Synthesis of Large-Pore Mesostructured Micelle-Templated Silicas as Discrete Spheres

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The synthesis of large-pore micelle-templated silica (MTS) materials as discrete spheres by pseudomorphic synthesis solves the double challenge: enlarging the pore size of MTS beyond the diameter of the micelles and controlling the morphology and the size of the particles. The pseudomorphic transformation of silica beads of the desired size into MTS is one of the more suitable routes to control both nanometric and micrometric scales of MTS synthesis. The most employed method to enlarge pore diameter of MTS synthesized from alkyltrimethylammonium surfactants is to use 1,3,5-trimethylbenzene (TMB) as a swelling agent in the micelles. Unfortunately this method leads to particle aggregation. By means of the pseudomorphic route combining an original set of chemical compositions (C_{18}TAB/decane/TMB/NaI), under mild conditions (low temperature, without autoclaving), we successfully synthesized nonaggregated MTS beads of 10 μm with pore diameter ranging from 7 to 9 nm, 900 m^2/g specific surface area, and 1.5 mL/g pore volume. To accommodate the large pore volume developed by large-pore MTS, highly porous silica beads of 10 μm and 300 m^2/g specific surface area have previously been synthesized by means of an emulsion/polymerization procedure. The control at nanometric scale, by means of surfactants, leads to improved textural properties compared to optimized silica gels, whereas the control of the micrometric morphology (discrete spheres) makes these supports suitable for column packing and chromatographic evaluation.

Introduction

The discovery of M41S type material in 1992,[1] such as MCM-41, has attracted considerable attention in adsorption studies. Thanks to their unique textural properties, these micelle-templated silica (MTS) materials represent a class of promising supports for advanced separation processes.[2] Their high specific surface area, high pore volume, and adjustable pore size should improve, respectively, the retention capacity, column permeability, and molecular selectivity by size-exclusion process. MTS materials have been proposed as possible stationary phases for capillary gas chromatography,[3] for size-exclusion chromatography (SEC),[4,5] for normal phase high-performance liquid chromatography (HPLC),[6−9] for chiral HPLC,[8,10,11] for reverse-phase HPLC (RP-HPLC),[2,8,9,12,13] and for proteins separation by RP-HPLC.[12,13]

To constitute an improved stationary phase for chromatography, MTS should present spherical and absolutely nonaggregated particles to ensure narrow chromatographic peaks (particle-size scattering seriously affects the chromatography peak width and consequently the separation process). Average particle size is given by chromatographic kinetic studies.[14,15] The kinetic properties of a material are

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of prime necessity to be used as stationary phase and reveal the solute dispersion into the column. The development of MTS materials in chromatography for separation of larger molecules such as peptides or proteins in applications such as diagnostic or proteomic requires large-pore stationary phase with pore size larger than 6 nm. Even if the preparation of MTS as discrete silica spheres by direct MTS synthesis has been the target of several research groups in the past few years for chromatographic purpose, all of these studies have led to particles aggregation as revealed by scanning electron microscopy images.[7,9,12,13,16−19] Most of these syntheses use nonionic alkyl-polyethylene-oxyde (C_nEO_m) surfactant near the isoelectric point of silica[9,16] or nonionic triblock-copolymer surfactant $EO_nPO_mEO_n$ in very acidic media,[19,20] or mixture of nonionic triblock-copolymer surfactant $EO_{20}PO_{70}EO_{20}$ and cetyltrimethylammonium bromide (CTAB) in very acidic media.[12,13,17,18] The later gives rise to large-pore MTS (9.8 nm pore size) but without avoiding particles aggregation. Other much heavier processes such as spray-drying even by MTS direct synthesis,[21−23] or by agglomeration of MTS nanoparticles[24] have been investigated, as well as oil-drop[25] which has been proposed to form spheres. However, no evidence has been brought yet that it would allow the synthesis of discrete spheres suitable for chromatographic studies. Pseudomorphic synthesis of MTS materials[15] is to our knowlegde the only way to readily synthesize MTS discrete spheres and furthermore to successfully reach the independent control of the nanometric and micrometric scales in MTS synthesis.

Our present study focuses on the development of large-pore mesoporous MTS formed by pseudomorphic synthesis for liquid chromatography applications. To enhance the possibility to use MTS in protein separation processes, one needs to increase the pore size beyond the diameter of the micelles at least to diameter larger than 6 nm, while preserving discrete nonagglomerated spheres of 10-μm particle size. Enlargement of the pore size of MTS is a technological challenge. The most employed method is the solubilization of a swelling agent (oil) in micelles.[1,26−31] In this case the template is not a plain surfactant micelle but instead a nanometric scale emulsion. The best oil to enlarge MTS pores and to keep them cylindrical in the range 6−10 nm is 1,3,5-trimethylbenzene (TMB)[28,30] or mixtures of TMB/decane.[31] This study concerns the control of the pseudomorphic synthesis of MTS using emulsion constituted by alkyltrimethylammonium surfactants and swelling agents such as TMB and decane and represents the double challenge to obtain large-pore MTS together with keeping discrete silica spheres.

