New routes to mesoporous silica-based spheres with functionalised surfaces†

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Mesoporous hybrid silica-based spheres with functionalised surfaces and abundant highly ordered domains are obtained using for the first time a simple synthetic route based on spray-drying processes.

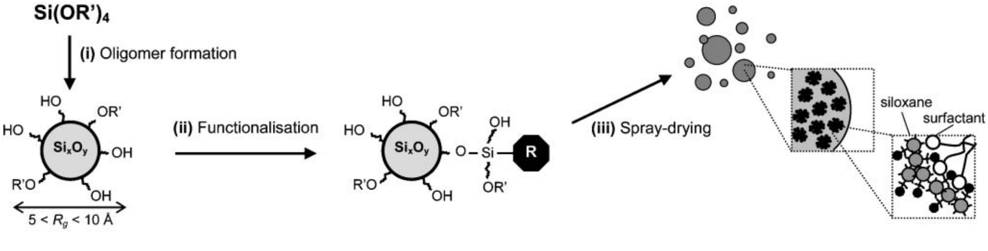
There is a great interest for a simple and robust synthesis of functionalised mesoporous oxide-based spheres adapted to specific applications such as heterogeneous catalysis, drug release, adsorption and separation techniques. For that purpose, Evaporation Induced Self-Assembly (EISA)[1] processes represent interesting alternatives because of their intrinsic characteristics: the use of sol–gel methods, the absence of macroscopic phase separation necessitating a further purification, and the simultaneous formation of the mesophase and the functionalised channel surface. In these processes, the solvent initially present in the solution is gradually evaporated from the atomised droplets. Meanwhile, the spherical droplet morphology can be retained, and the surfactant molecules can aggregate and self-assemble with the oxo-oligomers to form ordered textures. After preliminary tentatives,[2] the synthesis of mesoporous spheres using EISA was successfully demonstrated.[3] Since then, efforts have been made to better characterise and understand the underlying physico-chemical phenomena,[4–8] as well as to improve and expand the final properties and applications.[9] However, the direct synthesis of mesoporous spheres with functionalised surfaces has not been reported until now. It is known that solid formation during evaporation needs to be fast enough to maintain the spherical morphology, but also slow enough to allow the formation of mesophases from surfactant aggregates.[3] Additionally, the introduction of organic functions will have a perturbating effect on the size and shape of these surfactant aggregates rendering more difficult the synthetic task.

In this communication, we propose to solve these difficulties by a one-pot synthesis planned from the preliminary knowledge on mesoporous silica spheres, and conducted in three steps (Scheme 1): (i) the formation of oligomers with an optimal nanometric size, here by polycondensation of $Si(O...)_4$ Q units; (ii) the functionalisation by co-condensation, here between siloxane oligomers and $R–Si(O...)_3$ T units; (iii) the formation by spray-drying of micrometric spheres with nanometric mesophases and functionalised surfaces.

In the first step, tetraethoxysilane (TEOS), aqueous HCl (0.1 M), cetyltrimethylammonium bromide (CTAB), and isopropanol (^{i}PrOH) are mixed together in 1 : 5 : 0.12 : 20 molar proportions. The resulting clear solution is aged under stirring in a closed vessel at 293 K. The size of the siloxane oligomers is adjusted by varying the ageing time. A sol ageing time of 139 h for sample **1** will lead to oligomers with a mean radius of gyration $R_g \sim 6.9$ Å as deducted from previous SAXS data.[7] This value is in the range $5 < R_g < 10$ Å necessary to the formation of ordered mesoporous inorganic silica spheres. Sol ageing also minimises the quantity of non-hydrolysed alkoxy groups and facilitates further co-condensation reactions. For comparison, a sample **2** has been synthesised with a shorter ageing time of 43 h, resulting in $R_g \sim 4.8$ Å.

