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Micelle templating for the formulation of silica at the nanometer scale

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Abstract

The self-assembly of surfactant micelles and silica to form hybrid mesophases is a powerful tool to prepare silica formulations of unprecedented pore uniformity. The thermal stability of micelle-templated silicas (MTSs) is unexpectedly good, and they represent one of the stablest form of dispersed silica. An abacus for textural evaluation of the materials is given and a mechanism of degradation is proposed. Case histories exemplify the potential pitfalls of synthesis which can affect the quality of the final product. Metastabilities of the mesophase in the synthesis system, as well as instabilities during washing and calcination, can lead to broadening of the pore size distribution, spoiling the unique properties of MTSs. At present, the improvement of the stability of MTS towards hydrolysis probably represents the most important challenge to extend their field of application. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Micelle templating; MTS; MCM-41; Surfactant micelles

1. Introduction

The discovery of micelle-templated silicas (MTSs) represents a case history of gradual understanding of the general value of a new concept. The first disclosure of the self-assembly of silica and surfactant micelles was connected to the use of an extremely peculiar silica source, the layered sodium silicate kanemite [1,2]. The parallel work of Mobil's researchers brought to realize that ordered mesoporous materials, called M41s, could be prepared from several usual sources of silica in a wide field of synthesis conditions [3,4]. In a general way, the formation of hybrid ordered mesophases is the normal result of the interaction between a soluble silica source and a surfactant solution. Indeed, MCM-41-like materials had been prepared since the late sixties as low-density phosphor supports, but their ordered nature had not been properly characterized [5,6].

Further research on micelle-templating has been focused on the use of various surfactants and on the conditions of formation of mesophases with different topologies [7–13]. In the meanwhile, some alarm bells have been rung about the hydrothermal stability of these forms of silica [14–16]. Indeed, activated silica mesophases are characterized by a very high surface area and a corresponding extreme sensitivity to environmental conditions. The development of successful applications for MTS requires their properties to be tailored for each application and the preparation procedures to be scaled-up from laboratory to industrial scale. The purpose of this communication is to pinpoint some sensitive steps in the search for reliable preparations of stable materials.

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2. Texture of MTSs

MTSs are characterized by a very high surface area, often near or beyond 1000 $m^2 g^{-1}$. This corresponds to a very high dispersion of silica. In the case of spheres of bulky silica, a surface of 1000 $m^2 g^{-1}$ would correspond to a sphere diameter of about 3 nm, well below the usual limit of stability of the elementary particles of a silica sol, nearly 5 nm [17]. To give a clearer idea of the typical size-scale of MTS, the surface area of the hexagonal mesophase (for instance, MCM-41) can be correlated to the geometrical parameters of an hexagonal honeycomb [18,19]. The surface area S_g ($m^2 g^{-1}$) is

$$S_g = \frac{4 \times 10^3 (a - t)}{\rho_{Si} t (2a - t)}$$

where a (nm) is the parameter of the hexagonal cell, measured by powder X-ray diffraction, t (nm) the thickness of the silicate walls between pores, and ρ_{Si} ($g\,cm^{-3}$) the density of the silicate walls. The density of amorphous silica, $\rho_{Si} = 2.2\,g\,cm^{-3}$, is an acceptable value for the wall density [20]. Common textural sizes for MTS prepared in the presence of cetyltrimethylammonium are $a = 5$ nm and $t = 1$ nm, and allow to calculate a surface area of 1010 $m^2 g^{-1}$, in good agreement with experimental results. In Fig. 1, the surface area expected for hexagonal MTS with different wall thicknesses and cell parameters are reported. The surface area increases with the lattice parameter for materials templated by micelles of short-chain surfactants, usually corresponding to lattice parameters a between 3 and 4 nm. MTS templated by cetyltrimethylammonium or octadecyltrimethyl ammonium micelles usually present lattice parameters a larger than 5 nm. In this case, the thickness of the walls t is much smaller than a, and the formula for surface area is independent of the lattice parameter [19]:

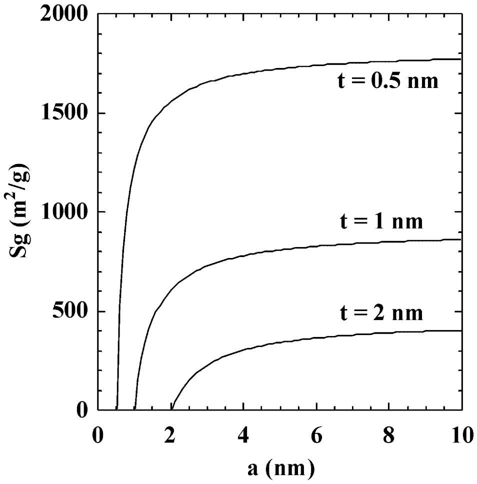

Fig. 1. Calculated surface area as a function of the lattice parameter a for hexagonal MTSs with different wall thicknesses.

$$S_g = \frac{2 \times 10^3}{\rho_{Si} t}$$

In silica walls 1 nm thick, half of the silica tetrahedra are directly exposed at the surface, nearly twice the fraction exposed on a silica sphere with a diameter of 5 nm. The stability of such a dispersed configuration is surprising and worth to be discussed.

