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# Mechanisms of Pore Size Control in MSU-X Mesoporous Silica

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Mesoporous silicas of the MSU-X type, made with nonionic polyethylenoxide-based (PEO) surfactants, were synthesized according to a two-step process that gives intermediary stable hybrid micelles. The influence of the various synthesis parameters, such as the silica concentration, the addition of a swelling agent (TMB: trimethyl-1,3,5 benzene), the condensation catalyst (NaF), and the temperature of silica condensation, was systematically explored, especially their influence on the material pore size. Surprisingly, changing the silica over surfactant ratio does not modify the silica wall thickness but the other parameters have a strong effect on the final pore size. Considering the model of hybrid micelles that was previously reported (Boissière et al. *Chem. Mater.* **2001**, *13*, 3580), we explained the effect of the different parameters by a classical swelling effect of the hydrophobic micelle core for TMB, whereas the modulation of the hydrophilicity of the PEO chains (for temperature) or that of the silica oligomers (for NaF) describes correctly the variations observed. Finally, the cumulative effect of these parameters is demonstrated and we show that materials with narrow pore size distributions tuned between 2.5 and 5 nm can be obtained without changing the surfactant nor adding any swelling agent, by varying only the synthesis parameters.

## I. Introduction

Since their first report in 1992, mesoporous materials exhibiting an ordered porosity, which one can call among several possible acronyms micelle templated structures (MTS), have been extensively studied, mostly because of their outstanding geometrical properties.[1−5] These materials, which are synthesized through an assembly mechanism between organic surfactants and inorganic precursors, exhibit a very large surface area ($>800\ m^2{\cdot}g^{-1}$), a high porous volume that can be higher than 1 $cm^3{\cdot}g^{-1}$, a monodisperse pore size tunable from 2 to more than 10 nm, and a regular porous arrangement. Since the first ordered mesoporous silica obtained by using electrostatic interactions between long-chain quaternary ammonium and silica,[1,3] a wide range of surfactants, including amines, gemini surfactants, nonionic surfactants, or copolymers, and various inorganic compositions was explored, especially for catalytic applications.[6−14] Among them, poly(ethylene oxide) (PEO) nonionic surfactants or block copolymers appeared to be potential candidates for industrial applications because of their low cost, their biodegradability, and their low toxicity. Moreover, since the first reports,[15−17] they allowed the formation of a wide range of geometries, from usual mesoporous MTS powders,[15,18] to spheres,[19] foams,[20,21] films,[22] rods,[23,24] monoliths,[25] and so forth. Besides, they can be prepared with 3D

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wormhole porosity[15,18,19] as well as hexagonal framework.[16,26−32]

Among various syntheses using nonionic assembly agents, different families have been identified, depending on their general synthesis conditions: SBA-15 silica is prepared mainly with block-copolymer Pluronic P123 under strong acidic conditions[27] and CMI silica, prepared with linear surfactants, gives hexagonal structure under judicious synthesis conditions,[32] whereas MSU-X silica (X refers to the nature of the surfactant: 1 for alkyl-PEO, 2 for alkylaryl-PEO, 3 for polypropyleneoxyde-PEO block copolymer, and 4 for Tween-type nonionic ethoxylated sorbitan esters) is prepared under neutral[15,18] or mild acidic conditions.[19] One specificity of MSU-X silica was the ability to modify the pore size of the final material by adjusting the synthesis temperature from room temperature to 80 °C.[18]

