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Preparation of Mesoporous/Macroporous Materials in Highly Concentrated Emulsions Based on Cubic Phases by a Single-Step Method

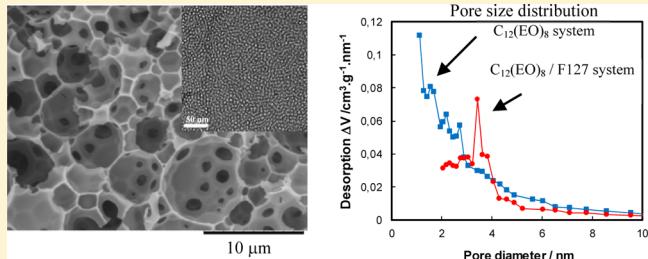
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S Supporting Information

ABSTRACT: A novel and simple single-step method for the preparation of meso/macroporous silica materials is described, which consists in templating in highly concentrated emulsions with a cubic liquid crystal in the continuous phase. Tetraethyl orthosilicate (TEOS) was solubilized in the aqueous continuous phase of highly concentrated emulsions stabilized by $C_{12}(EO)_8$ and a PEO–PPO–PEO block copolymer nonionic surfactant, with a cubic liquid crystalline phase of the $Fd\bar{3}m$ type. The resulting silica materials were characterized by small-angle X-ray scattering, nitrogen sorption and transmission electron microscopy. The results showed that a dual pore size distribution was obtained, consisting of mesopores in the nanometer range and macropores between 1 and 5 μm . These dual meso/macroporous silicas with bimodal pore size distribution can possess specific surface areas higher than 400 m^2/g .



INTRODUCTION

Inorganic solid foams are very important in technological applications such as catalysis and molecular separations. In the past decade, materials with dual meso- and macroporous structures (with bimodal pore size distributions) have attracted a great deal of attention because they combine the advantages of high specific surface areas with the good diffusion properties associated with macropores. Because of these dual properties, meso/macroporous materials are attracting widespread interest in many industrial applications,¹ including chromatographic adsorbents separation processes^{2,3} and photocatalysis.⁴ Other novel applications include fuel cells^{5–7} energy storage^{8,9} or heterogeneous catalysis for biodiesel production.¹⁰

The preparation of macroporous foams made of low-density organic polymers, by polymerizing in the external phase of highly concentrated emulsions, is known from 1982.^{11–18} The early works demonstrated that macroporous organic foams with very high pore volume ($>10 \text{ mL g}^{-1}$) and with well-interconnected macropores can be obtained by this approach.¹⁹ Highly concentrated emulsions are characterized by an internal phase volume fraction higher than 0.74, which is the critical value of closed-packed monodispersed undeformed droplets.^{20–22} Consequently, these emulsions have a foamlke structure, consisting of deformed and/or polydispersed droplets, separated each other by a thin film of continuous phase.^{20–23} Because of this morphology, highly concentrated

emulsions have a viscoelastic rheological behavior that provides them a gel appearance.^{24,25}

Therefore, highly concentrated emulsions can be very useful to obtain materials with high pore volume and interconnected macropores. The first research works focused on porous organic polymers,^{11–16} but porous inorganic oxides can also be obtained. Many examples show that applying sol–gel reactions in the external phase of concentrated and/or highly concentrated emulsions leads to the formation of macroporous and dual meso/macroporous inorganic oxides.^{19,26–38} The first inorganic porous materials, prepared in emulsions, were described in 1997 by Imhof and Pine.²⁶ In this early work, porous inorganic oxides materials with a narrow macropore size were obtained by adding the reagents to the external phase of isoctane-in-formamide emulsions.²⁶ Moreover, dual porosities (with bimodal pore size distributions) can be obtained by combining emulsion droplets with other kinds of templates. For example, dual inorganic oxide materials²⁷ and hybrid organo-inorganic materials^{19,30,33} can also be obtained by sol–gel processing in the external phase of highly concentrated emulsions.

Received: May 24, 2012

Revised: June 22, 2012

Published: June 26, 2012



The final materials possess a very open structure, with windows that interconnect macropores. In highly concentrated emulsions, the biliquid films located between adjacent droplets are very thin, and the precursor molecules are mainly located in the emulsion plateau borders. Consequently, connecting windows are usually formed across the biliquid films.^{27,31,33}

In most of the examples described above, the emulsions were prepared using surfactants as emulsifiers. However, it also has been reported that low-density inorganic oxide materials can be prepared in highly concentrated emulsions stabilized solely with solid particles, in the absence of surfactant (Pickering emulsions).³⁹ Moreover, one can obtain novel nanocomposite materials by polymerizing an organic monomer in Pickering emulsions, obtaining macroporous organic foams with inorganic nanoparticles, which are strongly adsorbed on the material surface.⁴⁰ A recent example of successful synthesis of macroporous material using highly concentrated emulsions stabilized solely with solid particles (Pickering HIPE's) has been described by Backov and coauthors.⁴¹