Table 1. Features of Starting Silicas: Unsized (Gn/II) and Sized (Gn/I) Highly Porous Silicas

sample	V (mL/g)	S (m^2/g)	D_{BdB} (nm)	d_p (μm)
G2/II	1.80	240	24	17 ± 10
G3/II	1.66	290	29	9 ± 8
G5/II	1.58	320	32	10 ± 9
G3/I	1.66	230	29	8.8 ± 3
G5/I	1.58	245	32	7.6 ± 4

Experimental Section

Large-Pore MTS Synthesis from Nonporous Silica. Before using preformed silica spheres to synthesize MTS with spherical particle shape, a study of the swelling effect of 1,3,5-trimethylbenzene (TMB) with a nonporous silica was performed. MTS samples were synthesized using Aerosil 200 (Degussa) as silica source, cetyltrimethylammonium or octyltrimethylammonium bromide (C_{16}TAB or C_{18}TAB, Aldrich), 1,3,5-trimethylbenzene (TMB, Aldrich), NaOH (SDS), and deionized water in the molar composition 1:0.1:0−1.3:0.25:0.035:20 SiO_2/C_{16}TAB/TMB/NaOH/$NaAlO_2$/H_2O. All reactants were added at the same time, stirred for 30 min at room temperature, and then autoclaved for 20 h in static condition at 115 °C. The resulting slurry was then filtered, washed with water until neutral pH, and dried overnight at 115 °C. The samples were then calcined at 550 °C for 8 h under air flow.

Pseudomorphic Large-Pore MTS Synthesis. The synthesis of large-pore MTS was realized according to the pseudomorphic synthesis procedure described previously.[15] Preformed silica spheres are the starting materials for the pseudomorphic synthesis of MTS materials, which transforms the interparticular porosity of the starting silica gel into the ordered porosity of MTS directly inside the silica beads without forming MTS in the solution. The sources of silica beads of ca. 10 μm used in this study are the so-called highly porous silica gels (called G2, G3, and G5 silicas in the present study) obtained by emulsion/polymerization as described below and that feature large pore volume as reported in Table 1. The MTS pseudomorphic synthesis performed with the highly porous silicas used a mixture of TMB/decane in different molar ratios of NaOH, C_{18}TAB, and NaI (SDS). The optimized molar ratio was the following: $0.3 < \text{NaOH/Si} < 0.4$, $0.075 < C_{18}\text{TAB/Si} < 0.1$, $0 < \text{NaI/Si} < 0.1$, while keeping constant TMB/C_{18}TAB $= 1.5$ and decane/C_{18}TAB $= 2$. Different experimental conditions were tested for the pseudomorphic synthesis to understand the behavior of the different reactants during the synthesis. For a typical experiment (MTS4) the molar ratio used was 1:0.075:0.1125:0.15:0.019:0.3:40 SiO_2/C_{18}TAB/TMB/decane/NaI/NaOH/H_2O. A first solution containing H_2O/NaOH/NaI/C_{18}TAB was stirred at 55 °C until a clear solution was obtained. Then the swelling agents decane and then TMB were added and the mixture was stirred at 55 °C for 1 h. The silica beads were added under

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low shear stirring and the temperature was raised to 90 °C. The mixture was then stirred for 4 h at 90 °C. The slurry was then filtered and washed with water until neutral pH was obtained. The samples were then dried at 100 °C for 24 h and calcined at 550 °C for 8 h under air flow.

Highly Porous Silica Gel Synthesis. The syntheses of highly porous silica particles were performed in three steps. (a) First polyethoxy siloxane (PES) was prepared by hydrolytic polycondensation of a prepolymerized tetraethoxysilane, labeled TES 40 (Wacker Chemie Gmbh, Burghansen), 1300 g of TES 40 was added to 280 g of ethanol and stirred, then 60 g of HCl (0.1 M) was added dropwise. Then ethanol was removed at 140 °C by a rotary evaporator under 50 mbar, and the remainder was put under nitrogen for 14 h at 140 °C. (b) Second, 550 mL of this PES was mixed with 33 g of dimethylformamide (DMF) and various amounts of cyclohexane. Higher amounts of cyclohexane induce higher pore volume to the final resulting silica gels: 150, 300, and 600 mL of cyclohexane were added to form G2, G3, and G5, respectively. Then the slurry was added to a mixture of 2700 mL of water and 1500 mL of 2-propanol and stirred. The mixture was emulsified for 5 min and then 250 mL of ammonia was added at once. After 30 min of stirring, the suspension was allowed to sediment for 24 h. The supernatant was then decanted and the residue was suspended in 8 L of water. Again, particles were allowed to sediment for 24 h. After the third sedimentation, the residue was suspended in 2 L of water. The suspension was then filtered on a Büchner funnel with a paper filter and washed with 3 L of water at room temperature and with 2 L of methanol. (c) Third, the silica was dried in a vacuum oven for 24 h at 140 °C under 20 mbar. A 150-g portion of this silica was suspended in 1500 mL of water under stirring at room temperature and 15 mL of 25% (w/w) ammonia was added. To maintain a pH of 7, it was necessary to heat the suspension for 8 h at 70 °C. The suspension was then filtered and washed with 5 L of water, 2 L of 2-propanol, and 1 L of methanol. The silica was then dried for 4 h at 150 °C under vacuum. Finally, silica was heated at 650 °C for 5 h, with a heat-up time of 1 °C/min.