3. Metastability of MTSs

During the synthesis, the high surface area is, more properly, an interface area and is stabilized by the interaction with the polar heads of the surfactant. In these conditions, the mesophase formed by the surfactant micelles in interaction with silica is at equilibrium with the synthesis system and can easily evolve in response at any evolution of the composition of the surrounding solution.

Metastability of MTS phases has been reported since the earliest research on the subject [21], and a clear effect of the pH of the synthesis system on the crystallinity of MTS has been observed [20,22]. This effect has been exploited to control the thickness of the silica walls, which is a function of the mass balance between surfactant and incorporated silica. At alkaline pH, higher solubility of silica leads to the formation of materials with thinner walls between micelles [23]. When a high concentration of silicate is present in the synthesis solution, disordered intermediates are formed at the beginning of the preparation by rapid condensation of silica with the isotropic micellar solution [24]. The slow transformation of the intermediates into the final crystallized MTS lengthens at a significant extent time of synthesis. Adjustments of pH allow to control the recrystallization process

[22]. Another source of metastability during the synthesis is the possible modification of the nature of the surfactant. Degradation of alkyltrimethylammonium is often observed in syntheses at temperature higher than 115°C and leads to a severe decrease of the yield of MTS. An interesting side-effect is that the products of degradation can swell the micelles formed by the fraction of undamaged surfactant, leading to materials with a larger pore size [25–28].

Modifications of the mesophase during the synthesis can seriously affect the homogeneity of the product. Materials prepared at room or near-room temperature up to 50–60°C can be easily affected by instability phenomena. The low synthesis temperature leads to less polymerized silica walls, quicker to follow any evolution of the surrounding solution. Systems washed at a temperature comparable to the synthesis temperature are especially liable to modifications during the washing process [29]. It is known that a significant fraction of cetyltrimethylammonium can be extracted from silicic MTS materials by ion exchange. In the case of materials formed at a temperature high enough to ensure a complete condensation of the silica walls, this property is exploited to extract a part of the surfactant and reduce the thermal effect of the following calcination [30]. Partial surfactant extraction is also possible during the washing at the end of the synthesis. The washing solution is much less alkaline and presents a low ionic strength than the synthesis solution. Both factors contribute to the protonation of the surface silanols and to the exchange of the surfactant cations, which are extracted from the solid. Silica lattices formed at lower temperature are not rigid enough to afford the lack of a template and collapse, with a decrease of the average pore size and a broadening of the pore size distribution [29]. The pore shrinking can be severe, and lead to the transformation of the mesopores into micropores, especially in the case of room-temperature syntheses in acidic conditions, where silica is less deprotonated and washing of alkyltrimethylammonium is easier [31].

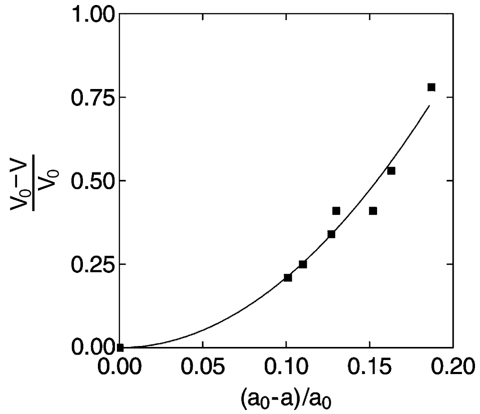

Fig. 2. Calcination at 550°C in air of hexagonal MTS. Decrease of pore volume as a function of the decrease of lattice parameter a for several samples.

4. Mechanism of degradation

The interaction between silica and the polar heads of the surfactant accounts for the stability of the interface. When the surfactant is eliminated, a high-energy silica surface is exposed, and the driving force for sintering is provided. Upon calcination, MTS features a significant decrease of the lattice parameter, with a decrease of pore size and volume and an increase of wall thickness [32,33]. It has been shown that the decrease of pore volume, reported in Fig. 2 for several samples of hexagonal MTS, is proportional to the second power of the decrease of lattice parameter, corresponding to a densification of the structure in the plane perpendicular to the pore length [29]. The best-fitting line reported in Fig. 2 corresponds to the equation

$$\frac{v_0 - v}{v_0} = 21\left(\frac{(a_0 - a)}{a_0}\right)^2$$

where v is the pore volume measured by t-plot from N_2 adsorption isotherms at 77 K, v_0 the micelle volume calculated from elemental analysis through some assumptions on the micelle and silica densities ($\rho_{\text{silica}} = 2.2\ \text{g cm}^{-3}$, $\rho_{\text{organics}} = 0.77\ \text{g cm}^{-3}$) [18], a and a_0 the lattice parameters of, respectively, the calcined and as-synthesized materials.