MSU-X materials possess regular pores diameters and wall thickness similar to MCM-41-type materials but they do not generally exhibit a long-range periodicity. Therefore, the single peak observed in their X-ray diffraction pattern cannot be related with any actual "*d*-spacing" of a crystalline cell. In a first-order approximation, we ascribed this peak to the most obvious periodic electron density contrast present in the material, that is, the correlation length between two pore centers.[18] Different strategies of synthesis have been applied since the first report.[15,18,32] We developed a two-step synthesis where the assembly step between surfactants and inorganic species is clearly set apart from the condensation step.[19,29,33] In a first step, the controlled hydrolysis of a silica precursor in the pH range 1−4 allowed us to obtain the assembly of both organic and inorganic reactants to form stable hybrid micelles, made of a hydrophobic core, a PEO organic palisade, and an inorganic poorly condensed silica layer interacting with the PEO part by hydrogen bonding.[24] In the second step, the addition of a fluoride salt activates the silica condensation in the hybrid micelles to form, after surfactant removal, the silica network.[34] We reported already that both the condensation step temperature and the fluoride amount were able to influence the pore size[19] but these parameters have not been extensively studied yet. The aim of this work was thus to explore how the variation of different parameters of the synthesis may help to modify the structure of the MSU-X silica and how the hybrid micelle model that we reported previously may help to explain the mechanisms that direct these behaviors. We report hereinafter the influence of four synthesis parameters: the addition of a swelling agent (trimethyl-1,3,5 benzene: TMB), the influence of the condensation temperature, that of the sodium fluoride, and the influence of the silica over surfactant ratio on the final structure of the material.

## II. Experimental Section

The materials were synthesized with two families of PEO surfactants: Tergitol 15-S-$N$ ($N$ = 9, 12, 15) ($CH_3-(CH_2)_{15}-(CH_2CH_2O)_N-OH$) (kindly provided by Union Carbide Co., Belgium) and Tween surfactants including Tween 20 (PEO sorbitan monolaurate) (Fluka Chemicals), Tween 40 (PEO sorbitan monopalmitate) (Sigma Chemicals), Tween 60 (PEO sorbitan monostearate) (Sigma Chemicals), and Tween 80 (PEO sorbitan monooleate) (Acros Chemicals). The silica source was tetraethyl orthosilicate (TEOS: $Si(OCH_2CH_3)_4$) (Acros Chemicals). We used sodium fluoride as a silica condensation catalyst (Fluka Chemicals). All reagents were used as received.

We prepared the different series of compounds according to the two-step synthesis already published.[19,29] A 0.02 $mol\cdot L^{-1}$ aqueous solution of surfactant was prepared (by example 1.476 g of T15S12 with 98 mL of water) and its acidity was adjusted to pH 2 by adding 2 mL of a hydrochloric acid solution (N). At this step, TMB could be added with a different TMB/surfactant molar ratio. TEOS (3.33 g) was added under magnetic stirring to reach a final TEOS/surfactant molar ratio of 8. The fast hydrolysis of TEOS at this pH, which is not followed by any condensation of silica, broke the emulsion made of unreacted TEOS drops in water, within several minutes, and a clear solution of hybrid organic−inorganic micelles was obtained.[24] That solution was left at rest overnight, thereafter placed in a thermostated shaking bath adjusted at the desired temperature between 5 and 75 °C, and maintained under slow shaking (40 rpm). A few drops of a solution of sodium fluoride (0.25 $mol\cdot L^{-1}$) were finally added to obtain a final NaF/TEOS molar ratio varying between 0% and 6%. Depending on the respective concentrations, the silica condensation started within 10−30 min but the mixture was kept under slow shaking for 3 days at the condensation temperature. Afterward, it was filtered, dried, and calcined (3 $°C\cdot min^{-1}$) at 620 °C for 6 h after a 6-h step at 200 °C. Reaction yield was always higher than 95%.

All measurements were performed on calcined powders. They were characterized by X-ray diffraction and nitrogen adsorption/desorption. Nitrogen adsorption isotherms were measured at 77 K on a Micromeretics 2010 Sorptometer using standard continuous procedure. Surface areas were determined by the Brunauer−Emmett−Teller (BET) method within a 0.05−0.2 relative pressure range. Pore size distributions were calculated—only for sizes above 2.5 nm—from the desorption branch by a polynomial correlation between relative pressure and pore diameter, deduced from the Broekhoff and de Boer (BdB) model.[35−37] To ease comparison, we displayed the reduced adsorption curves (isotherms divided by the amount adsorbed at a relative pressure of 0.8).[30] X-ray diffraction patterns were recorded with a Siemens D5000 diffractometer in the Bragg−Brentano reflection geometry. Cu $L_{3,2}$ radiation was employed and monochromatized by a