Characterization. Materials were characterized by nitrogen adsorption−desorption at 77 K (Micromeritics ASAP 2000) and by thermogravimetric analyses (Setaram 90C). Average pore diameters have been evaluated from the nitrogen desorption branch according to the Broekhoff and De Boer method;[32] as this method is one of the best to evaluate pore size of MTS materials.[33] Particle size distributions were made by granulometric analysis (Malvern Instruments Mastersizer 2000). Scanning electron microscope (SEM) examination of the particles was performed using a Hitachi S-4500 I. Sizing of highly porous silicas into ca. 10-μm fractions was performed by air elufriction using a zigzag siever (M100 by Alpine AE, Aussburg, Germany).

Results and Discussion

Large-Pore MTS Synthesis from Nonporous Silica. Before using preformed porous silica spheres as silica source for the synthesis of large-pore MTS, synthesis conditions and swelling mechanisms have been investigated from less expensive nonporous silica. TMB is the swelling agent most used in the literature to increase the average pore diameter of MTS.[1,26,27,30] We have observed that an increasing amount of TMB between $0 < \text{TMB/C}_{16}\text{TAB} < 13$ in the synthesis gel increases the average pore diameter of MTS from 3.9 to 9 nm (Figure 1), and the pore volume from 0.8 to 1.9 mL/g with a similar specific surface area of ca. 1000 m^2/g. A constant specific surface area is characteristic of a constant wall thickness controlled by the alkalinity and the surfactant ratio[34,35] and in this case corresponds to wall thickness of 1.2 nm. From the XRD pattern,[33] large-pore MTS revealed a disordered hexagonal structure. The increase of average pore diameter as a function of the amount of TMB used in the synthesis is not linear, but shows three steps (Figure 1): (a) for a ratio $0 < \text{TMB/C}_{16}\text{TAB} < 1.6$, the diameter remains the same as the synthesis without TMB around 4 nm, TMB does not swell the micelles; (b) for $1.6 < \text{TMB/C}_{16}\text{TAB} < 5$, the average pore diameter increases rapidly to 8.5 nm, TMB swells the micelles; (c) for TMB > 5, the average pore diameter remains almost constant at 9 nm, the solubilization limit of TMB in C_{16}TAB micelles is reached. A more hydrophobic micellar interface achieved by changing the surfactant counterion permits increasing the amount of TMB in the micelle and therefore increasing the pore size. A lower pore diameter (7 nm) is obtained by using cetyltrimethylammonium chloride (C_{16}TACl)[26] instead of bromide (C_{16}-TAB), and a higher pore size (10 nm) was reached by exchanging 25% of bromide by iodide anions in C_{16}TAB micelles. This maximum pore diameter can be further enlarged to 15 nm by using octyltrimethylammonium bromide C_{18}TAB (Figure 2) instead of C_{16}TAB. A more hydrophobic surfactant allows solubilization of more TMB molecules.

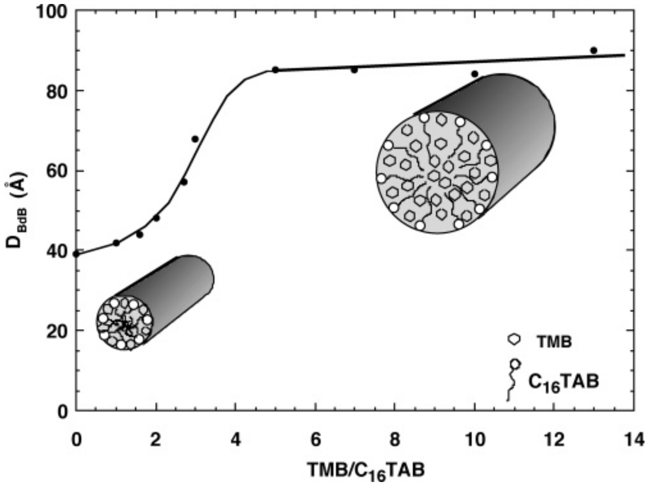

Figure 1. Evolution of MTS average pore diameter as a function of TMB amount introduced in the synthesis mixture of MTS synthesized from nonporous silica at the molar composition 1:0.25:0.1:x:0.035:20 $\text{SiO}_2/\text{NaOH}/\text{C}_{16}\text{TAB}/\text{TMB}/\text{NaAlO}_2/\text{H}_2\text{O}$. At low TMB content (TMB/CTAB < 1.6), TMB solubilized around the headgroups of the surfactants; at high TMB content, TMB penetrates in the core of the micelle and swells the micelle.

