# A double step synthesis of mesoporous micrometric spherical MSU-X silica particles

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**Spherical particles of mesoporous MSU-X silica in the micrometric size range have been obtained through a new double step process that led to an easy and highly reproducible synthesis pathway giving micelle templated structures with a large surface area and narrow pore size distribution**

Micelle templated structures (MTS), like the mesoporous alumino-silicates M41S (MCM-41, MCM-48) are synthesized through an assembly mechanism between long chain quaternary ammonium compounds and inorganic species. They exhibit desirable properties such as high surface area (*ca*, 1000 $m^2 g^{-1}$) and narrow pore size distribution in the range 20–100 Å.[1,2] Since their discovery, many groups have succeeded in expanding this new field to other ionic surfactants.[3] The possibility of using non-ionic surfactants such as those based on polyethylene oxide and block-copolymers was also demonstrated,[4–9] which led to a whole family of mesoporous silicas such as MSU-V,[10] MSU-G[11] and MSU-*X* ($X$ = 1–4), where $X$ refers to the non-ionic surfactant molecules that can be either alkyl PEO, alkyl–aryl PEO, polypropylene oxide PEO block copolymers or ethoxylated derivatives of sorbitan fatty esters (Tween™).[4] Although some reactions proceed in acidic or basic media,[12] syntheses of MSU-X materials were generally reported to occur at neutral pH even though syntheses using non-ionic block copolymers under highly acidic conditions (SBA-type materials) were also successfully explored.[8,13]

Whatever the nature of the template, among possible applications such as catalysts, grafting supports, or filtration materials, the use of MTS for chromatography applications has been claimed for years. However, this latter application requires the ability to synthesize homogeneous batches of spherical particles with a mean diameter of at least 5 μm.[14] Even if such particles have been observed once in a pH-dependent synthesis of MCM-41 particles,[15] until now the only specific syntheses have been of sub-μm particles of MCM-41 or MCM-48 materials[16–18] or 2 μm HMS particles.[19] Here, we describe the synthesis of MSU-X silica with perfectly controlled size and shape that would be suitable for liquid phase chromatography applications.

Our synthesis is based on a sodium fluoride aided hydrolysis of tetraethoxysilane dissolved in a dilute solution of non-ionic polyethylene oxide-based surfactants.[6,20] Depending on the initial mixing conditions, a milky mixture is usually obtained that settles to give a colorless microemulsion if conditions are carefully chosen. The final product contains aggregates of small particles (*ca.* 300 nm) with a 3D worm-hole porous structure.[21] We modified this synthesis process by an apparently slight but actually drastic change in the preparation. The main feature of this new approach lies in the capability to discriminate the assembly step from the hydrolysis step. To this purpose we added an intermediate step that utilises a mild acidic medium (pH *ca.* 2–4) in which, prior to the reaction, a stable colorless microemulsion containing all reactants is obtained. Hence, whatever the initial homogeneity of the surfactant–TEOS mixture, the homogeneity at the molecular level is always attained before the reaction starts. Moreover, one can use a TEOS/surfactant molar ratio of up to 25 or a swelling agent such as 1,3,5-trimethylbenzene and still obtain a stable colorless microemulsion, without any reaction. Hence, this approach does not proceed from previously reported systems such as for the synthesis of SBA materials that use block copolymers[8,13] or the synthesis of modified MSU-X materials through an acid $[N^0(N^+)X^-I^-]$ pathway[12] because these syntheses used acid as the hydrolysis catalyst whereas we use it only as an emulsion breaker (actually, a slight hydrolysis is observed but only after several days). As previously reported, the actual catalyst of the hydrolysis still remains sodium fluoride.[6]

In a typical synthesis, TEOS (Aldrich Chemicals) was dispersed in a 0.02 M solution of Tergitol 15S12 ($CH_3(CH_2)_{14}(EO)_{12}$, Union Carbide Chemicals) up to a molar ratio TEOS/surf. = 8. A milky emulsion was obtained, but the addition of 0.25 M hydrochloric acid (final pH between 2.0 and 4.0) destroys this emulsion within minutes, giving a perfectly colorless microemulsion composed of 6–7 nm monodisperse particles containing both surfactant and TEOS, as observed by dynamic light scattering experiments.[22] The solution was left to stand for 18 h and the hydrolysis of TEOS was induced by the addition of a small amount of sodium fluoride [NaF/TEOS = 1–4 (mol%)]. The reaction begins after *ca.* 1 h and although it is almost totally complete after 6 h, the mixture was allowed to stand for 3 days at 35 °C. A white powder was obtained with a yield close to 100% which was filtered off, dried and calcined at 620 °C for 6 h after a 6 h step at 200 °C (heating rate of 3 °C $min^{-1}$). This new process was successfully applied to the whole family of nonionic surfactants and block-copolymers of MSU-*x* ($x$ = 1–4) materials and preparation of large batches was also successful.