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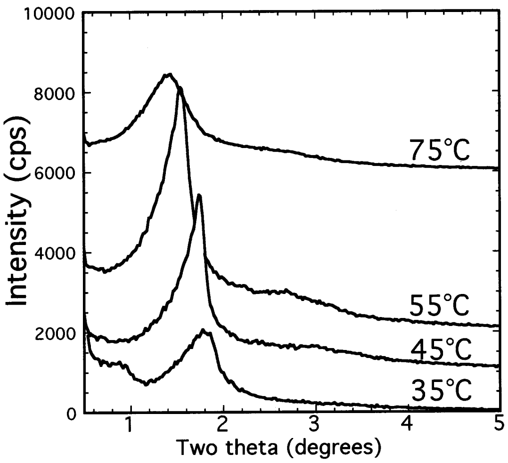

**Figure 1.** X-ray patterns of calcined MSU-4 silica prepared with Tween 40 at different temperatures of silica condensation. The patterns were vertically shifted for clarity.

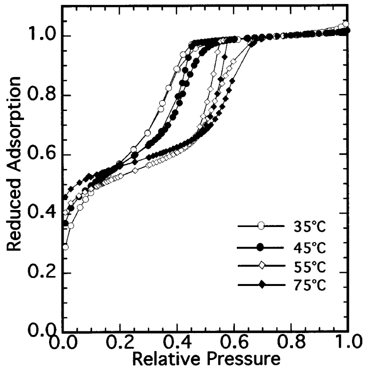

**Figure 2.** Reduced nitrogen adsorption (line)/desorption (dashed) isotherms of calcined MSU-4 silica prepared with Tween 40 at different temperatures of silica condensation. (The isotherms were divided by the amount adsorbed at a relative pressure of 0.8.)

graphite single crystal in the diffracted beam. Most patterns exhibit a single diffraction peak that we assigned to a correlation length between pores.[18] This "pore center to pore center" correlation length will be named "*d*-spacing" in the following.

## III. Results

The influence of temperature is illustrated by syntheses of MSU-4 performed with Tween 40 at synthesis temperatures adjusted in the shaking bath between 35 and 75 °C. The X-ray patterns displayed in Figure 1 exhibit a progressive shift of the diffraction peak toward lower angles, characteristic of the increasing *d*-spacing.[18] A parallel trend is observed for the nitrogen adsorption/desorption isotherms (Figure 2), with the adsorption jump shifted toward higher relative pressures, which is characteristic of an increasing pore size. Similar results are observed with MSU-1 materials. The evolutions of both the *d*-spacing and the pore diameter as a function of the synthesis temperature for MSU-1 and MSU-4 materials prepared with Tergitol 15-S-*N* and Tween, respectively, are plotted in Figure 3. For both families, an average increase of 1.0 nm is observed for the *d*-spacing as well as for the pore diameter, when the synthesis temperature varies between 35 and 75 °C. These observations confirm that the pore size dependence as a function of the synthesis temperature is a general feature in the two-step synthesis process. If one takes into account that the *d*-spacing describes the pore center to pore center correlation length, the silica wall thickness value can be deduced by subtracting the pore diameter value from *d*-spacing. The evolution of the silica walls thickness as a function of the temperature is plotted in Figure 4. Except a possible slight decreasing observed for MSU-1 materials, it appears that the silica wall thickness remains constant whatever the synthesis temperature.

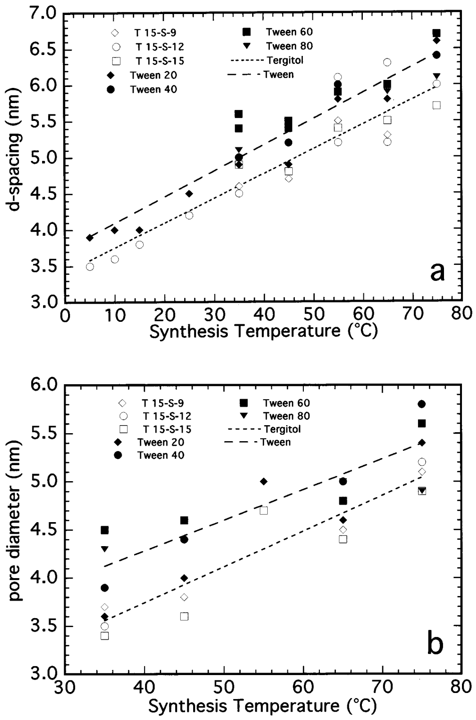

**Figure 3.** Evolution as a function of the silica condensation temperature of (a) the *d*-spacing and (b) the pore diameter of calcined MSU-1 and -4 silica prepared with different assembly agents of Tergitol 15-S-*N* and Tween, respectively. Dashed line: linear fit of the evolution of the parameters, calculated with the whole set of samples of MSU-1 and MSU-4.