The nonlinear evolution of average pore diameter as a function of TMB amount (Figure 1) is explained by the different sites of TMB solubilization in the C_{16}TAB micelles. For $0 < \text{TMB/C}_{16}\text{TAB} < 1.6$, no swelling is observed due to preferential adsorption of low-substituted aromatic mol-

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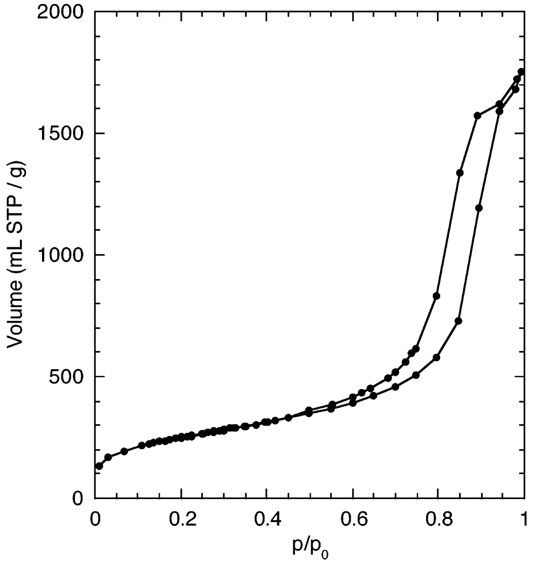

Figure 2. Nitrogen adsorption−desorption isotherm at 77 K of large-pore MTS synthesized from nonporous silica as silica source with $C_{18}TAB$ at the molar composition 1:0.25:0.1:1.3:0.035:20 $SiO_2/NaOH/C_{18}TAB/TMB/NaAlO_2/H_2O$ (average pore diameter of 15 nm, pore volume of 2.5 mL/g, specific surface area of 913 m^2/g).

ecules near the quaternary ammonium headgroups due to cation−π interactions.[36] Then for $1.6 < TMB/C_{16}TAB < 5$, TMB swells the $C_{16}TAB$ micelles, TMB is solubilized in the core of the micelles, and MTS average pore diameter increases. The incorporation of TMB in the core of the micelle is facilitated by the more hydrophobic environment at the micellar interface given by the TMB in interaction with the ammonium headgroups. For $5 < TMB/C_{16}TAB < 13$, no additional amount of TMB is incorporated in the micelle, and no swelling effect is observed, but a better organization in the material is noticed. The pore size distribution becomes narrower for the highest amount of TMB ($TMB/C_{16}TAB = 13$), so pores are more homogeneously cylindrical.

The better organization of the materials and the more cylindrical pores for the highest amount of TMB can be explained by the thermodynamics of the nanoemulsion which are controlled by the elasticity properties of the surfactant layers. In emulsion, oil/water/surfactant systems, phase diagrams (Figure 3) exist as a function of two parameters:[37] $W = (\Phi/\Phi_0)/(C_0 l_0)$ where Φ is the surfactant volume fraction, Φ_0 is the oil volume fraction, C_0 is the spontaneus curvature (which is close to the surfactant packing parameter (g) defined by Israelachvili[38,39] where $g = V/a_0 l_0$), l_0 is the surfactant chain length, a_0 is the area of the surfactant head, and K id called the deformation modulus which is approximately proportional to a^{-2}, with a being the area of the alkyl chain end.[40] If Φ_0, the fraction of oil, is taken as oil volume per surfactant when $V = \Phi$, W will be close to $W = a_0/\Phi_0$.

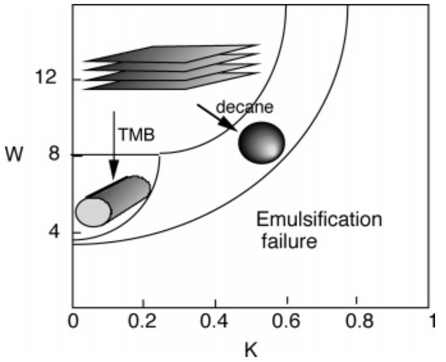

Figure 3. General emulsion phase diagram of oil/water/surfactant mixtures as a function of $W = (\Phi/\Phi_0)/(C_0 l_0)$ where Φ is the surfactant volume fraction, Φ_0 is the oil volume fraction, C_0 is the spontaneus curvature, l_0 is the surfactant chain length, and K is the deformation modulus (see text). Lamellar, cylindrical, and spherical phases stabilities are given.