In the second step, functionalisation is realised by addition of an organosilane to the same pot. Methyltriethoxysilane (MTES) is chosen here with an initial molar ratio MTES : TEOS fixed to 1 : 9.‡ The other chemicals are added to maintain the molar proportions 1 : 5 : 0.12 : 20 between silicon precursors (TEOS + MTES), HCl 0.1 M, CTAB, and ^{i}PrOH. Prior to spray-drying, a second but shorter ageing time of 5 h is introduced (identical for both samples **1** and **2**). This ageing allows co-condensation between Q and T units to proceed without increasing significantly the final oligomer size.

In the third step, the clear solution is spray-dried at a moderate inlet temperature (383 K) using the experimental setup employed



Scheme 1 Synthetic route.

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† Electronic supplementary information (ESI) available: Determination of the volumic percentage of ordered domains by TEM, quantification and spatial localisation of Si–Me groups by solid state NMR. See http://www.rsc.org/suppdata/cc/b4/b418191c/
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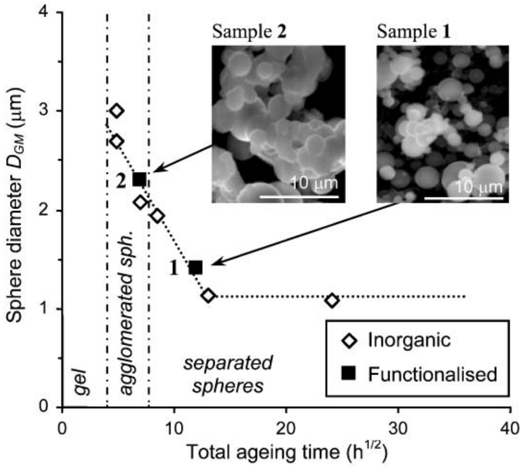

Fig. 1 Geometric mean diameters D_{GM} of inorganic and functionalised hybrid spheres as a function of the square root of total ageing time. D_{GM} result from the simulation by log–normal functions of the diameter size distributions. Insets represent SEM micrographs for samples **1** and **2**. They were recorded under low variable water pressure (0–1 Torr) on a Philips ESEM apparatus.

for mesoporous silica spheres.[7] The collected powders are dried overnight at 383 K and analysed as synthesised.

Micrometric separated spheres are observed by SEM for sample **1** instead of slightly agglomerated spheres for sample **2** (Fig. 1). This difference is related to the rate of solid formation during spray-drying. In the case of sample **1**, siloxane oligomers are large enough to solidify the droplets before agglomeration. The dependency of the morphological properties (dimension, agglomeration state) on the ageing time necessary to oligomer formation coincides with that previously found for mesoporous inorganic silica spheres (Fig. 1).[7] In that sense, morphological rules established for inorganic spheres can be transposed to spheres functionalised at a moderate level.

Typical XRD patterns of 2D hexagonal phase (*p*6*mm*) are observed for samples **1** (Fig. 2) and **2**. TEM analysis of sample **1** revealed the presence at the spheres' surface of highly ordered hexagonal domains (Fig. 2) representing at least 60% of the volume (ESI†). XRD characteristic distances *d* of the functionalised hybrid samples (corresponding here to the d_{100}-spacing) plotted as a function of the total ageing time (Fig. 2) are outside the correlation found for their inorganic analogs.[7] The deviation ($\sim$1 Å for sample **1**) might reflect the perturbating effect on surfactant aggregation of hydrophobic methylsilane groups (Si–Me) when replacing part of the hydrophilic silanol groups located at the siloxane–surfactant interface.