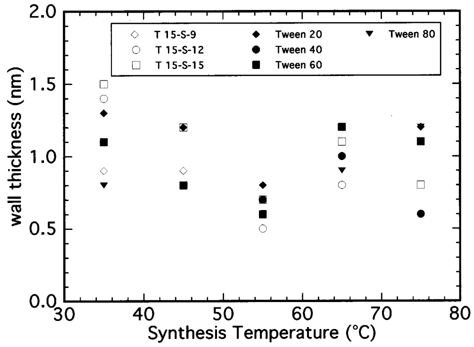

**Figure 4.** Evolution as a function of the temperature of silica condensation of the silica wall thickness for MSU-1 silica prepared with Tergitol 15-S-*N* surfactants and MSU-4 silica prepared with Tween surfactants.

The influence of the NaF/Si molar ratio was studied through two similar sets of syntheses with the NaF/Si molar ratio adjusted between 0 and 6%, the condensation temperature, and the Si/surfactant molar ratio being kept constant and equal to 35 °C and 8, respectively. Though only a slight decrease of the diffraction line position toward lower angles is noticed, the main evolution is highlighted in the nitrogen adsorption/

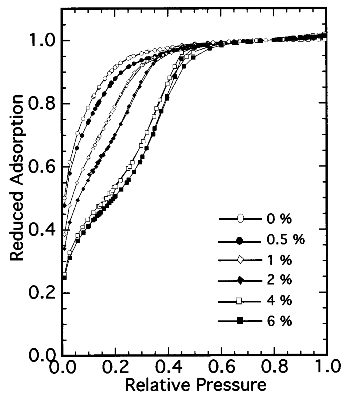

**Figure 5.** Reduced nitrogen adsorption (line)/desorption (dashed) isotherms of calcined MSU-1 silica prepared with Tergitol 15-S-9 and different NaF/Si molar ratios.

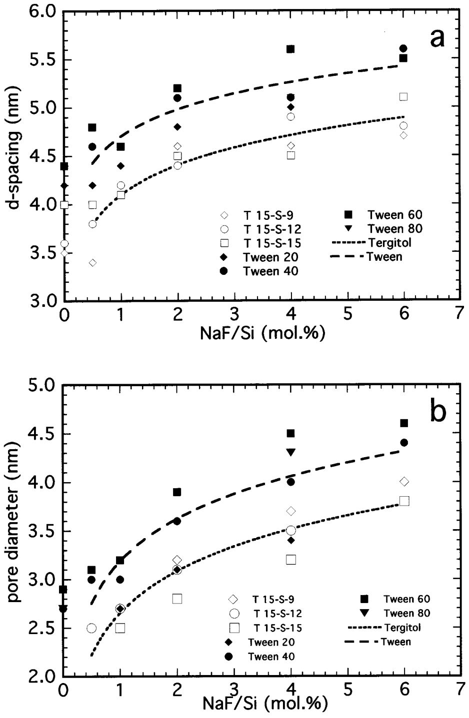

**Figure 6.** Evolution as a function of the NaF/Si molar ratio of (a) the *d*-spacing and (b) the pore diameter of calcined MSU-1 and -4 silica prepared with different assembly agents of Tergitol 15-S-N and Tween, respectively. Dashed line: Log fit of the evolution of the parameters, calculated with the whole set of samples of MSU-1 and MSU-4.

desorption isotherms (Figure 5) that shows that the adsorption step shifts toward higher pressure values up to NaF/Si = 4%, which means that the pore size increases with the amount of sodium fluoride. For both series, the evolution of the *d*-spacing and pore diameter follows roughly logarithm functions in the NaF/Si ratio range studied (Figure 6), and it appears that the pore diameter increases within at least 1.0 nm when the NaF/Si molar ratio is changing from 1% to 6%. We plotted the evolution of the silica wall thickness as a function of the NaF/Si molar ratio (Figure 7). For both series of samples, one observes a similar decrease of this value.