For TMB/CTAB > 5, the increase in TMB amount increases the oil volume per surfactant for a constant surfactant head and a constant surfactant end area; therefore for a constant K, W decreases. The better organization of the pore given by a narrower pore size distribution of cylindrical pores by increasing TMB amount comes to the fact that the synthesis conditions are close to the frontier between lamellar and cylindrical phases of the nanoemulsion, and a higher amount of TMB allows the transition between these two phases and stabilizes the cylindrical phase of the nanoemulsion. In the literature, the transition from lamellar phase to cylindrical phase has been effectively observed by increasing the amount of oil.[41]

Pseudomorphic Large-Pore MTS Synthesis. The pseudomorphic synthesis of MTS transforms the intergranular porosity of amorphous porous silica gels into ordered porosity.[15] Each silica particle acts as a nanoreactor where silica inside the particle is dissolved under basic condition and is reprecipitated immediately with surfactant molecules present in the particle. Mesostructured silicas obtained by pseudomorphic synthesis are metastable phases, therefore the pseudomorphic synthesis is kinetically controlled and the transformation is progressive. For pseudomorphic syntheses without swelling agent, 24 h at 115 °C is necessary to transform all intergranular porosity into ordered porosity. The rate of pseudomorphic transformation depends on the synthesis conditions. Nevertheless, some limitations exist: (a) particles explosion can occur if the transformation is too fast, for instance if $C_{18}TAB$ is used instead of $C_{16}TAB$ since a longer alkyl chain of alkyltrimethylammonium increases the synthesis rate of MTS,[42] or if the pore volume of the precursor silica source is too low to accommodate the large pore volume developed by MTS synthesis; (b) outside particle nucleation (Ostwald ripening) can occur if the synthesis time is too long, some silicate species outside the particles start to nucleate at the outer surface of the particles and form noodles with hexagonal section; (c) particle aggregation occurs if the particles suspension is too concentrated. All kinetic conditions have to be controlled to overcome these limitations in pseudomorphic synthesis.

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Table 2. Features of MTS Materials Produced by Pseudomorphic Transformation from Unsized Highly Porous Silica G2/II ($d_p = 17 \pm 10$)

sample	NaOH/Si	C_{18}TAB/Si	NaI/Si	V (mL/g)	S (m^2/g)	D_{bdB} (nm)	d_p (μm)	aggregation[a]
MTS1	0.3	0.1	0.025	1.34	890	6.8 ± 1.5	39 ± 13	A
MTS2	0.3	0.087	0.022	1.24	875	5.8 ± 1.0	14 ± 8	NA
MTS3	0.3	0.081	0.020	1.20	750	6.8 ± 0.7	14 ± 10	NA
MTS4	0.3	0.075	0.019	1.48	790	8.4 ± 0.9	14 ± 6	NA
MTS5	0.35	0.075	0.019	1.81	910	8.7 ± 0.9	27 ± 18	A
MTS6	0.35	0.1	0.025	1.94	1016	7.9 ± 0.8	41 ± 26	A
MTS7	0.4	0.1	0.025	1.96	1070	7.4 ± 0.9	30 ± 17	A
MTS8	0.3	0.075	0	1.43	795	7.3 ± 1.0	10 ± 5	NA
MTS9	0.3	0.075	0.037	1.46	700	9.2 ± 1.0	25 ± 15	A
MTS10	0.3	0.075	0.056	1.43	685	9.6 ± 1.2	31 ± 20	A

[a] A, aggregated; NA, nonaggregated.

To synthesize large-pore MTS, which developed very high pore volume (ca. 2 mL/g), it was necessary to start from highly porous silica materials. By using the protocol described in the Experimental Section, three batches of highly porous silica spheres called G2/II, G3/II, and G5/II of ca. 300 m^2/g specific surface area, 1.8 mL/g pore volume, and 30-nm average pore diameter were obtained (Table 1). The particle size distribution of these silicas is quite broad (ca. 10 ± 10 μm). Some further sizing has been performed on two batches (G3/II and G5/II) leading to two sized silica beads (G3/I and G5/I) with particle sizes of $d_p = 8 \pm 3$ μm (Table 1).