The X-ray pattern (Fig. 1) exhibits a single narrow peak assigned to the pore center to center correlation length, characteristic of a worm-hole structure of the porous framework of MSU compounds.[4,6] Transmission electron microscopy (not shown here) reveals that the whole material is made of such a porous framework and that there is no amorphous component. As shown in Fig. 2, the nitrogen adsorption–desorption

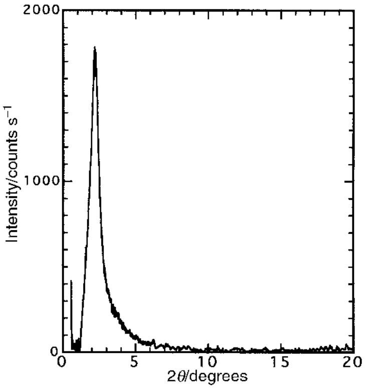

**Fig. 1** X-Ray patterns of calcined MSU-1 silica obtained with Tergitol 15S12 and a NaF/TEOS ratio of 4 mol%. The pattern was recorded with a Bruker D5000 diffractometer in Bragg–Brentano reflection geometry. Cu-$L_{3,2}$ radiation was employed that was monochromatized by a graphite single crystal in the diffracted beam.

isotherm is typical of a well defined porous framework without any textural porosity, but the pore size is very dependent on the amount of fluoride. Keeping other parameters constant, the sample synthesized with a 1 mol% NaF/TEOS ratio exhibited a surface area of 910 $m^2 g^{-1}$ and a pore diameter of 24Å (according to the Broekhoff and de Boer model[23]) whereas the sample synthesized with a NaF/TEOS ratio of 4 mol% gave a material with a pore diameter of 35 Å (surface area 1053 $m^2 g^{-1}$). Along with the higher crystallinity of the calcined material, the ability to increase the pore size by 10 Å by simply changing the amount of fluoride is one of the new features of this synthesis, which makes it different from previous reaction pathways.[4,6,12] This cannot be assigned to a salt effect since adding large amounts of NaCl does not affect the pore size.

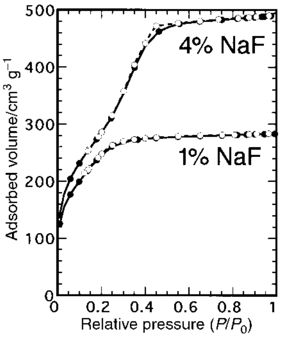

**Fig. 2** Nitrogen adsorption (●) and desorption (○) isotherms of MSU-1 silica synthesized with Tergitol 15S12 and different NaF/TEOS molar ratios. Nitrogen adsorption isotherms were measured at 77 K on a micromeretics 2010 Sorptometer using standard continuous procedures and samples degassed at 150 °C for 15 h.

Since the reaction begins in a homogeneous medium, the final shape and size of particles will depend on the respective kinetics of the nucleation and aggregation processes. This competition depends on the quantity of nucleation seeds, and hence upon the NaF/TEOS ratio and on the concentration of the reagents. At low concentrations ([Tergitol 15S12] = 0.02 M), the aggregation process leads to spherical particles as shown by SEM (Fig. 3). The low rate of nucleation (NaF/TEOS = 1–2 mol%) allows the particles to grow up to the micrometer range and the homogeneity of the starting mixture leads to a quite narrow size distribution. Indeed, the mean size of the spherical particles displayed in Fig. 3(A) is 7 μm. A particle size analysis shows that while 98% of the powder volume is comprised of particles < 10 μm, 83% lie in the 3–8 μm size range. However, since the synthesis was not optimized for the preparation of isolated single particles, some of them that grew too closely together are stuck by grain boundaries that appeared during the particle growth.