TMB is a swelling agent of the micelle hydrophobic core that has been widely used as a pore expander in almost all syntheses of MTS materials as well as MSU-X-type materials.[33] Syntheses of a MSU-1 silica, implying Tergitol 15-S-12, confirm that TMB is also effective in the two-step synthesis of MSU-X materials: a 0.5 nm increasing of the pore diameter is observed for a TMB/surfactant molar ratio varying from 0 to 2, but the silica wall remains unchanged (Figure 8).

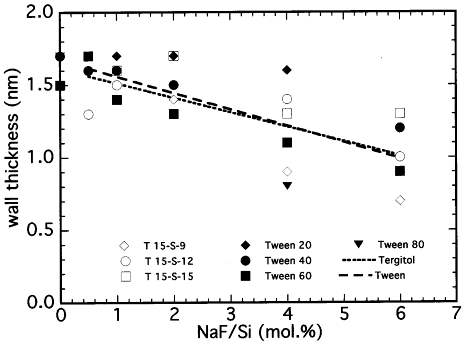

**Figure 7.** Evolution as a function of the NaF/Si molar ratio of the silica wall thickness for calcined MSU-1 and -4 silica prepared with different assembly agents of Tergitol 15-S-*N* and Tween, respectively. Dashed line: linear fit of the evolution of the parameters, calculated with the whole set of samples.

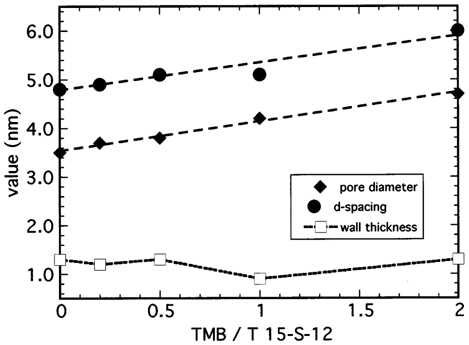

**Figure 8.** Evolution as a function of the TMB/surfactant molar ratio of the *d*-spacing, pore diameter, and wall thickness for calcined MSU-1 silica prepared with Tergitol 15-S-12. Dashed lines: linear fit of the evolution of the parameters.

The influence of the Si/surfactant molar ratio, adjusted between 4 and 12, was also studied. A small increase of the *d* spacing and pore diameter is only observed, which cannot be compared in magnitude, with those observed with the other parameters. However, even though such results must be carefully considered in the lack of precise quantitative determination, we observe a continuous increasing intensity of the diffraction line when Si/surfactant varies from 4 to 10, which cannot be only assigned to random experimental conditions: the area of the diffraction line becomes 1.5 larger for Si/surfactant = 10 than for Si/surfactant = 4, without any change of its width. The increasing intensity of the diffraction line must be understood in the light of an increasing contrast of the electron density in the material, that is, of the silica density itself, compared with the empty pore.[38]

## IV. Discussion

We have demonstrated previously that the assembly step of this two-step synthesis of MSU-X silica leads to spherical hybrid micelles that exhibit an additional low-