Pseudomorphic large-pore MTS synthesis performed with the synthetic conditions optimized for nonporous silica using C_{16}TAB or C_{18}TAB and TMB as swelling agent with a ratio TMB/surfactant = 13 have successfully led to large-pore MTS with ca. 10−15 nm average pore diameter, but, unfortunately, particle aggregation could not be avoided. To some extent TMB acts as a "glue" for silica particles by decreasing the repulsion between silica particles by changing ionic forces in water induced by a higher hydrophobic character of the synthesis medium. The use of TMB is another limitation to the pseudomorphic transformation. At this point the challenge was to optimize the synthesis conditions to limit the use of TMB. Replacing TMB with another swelling agent such as decane does not lead to cylindrical pore geometry but to spherical pore geometry by decreasing the surfactant end area *a* which leads to a cone shape for the surfactant favoring spherical micelles (Figure 4). With decane as swelling agent, the pores appear to be a succession of interconnected spheres, and, furthermore the maximum average pore diameter reached is 4.9 nm.[30] To obtain pores with cylindrical geometry without particle aggregation, one needs to maintain a large surfactant head surface with a minimum amount of TMB. The amount of TMB around the headgroup of surfactant has been determined by the study using nonporous silica as silica source and has been revealed to be TMB/surfactant = 1.6 (Figure 1). Therefore, TMB/surfactant ratio = 1.5 has been chosen as the minimum amount of TMB and the swelling effect has been ensured by adding decane, with decane/TMB = 2 as recommanded by Blin et al.[31] The geometry of the surfactant as a truncated cone will be in accordance with a cylindrical shape of the resulting micelles (Figure 4). To get the highest pore size, C_{18}TAB has been used instead of C_{16}TAB and 25% of iodure anions have been added to the C_{16}TAB micelles. NaI has been added to favor the penetration of TMB and decane in the micelles. An amount of water twice that engaged in the synthesis from nonporous silica has been used to prevent aggregation. Note that an amount of water too high leads to an emulsion failure, and as a consequence, to the formation of small pores of 4 nm. As previously mentioned, too fast an MTS synthesis could lead to a failure in pseudomorphic transformation. The use of TMB accelerates the synthesis of MTS materials,[43] so to slow the reaction a lower synthesis temperature was used: 90 °C for 4 h instead of 115 °C for 24 h. The optimization of the synthesis in terms of surfactant, NaOH, and NaI concentration was performed with the highly porous silica named G2/II possessing a large particle size distribution 17 ± 10 μm, using nitrogen adsorption measurements, SEM, and granulometry as diagnostic (Table 3, Figures 5 and 6). All MTS possess large cylindrical pores with average pore diameter between 6 and 10 nm, high specific surface areas between 700 and 1000 m^2/g, and high pore volume between 1.20 and 1.96 mL/g, but with different states of particles aggregation. All syntheses lead to a silica yield around 55% and surfactant yield around 100%. Almost half of the native silica is dissolved and remains as silicate species in the suspension available for making necks between silica beads.

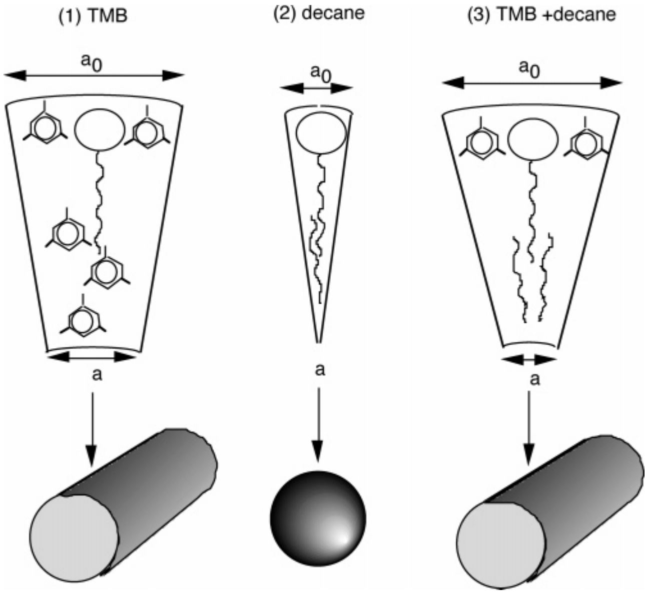

Figure 4. Schematic representation of the surfactant geometries developed by mixtures of (1) TMB/CTAB, (2) decane/CTAB, and (3) TMB/decane/CTAB; with a_0 and a being the areas of the surfactant head and tail, respectively, giving rise to cylindrical or spherical swelled micelles.

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(43) Ottaviani, M. F.; Moscatelli, A.; Desplantier-Giscard, D.; Di Renzo, F.; Kooyman, P. J.; Alonso, B.; Galarneau, A. *J. Phys. Chem. B* **2004**, *108*, 12123.