The key of this reaction is the ability to separate the assembly step from the condensation step. This approach defines not only an improvement of previously reported syntheses of MSU-X materials, but also a different concept, which is particularly illustrated by the different behavior of some synthesis parameters such as sodium fluoride content. Similarly, syntheses using ethoxylated sorbitan molecules (Tween surfactants), which lead to nanometric particles when synthesized by the usual process,[7] also gives micrometric spherical particles when this new process is applied [Fig. 3(B)]. This makes this synthesis a new example of the versatility of the non-ionic route for the synthesis of MTS materials. Both the simple synthetic pathway along with the possibility to control all steps of the reaction, and the well defined morphology and nanostructure of the resulting powders make them suitable for future liquid phase chromatography applications that are currently being investigated.

## Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

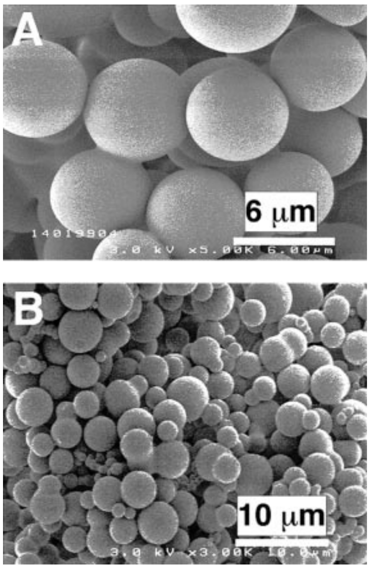

**Fig. 3** SEM photograph of (A) calcined MSU-1 silica obtained with Tergitol 15S12, a molar ratio TEOS/surfactant = 8 and NaF/TEOS = 1 mol% and (B) calcined MSU-4 silica obtained with Tween 20, a molar ratio TEOS/surfactant = 4 and NaF/TEOS = 2 mol%. Spherical micrometric particles can be obtained with both surfactants but the mean size depends on various synthesis parameters, especially the TEOS/surfactant and NaF/TEOS ratios. SEM micrographs were obtained on a Hitachi S-5400 FEG microscope.

2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.
3 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.
4 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
5 S. A. Bagshaw and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 1102.
6 E. Prouzet and T. J. Pinnavaia, *Angew. Chem., Int. Ed. Engl.* 1997, **36**, 516.
7 E. Prouzet, F. Cot, G. Nabias, A. Larbot, P. J. Kooyman and T. J. Pinnavaia, *Chem. Mater.*, 1999, **11**, 1498.
8 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
9 G. S. Attard, J. C. Glyde and C. G. Göltner, *Nature*, 1995, **378**, 366.
10 P. Tanev and T. J. Pinnavaia, *Science*, 1996, **271**, 1267.
11 S.-S. Kim, W. Zhang and T. J. Pinnavaia, *Science*, 1998, **282**, 1302.
12 S. A. Bagshaw, T. Kemmitt and N. B. Milestone, *Microporous Mesoporous Mater.*, 1998, **22**, 419.
13 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
14 R. Rosset, M. Caude and A. Jardy, *Manuel Pratique de Chromatographie en Phase Liquide*, Masson, Paris, 1996.
15 H. Yang, G. Vovk, N. Coombs, I. Sokolov and G. A. Ozin, *J. Mater. Chem.*, 1998, **8**, 743.
16 M. Grün, I. Lauer and K. K. Unger, *Adv. Mater.*, 1997, **9**, 254.
17 M. Grün, K. K. Unger, A. Matsumoto and K. Tsutsumi, *Microporous Mesoporous Mater.*, 1999, **27**, 207.
18 K. Schumacher, M. Grün and K. K. Unger, *Microporous Mesoporous Mater.*, 1999, **27**, 201.
19 G. Büchel, M. Grün, K. K. Unger, A. Matsumoto and K. Tsutsumi, *Supramol. Sci.*, 1998, **5**, 253.
20 A. C. Voegtlin, F. Ruch, J. L. Guth, J. Patarin and L. Huve, *Microporous Mater.*, 1997, **9**, 97.
21 F. Cot, P. J. Kooyman, A. Larbot and E. Prouzet, in *Mesoporous Molecular Sieves 1998*, ed. L. Bonneviot, F. Beland, C. Danumah, S. Giasson and S. Kaliaguine, Elsiever Science, Amsterdam, Lausanne, New York, Oxford, Shannon, Singapore, Tokyo, 1998, vol. 117.
22 C. Boissière, A. Larbot and E. Prouzet, unpublished work.
23 J. C. P. Broekhoff and J. H. de Boer, *J. Catal.*, 1968, **10**, 377.

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