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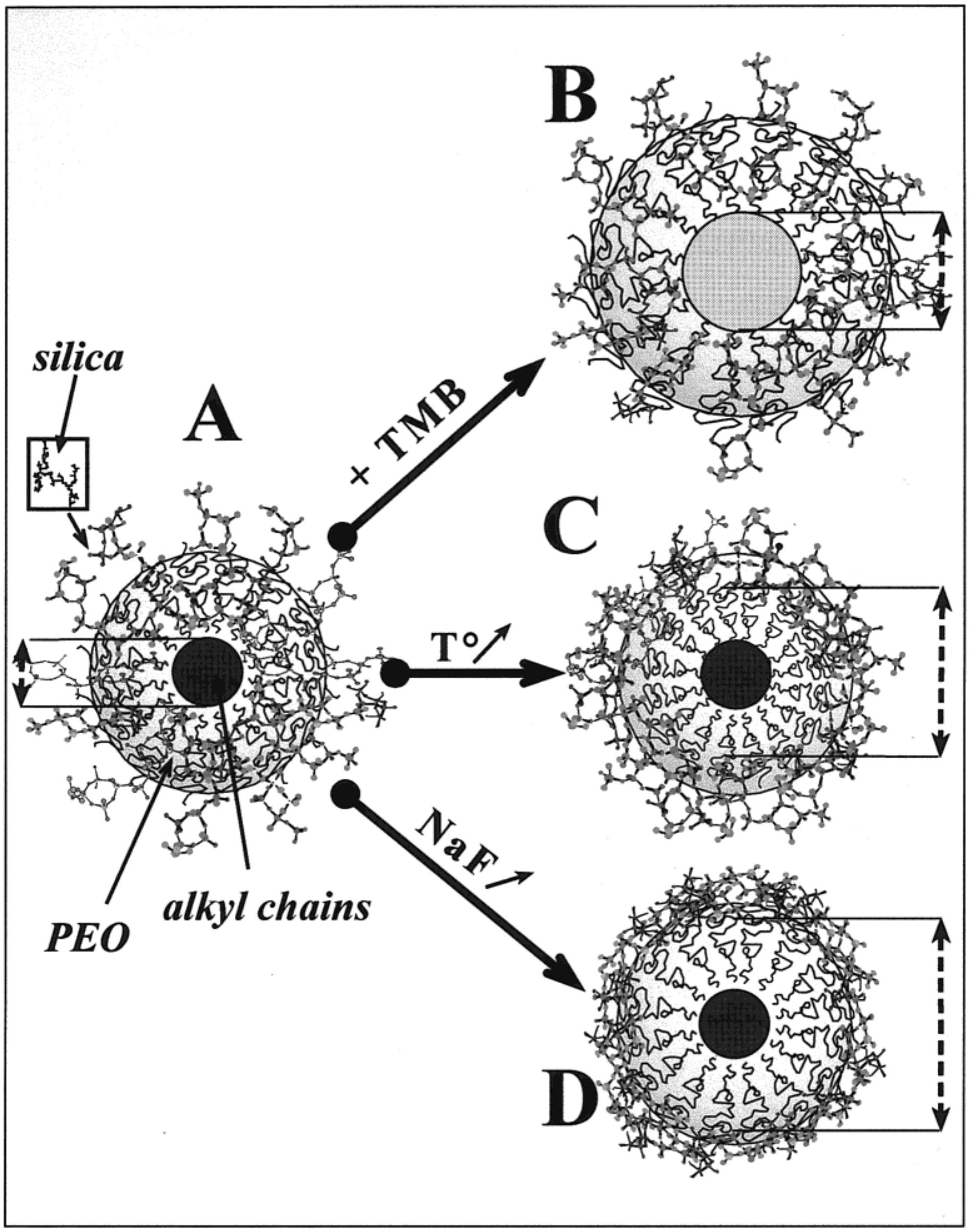

**Figure 9.** Model describing the influence of the different parameters on the hybrid micelle structure: (A) initial structure, (B) the addition of TMB swells the alkyl core, (C) increasing temperature increases the hydrophobicity of PEO chains, and (D) increasing the NaF/Si ratio increases the hydrophobicity of silica. Dashed double arrows: new silica-free core diameter.

density silica (fractal dimension of 1.9) outer shell around the micelle, whose thickness varies linearly with the Si/surfactant molar ratio between Si/surfactant = 4 and Si/surfactant = 20.[24,39] Its structure is illustrated in Figure 9A: this hybrid micelle is built with a central hydrophobic core made of the surfactants alkyl tails, surrounded by the hydrophilic palisade made of PEO chains plus a third outer shell made of the low reticulated silica network growing out from the PEO shell. The interactions between silica oligomers and PEO groups are based on hydrophilic hydrogen-bonding-type interactions. Upon the addition of fluorine, the silica shell condenses and the hybrid micelles merge, with silica building walls whereas the non-silicated center of the micelle creates the porosity. Even if the condensation step implies more drastic changes—which will not be discussed in this report—than a simple “aggregation” model between spherical micelles, the hybrid micelles remain the center of all processes involved during the silica condensation since they are the starting brick of the condensation process. Obviously, the future shrinkage during drying and calcination cannot allow us to deduce directly, from the dimensions of the pristine micelle, what will be the final pore size, but a homothetic behavior is expected. Variations in the structure of the hybrid micelle before or during the first steps of the condensation must lead to correlated modifications in the structure of the final material. Adding a swelling agent such as TMB or changing the length of the surfactant hydrophobic chain is a way to modify the hydrophobic core dimension. They are well-known to be