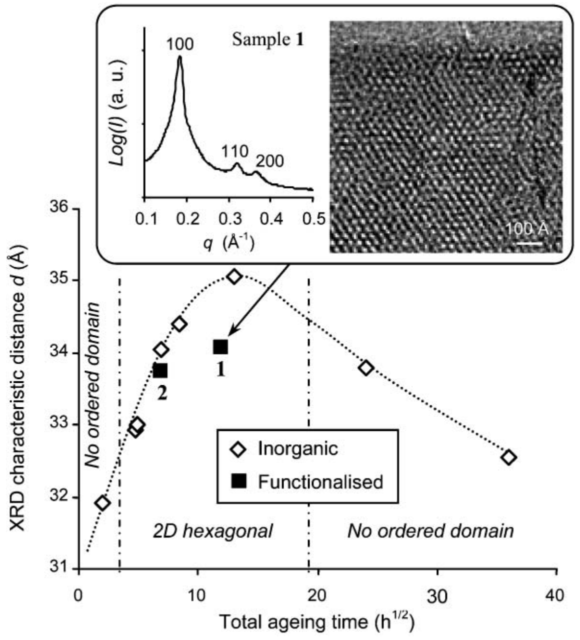

Fig. 2 XRD characteristic distances *d* of inorganic and functionalised hybrid spheres as a function of the square root of total ageing time. The inset represents an XRD pattern and a TEM micrograph for sample **1**. XRD patterns were recorded on the D43 instrument using the synchrotron radiation emitted by the DCI ring of LURE. TEM micrographs were obtained with a Philips Apparatus operating at 200 kV. The analysed slices were cut by ultramicrotome from a resin mixed with sample **1**.

This feature is established by ^{1}H and ^{29}Si solid state NMR. Both alkoxy (Si–OR′) and Si–Me groups have been quantified (ESI†). From the quantity of Si–Me, the final molar ratio $T:Q$ are: 0.7 : 9.3 for sample **1** (70% of incorporation) and 0.4 : 9.6 for sample **2** (40% of incorporation). Differences between the two samples illustrate the necessity of an extended hydrolysis during the first step for the formation of a maximum of *Q*–O–*T* bonds. In addition, we found that the total quantity of Si–Me and Si–OR′ matches the correlation, evidenced for mesoporous inorganic spheres,[7] between textural properties (degree of ordering, characteristic XRD distance) and Si–OR′ at the siloxane–surfactant interface (Fig. 3). Furthermore, double quantum ^{1}H NMR experiments on sample **1** demonstrated the localisation of Si–Me at this interface (ESI†). Therefore, the effect of Si–Me on surfactant aggregates is similar to that of Si–OR′, and will also determine the textural properties.

In conclusion, we have been able to directly synthesise mesoporous silica-based spheres with functionalised siloxane

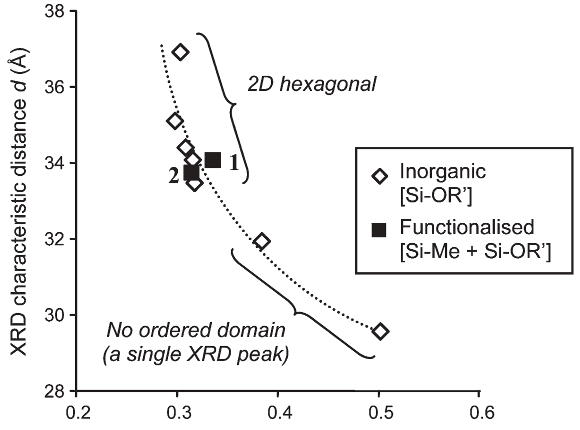

Fig. 3 XRD characteristic distances *d* of inorganic and functionalised hybrid spheres as a function of the molar proportions of organic groups bound to silicon calculated from ^{1}H NMR data (ESI†). Sol ageing times are here below 170 h.

surfaces using for the first time spray-drying techniques. We have proven that the final properties are determined by two adjustable parameters: the size of the siloxane oligomers prior to spray-drying, and the quantity of organic groups bound to the siloxane surface. The former parameter influences the rate of solid formation and thus the particle morphology, but might also impose geometrical constraints for the texture (work in progress). The latter influences surfactant aggregation necessary to the formation of ordered textures. Moreover, we used hydrolysis and condensation reactions for the formation of oligomers with optimal nanometric size (step (i)), but other silica or metal oxide sources could be used. In addition, this synthetic route might be extended to other functions by simply changing the nature of the organic group. First results in this direction obtained with phenyl or mercaptopropyl functions are promising (work in progress). We anticipate that this kind of synthesis would be of great use for the design of mesoporous spheres with functionalised surfaces.

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Notes and references

‡ We want to emphasise that adding MTES from the beginning (other parameters being equal) results in more agglomerated spheres and less ordered textures.

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