Notwithstanding the cell shrinking, the hexagonal honeycomb of the better materials remains stable if the temperature of calcination does not exceed 800 or 900°C [32]. This temperature limit corresponds to the Tamman temperature of quartz (846°C), and it is interesting that a highly dispersed material, like MTS, and the equivalent bulky crystalline phase present the same threshold of thermal stability.

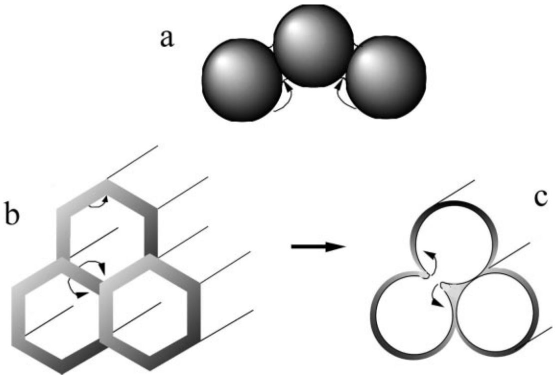

Fig. 3. Sintering mechanism: (a) packing of spheres, (b) MTS before and (c) during degradation.

The usual mechanism of sintering passes through the mass transport from surfaces with a positive curvature radius towards surfaces with a negative curvature radius, as represented in Fig. 3a in the case of contacting spheres [34]. In the case of MTS, a thermal instability is expected due to different values of the curvature radius: small positive radii (of the order of $\frac{1}{2}t$) at the pore mouth made the outer rim of the grain specially unstable. On the other hand, negative curvature radii inside the pores should make the inner surface an extremely effective sink for diffusing species.

To evaluate this effect, the peculiar shape of the pores of MTS has to be taken into account. The pore section is not cylindrical, but properly hexagonal [35], as a result of a mechanism of formation which equilibrates any tension between adjacent micelles, exactly like the flat surfaces observed at the interface between two soap bubbles [36]. As a consequence, the inner surface alternates flat surfaces, corresponding to the sides of the hexagon, and grooves with a very small negative curvature radius, in correspondence with the 60° corners of the hexagon (Fig. 3b). These grooves can be expected to be extremely effective sinks for diffusing silica species, but recent findings probably justify why they are not. It has been shown that also before the extraction of the surfactant, the 60° corners of the hexagonal pores are extremely rich of siloxane bridges, and present an especially low concentration of silanols [37]. In some way, the geometry of silica tetrahedra around the pore corners corresponds to the geometry of tetrahedra around zeolite micropores, and generates a completely condensed silica surface. Such a surface is an extremely poor acceptor of migrating species, and migration from the instable pore mouths is effectively prevented by lack of a suitable sink.

When the temperature of thermal treatment exceeds the Tamman temperature, tetrahedra are mobile enough to allow viscous sintering to occur. In analogy with the sintering behavior of foams [38], migration of silica takes place from the pore sides towards the corners, and walls can become thin enough to allow the opening of gaps between pores (Fig. 3c), with a severe broadening of the pore size distribution [33]. Materials formed in less than optimal conditions present a lower stability. It is the same case for MTS formed at very high [33] or very low pH [20]. In both cases, very thin silica walls (∼0.5 nm) are formed, and calcination at 550°C often brings about a severe decrease in pore volume and broadening of the pore size distribution.

5. Hydrothermal stability

For all MTS, the presence of water seriously affects the stability of the material. When the presence of an adsorbed water phase makes available an efficient mass transfer mechanism, the effects of surface ripening at room temperature can closely parallel the effects of sintering at high temperature. Liquid water [14] as well as water vapor, both at room temperature [16] and as superheated steam [15], have been shown to rapidly destroy the structure of MTS. The effect of water can be easily accounted for by the degradation mechanism schematized in Fig. 3. It has been shown that surface siloxanes of MTS are easily hydrolyzed in the presence of water vapor [39,40]. The formation of silanols at the pore corners makes these portions of the surface liable to react with diffusing silica species, and provides the silica sink needed to trigger the ripening of the surface.

It has been shown that small amounts of aluminium in the silica lattice significantly improve the hydrothermal stability of the material [41]. This effect confirms that the stability of MTS cannot be addressed at by general considerations alone; the reactivity of each material critically depends on the composition and the conditions of synthesis and activation.

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