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efficient in the pore size modification, whatever the nature of the templating surfactant. Changing the temperature of silica condensation in a moderate temperature range as well as modifying the amount of catalyst (NaF) are efficient only with nonionic surfactant—as far as the two-step synthesis process that allows a quasi-thermodynamic equilibrium of the hybrid micellar object is applied.[29] We will demonstrate thereinafter that a single mechanism, the shift of the boundary between the hydrophobic core and the hydrophilic shell, can explain the influence of these latter parameters.

TMB swells the alkyl core without disturbing the hydrophilic shell, region of the silica framework to be (Figure 9B). The resulting material will exhibit a larger pore with an unchanged silica wall, as was observed (see Figure 8). This method is applied to relatively small amounts of TMB since it must dissolve in the alkyl core but stable microemulsions were also prepared, which played the part of a template of mesostructured cellular foams.[40−42]

Temperature raising leads also to the pore diameter expansion (Figure 3) but its influence on the wall thickness is not obvious. This pore size variation cannot be linked anyway with the pore size increase mechanism observed when postsynthesis treatments of MTS using cationic surfactants are applied because, in this latter case, it depends mostly on dissolution and recrystallization processes in the hybrid phase.[26,43] Unlike cationic surfactants that exhibit a thin hydrophilic surface made of ionic heads, the hydrophilic shell of nonionic surfactants is thicker and largely swelled by water molecules, with an increasing amount of water as one goes from the center toward the outer surface of the micelle.[44,45] In parallel, it has been shown that the hydration degree—hence the hydrophilicity—of the ethylene oxide group decreases as the temperature increases.[46] The increasing hydrophobicity of PEO groups with temperature tends to expel more and more water molecules from this shell and the hydrophobic EO groups will be stretched (the size of nonionic micelles increases upon temperature rising). Besides, another parameter, the brownian motion induced by temperature, will lessen the strength of hydrogen bondings linking silica with PEO chains. Hence, silica will be more and more kept apart from the inner region of the hydrophilic shell and this internal part, freed from silica, will add with the hydrophobic core to contribute to greater porosity (Figure 8C). This behavior shows that temperature modifies the level of hydrophobicity of the PEO shell in the hybrid micelle, which shifts the position of the limit between the hydrophobic internal zone and the external hydrophilic shell that contains EO groups, water, and silica oligomers.

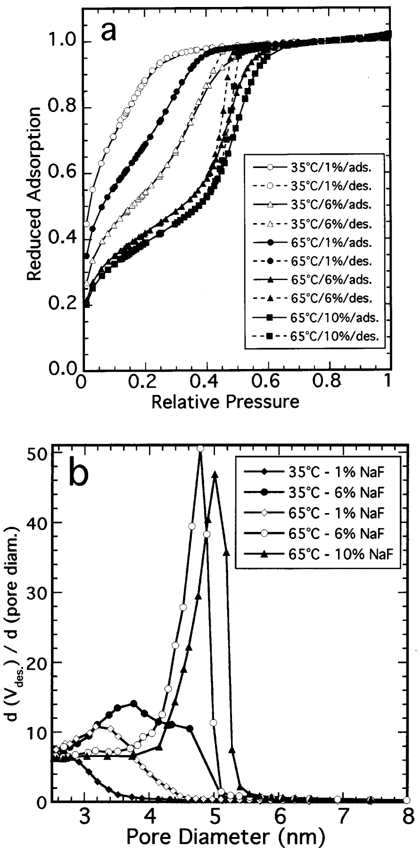

**Figure 10.** (a) Reduced nitrogen adsorption/desorption isotherms of calcined MSU-1 silica prepared with Tergitol 15-S-12, at 35 or 65 °C and different NaF/Si molar ratios (1, 6, and 10%). (b) Pore size distribution deduced from the nitrogen desorption branch.