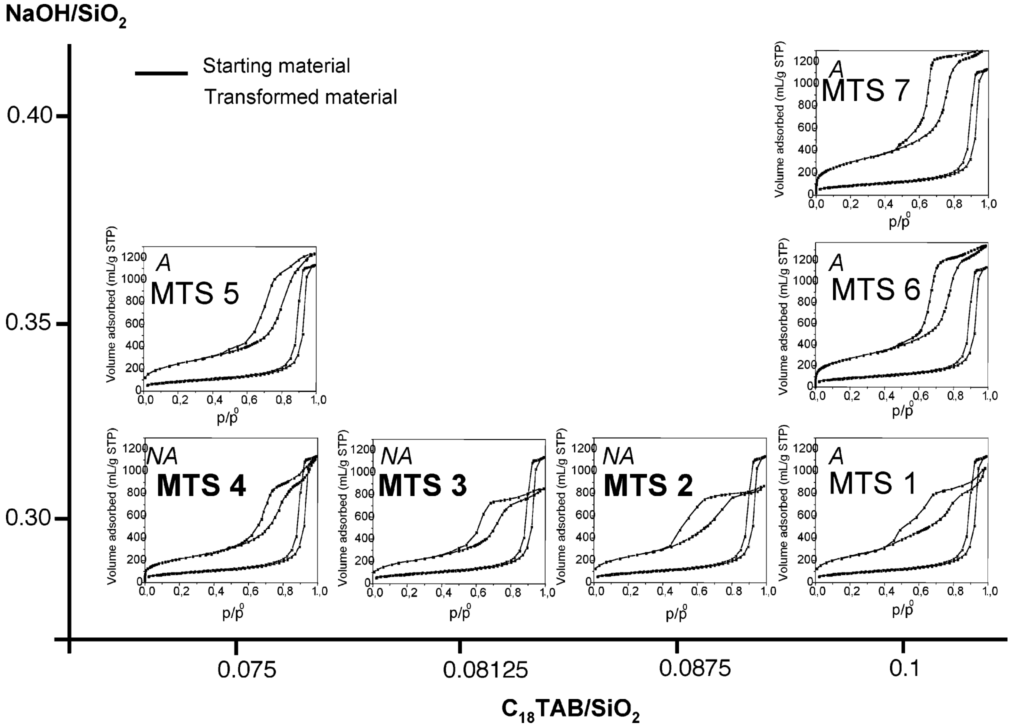

Figure 5. Nitrogen sorption isotherms at 77 K of MTS synthesized from pseudomorphic transformation from G2/II with varying amounts of $C_{18}TAB$ and NaOH in the molar composition 1:*x*:*x*/4:1.5*x*:3*x*:*y*:40 $SiO_2/C_{18}TAB/NaI/TMB/decane/NaOH/H_2O$, with $0.075 < x < 0.1$ and $0.3 < y < 0.4$. *A*, aggregated particles, and *NA*, nonaggregated particles.

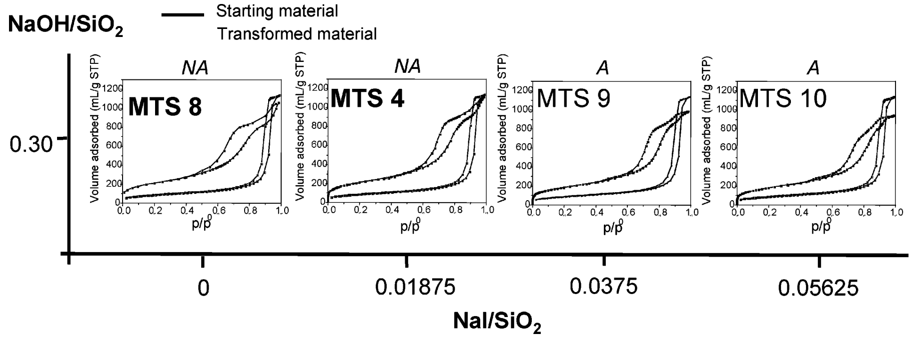

Figure 6. Nitrogen sorption isotherms at 77 K of MTS synthesized from pseudomorphic transformation from G2/II with varying amount of NaI in the molar ratio: 1 SiO_2/0.075 $C_{18}TAB$/x NaI/0.1125 TMB/0.225 decane/0.3 NaOH/40 H_2O, with $0 < NaI < 0.1$. *A*: aggregated particles, and, *NA*: nonaggregated particles.

Table 3. Features of Large-Pore MTS Showing No Particles Aggregation Produced by Pseudomorphic Transformation of Different Highly Porous Silicas under the Optimized Condition 1:0.075:0.019:0.112:0.225:0.3:40 $SiO_2/C_{18}TAB/NaI/TMB/Decane/NaOH/H_2O$

sample	starting silica	*V* (mL/g)	*S* (m^2/g)	D_{BdB} (nm)	d_p (μm)
MTS4	G2/II	1.48	790	8.4 ± 0.7	14 ± 6
MTS11	G3/II	1.37	750	7.4 ± 1.0	8 ± 7
MTS12	G5/II	1.47	890	6.7 ± 0.9	10 ± 9
MTS13	G3/I	1.41	780	6.6 ± 1.5	8 ± 3
MTS14	G5/I	1.35	804	6.6 ± 1.3	7 ± 3

In Figure 5 are represented the nitrogen adsorption–desorption isotherms of the initial silica G2/II together with the isotherms of its pseudomorphic transformations in the optimized synthesis mixtures corresponding to the following molar ratios: 1:*x*:*x*/4:1.5*x*:3*x*:*y*/40 $SiO_2/C_{18}TAB/NaI/TMB/decane/NaOH/H_2O$, with $0.075 < x < 0.1$ and $0.3 < y < 0.4$. The MTS synthesized with $C_{18}TAB/SiO_2 = 0.1$ at $NaOH/SiO_2 = 0.3$ (sample MTS1), gives a bimodal pore distribution and aggregated particles. Increasing the amount of sodium hydroxide increases the pore volume (1.95 mL/g) and the specific surface area (1070 m^2/g), and gives a narrower pore size distribution (7.5 ± 0.9 nm) (Table 2). Unfortunately, MTS (MTS7 and MTS6) materials obtained under these synthesis conditions show particles aggregation maybe due to too high an amount of TMB associated with the surfactant in the synthesis mixture compared to silica. As already mentioned, TMB by its hydrophobic behavior decreases the polar state of the silica particles, diminishes their repulsion, and then favors their agglomeration. Decreasing the amount of surfactant in the synthesis effectively avoids particles aggregation as observed for MTS2, MTS3, and MTS4 (Figure 5). The amount of TMB/SiO_2 should be inferior to 0.13. The pore volumes for these nonaggregated large-pore MTS are approximately 1.3 mL/g, specific surface area of 800 m^2/g, and average pore diameter approximately 7−8 ± 0.6 nm. MTS4 synthesized with the lower amount of surfactant ($C_{18}TAB/SiO_2 = 0.075$) shows the larger pore size and the narrower pore size distribution ($D = 8.4 \pm 0.9$

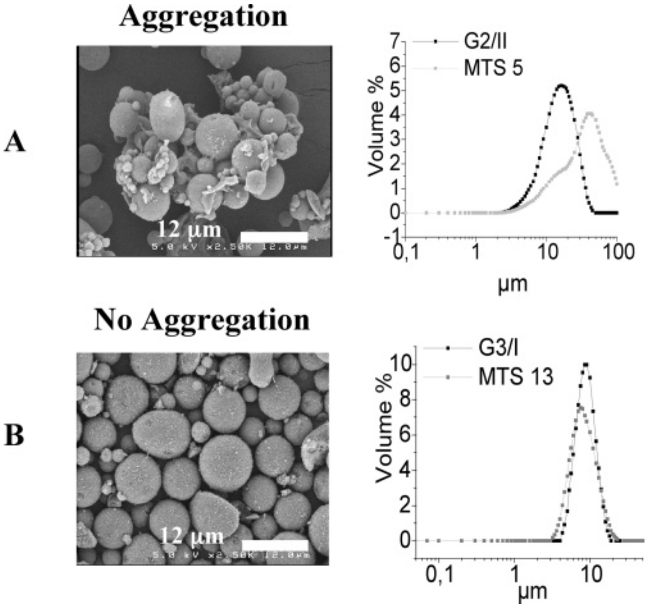

Figure 7. SEM pictures and particle size distributions of the products MTS5 and MTS13 of pseudomorphic transformation of (A) unsized G2/II and (B) sized G3/I, respectively, showing no particles aggregation in the case of MTS13.

nm). Increasing the amount of sodium hydroxide in this synthesis leads to a MTS (MTS5) of 8.7-nm average pore diameter with higher pore volume (1.81 mL/g) and higher specific surface area (900 m^2/g) than previously noticed, but for this sample particles are aggregated (Figure 7). For high amounts of sodium hydroxide, the yield of silica decreases slightly from 55 to 50%, leaving even more silicates in solution available to form silica necks between particles. There is a compromise between high specific surface area and particle aggregation governed by the sodium hydroxide amount. The best MTS is then MTS4 with $V = 1.48$ mL/g, $S = 790$ m^2/g, and $D = 8.4 \pm 0.9$ nm. Increasing the amount of NaI compared to this synthesis (Figure 6 and Table 2) leads to the increase of MTS average pore diameter. An average pore diameter of $D = 9.6 \pm 1.2$ nm (MTS10) has been obtained for the higher amount of NaI, but unfortunately, this synthesis also leads to particles aggregation. By having a more hydrophobic interface, TMB may more easily play its role of glue between particles, by decreasing repulsion between particles. Removing NaI from the synthesis (MTS8) leads to smaller average pore diameter of 7.3 nm, without particle aggregation. The best synthesis conditions to obtain large-pore MTS without particles aggregation are the following (corresponding to MTS4): 1:0.075: 0.01875:0.1125:0.225:0.3:40 SiO$_2$/C$_{18}$TAB/NaI/TMB/Decane/NaOH/H$_2$O.

These optimum experimental conditions for large-pore MTS synthesized by pseudomorphic transformation have been applied to 3 unsized and 2 sized highly porous silicas (Table 3). Results similar to those of MTS4 with nonaggregated particles have been obtained. Two large-pore MTSs obtained from sized precursor (MTS13 and MTS14) possess a narrow particle size distribution ($d_p = 8 \pm 3$ μm), same as the parent silicas (Figure 7), and pore volumes of 1.4 mL/g, specific surface areas of 800 m^2/g, and average pore diameter of 6.6 ± 0.9 nm.

Conclusion

We successfully developed new advanced MTS supports with large mesopores (7−9 nm pore diameter) for chromatography purposes by means of the pseudomorphic route combining an original set of chemical compositions (C$_{18}$TAB/decane/TMB/NaI) under mild conditions (low temperature, without autoclaving) to avoid particles aggregation. The main difficulty we had to solve arises from the availability of dissolved silicates species in the synthesis mixture, which are responsible for the formation of silica necks between particles. A low amount of TMB and an adequate amount of NaOH are required to avoid particle aggregation. This synthesis procedure has been successfully scale-up at hundred grams scale. The control at nanometric scale, by means of surfactants, leads to improved textural properties compared to optimized silica gels, whereas the control of the micrometric morphology (discrete spheres) makes these supports suitable for column packing and chromatographic evaluation (under testing).

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