We found that fluoride has an unexpectedly strong effect, both on the pore diameter (Figure 6) and on the silica wall thickness (Figure 7). This effect was not noticed either in our initial synthetic pathway[18] or in related works using fluoride ion.[17,23] The influence of the sodium fluoride addition on the structure of MSU-X materials mut be explained by its catalytic oxolation properties: the more fluoride added, the faster the oxolation reaction proceeds, which leads to a progressive decrease of the amount of hydroxo groups linked to silica oligomers. A correlated increasing of the hydrophobicity of the silica framework will then appear.[34,47] In this case, silica cannot enter as deep as expected into the hydrophilic PEO shell because the silica oligomers, as they are more reticulated in the first steps of the reaction, become less flexible and more hydrophobic. This will tend to increase the non-silicated region in the PEO shell, with the same effect as for temperature, but for a different reason (Figure 8D). However, in this case, the higher condensation of silica must lead to a thinner thickness of the walls, which is actually observed (Figure 7). These two mechanisms are different in nature because the temperature influences the thermodynamics of the hybrid micelle—quasi-elastic light-scattering measurements have shown that the swelling/shrinking behavior of the hybrid micelle with temperature is reversible—whereas the sodium fluoride acts on the kinetics of the silica condensation and leads to an irreversible process. Moreover, temperature affects the

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PEO chains and sodium fluoride modifies the silica oligomers.

Since one mechanism modifies the properties of the organic part whereas the other modifies those of the inorganic part, we might expect that both should be cumulative. We checked this assumption by performing a set of syntheses of MSU-1 silica, prepared with Tergitol 15-S-12 (Si/surfactant = 8), at two temperatures (35 and 65 °C) and different NaF/Si molar ratios (1 and 6%). The nitrogen adsorption/desorption isotherms of the materials are displayed in Figure 10. An increasing shift ot the adsorption step, with either the NaF/Si ratio or the temperature, is actually observed. Compared with the “reference” synthesis performed at 35 °C with NaF/Si = 1 mol %, the syntheses performed by either raising the temperature (65 °C, NaF/Si = 1%) or the sodium fluoride amount (35 °C, NaF/Si = 6%) give a rather similar shift in the adsorption edge. When both parameters are combined (65 °C, NaF/Si = 6%), one observes, as expected, a cumulative effect. We increased the NaF amount up to 10% (65 °C, NaF/Si = 10%), which helped us to further increase the nitrogen adsorption step shift. The pore size distributions deduced from these isotherms are displayed in Figure 10. It appears that, with the same surfactant and the same ratio of silica over surfactant and without any swelling agent, the rational choice of the synthesis parameters (temperature and catalyst) allows us to prepare MTS materials with a pore diameter adjustable between 2.5 and 5.0 nm. This latter value appears to be the upper limit with this kind of surfactant.

Finally, syntheses performed with various Si/surfactant ratios reveal that increasing the amount of silica does not modify the silica layer thickness but its density. Even though these are preliminary results that will require accurate quantitative measurements, one may notice that similar results were also observed for MCM-41 materials[48] that allow us to try to propose a first explanation for this behavior. The silica shell of the hybrid micelle, prior to the condensation step, forms a low-density framework whose density does not depend on the amount of silica.[39] Once the reticulation is induced by the addition of sodium fluoride, the silica network will be constrained by steric confinements between micelles, which will help to shrink this layer and to build a denser silica layer. These preliminary results let us think that the final silica wall thickness seems mostly defined by the geometrical constraints provided by the micelles packing than by the initial amount of silica.

We showed previously that the pore size of the final material can be dependent not only on the surfactant alkyl chain length or the addition of a swelling agent but also on the temperature synthesis.[18] A new effect, that of the fluoride ion, was revealed too.[19] We show in this report that both effects are acting with different kinds of surfactants, as far as a two-step synthesis is followed, and that they are cumulative. The knowledge of the unit brick of the synthesis, that is, the hybrid micelle built during the assembly step, allowed us to understand the mechanisms involved by these two parameters.

**Supporting Information Available:** Seven tables describing the structural parameters (pore diameter, *d* spacing, $S_{BET}$, and porous volume) of the samples used in this study (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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