Meso/macroporous dual materials, with independent control of the size of macropores and mesopores, can be obtained by applying two-step methods. In these methods, macroporous foams are used as sacrifice scaffolds to template the macroporous structure.^{42–47} These organic foams can be prepared, in a first step, by polymerizing in the external phase of W/O highly concentrated emulsion^{42,43} or in multiple emulsions.⁴⁵ The final meso/macroporous dual inorganic materials are obtained, after a second step, in which the organic macroporous foams are impregnated with sol–gel solutions that contain the inorganic oxide precursors and surfactants. The cooperative self-assembly of surfactant molecules and silica species leads to the formation of ordered mesopores. One of the examples is the preparation of dual meso/macroporous materials,⁴² by polymerizing in highly concentrated emulsions to obtain polystyrene solid foams,⁴⁴ which were later impregnated with inorganic precursor solutions containing block copolymer surfactants to form the mesopores. Another example is the use of commercial polyurethane foam as a sacrificial scaffold, which is impregnated with a mixture of F127 surfactant with TEOS.⁴⁷

However, in industrial applications it is very important to obtain such materials by simple and cost-effective methods. The two-step methods described above are rather time-consuming and cannot be adapted easily to industry for mass production. In this context, simple single-step processes would be preferred, in which sol–gel reactions are carried out directly in the external phase of the emulsions.

In single-step methods, a great variety of surfactants can be used, including block copolymer,²⁶ cationic,^{31,34} and ethoxylated nonionic surfactants,^{32,48,49} and the continuous phase of the emulsions can be either a microemulsion³¹ or a liquid crystal.³⁴ However, the phase behavior of the systems composed of surfactant/precursor/solvent has not been investigated in detail. Although it is generally assumed that emulsions consist of “simple” liquid phases being the droplets stabilized by a surfactant monolayer, the continuous phase can be either a microemulsion⁵⁰ or a liquid crystalline phase,^{51,52} and thus highly concentrated emulsions can be classified in two types, with either microemulsion or liquid crystal in the external continuous phase.

In highly concentrated emulsions based on liquid crystals, surfactant aggregates cover the emulsion droplets and prevent their coalescence. The selection of the most appropriate

surfactant system is very important because hydrolysis of TEOS (commonly used tetraethyl orthosilicate) produces ethanol, which may greatly influence the nanostructure of the emulsion continuous phase and therefore can decrease emulsion stability.^{53–55}

In the present work, we propose to use highly concentrated emulsions based on cubic liquid crystals as scaffolds to obtain materials with meso- and macroporous dual structures in a simple single-step procedure. The advantage of this method is that the structure of such emulsions can be regarded as dual: micrometer-sized emulsion droplets and nanometer-sized aggregates. Therefore, the emulsion droplets would template the formation of macropores whereas the cubic liquid crystal, present in the continuous phase, would template the formation of the mesopores, as shown in the formation of cubic mesoporous materials.^{56–58} The surfactant used in this study is a polyoxyethylene-chain nonionic compound, surfactant, which has a well-known phase behavior.^{59,60} This kind of surfactant forms cubic discontinuous phase, in which surfactant aggregates are packed in a cubic array,⁶⁰ is highly viscous, and ensures a very good stability to the emulsions. The phase behavior of these systems has been extensively studied in the past decade by Kunieda and co-workers.^{51,60–62}

On the basis of the knowledge of the inorganic–organic mesophase structures in the case of polyoxyethylene-chain nonionic surfactants and the formation of mesoporous materials in acidic pH,^{48,49,58,63,64} we chose to investigate the addition of the block copolymer surfactant F127 ((EO)₁₀₀(PO)₇₀(EO)₁₀₀) to the above system, in order to control the size of mesopores. Small-angle X-ray scattering, nitrogen sorption, and transmission and scanning electron microscopy were applied for a detailed structural and chemical characterization of the obtained materials. The results indicate that dual meso/macroporous structures could be obtained directly in such systems.

MATERIALS AND METHODS

Materials. The nonionic ethoxylated surfactant octaethylene glycol mono-*n*-dodecyl ether, abbreviated C₁₂(EO)₈, was purchased from Nikko Chemicals Co. (Japan). The poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer surfactant (EO)₁₀₀(PO)₇₀(EO)₁₀₀ (Pluronic F127) was supplied by BASF. Both surfactants were used without further purification. Tetraethyl orthosilicate (TEOS), 99.999%, was supplied by Aldrich. Hydrochloric acid (5 mol dm⁻³) was purchased from Junsei (Japan), and Milli-Q purified water was used in all the experiments. Decane was supplied by Aldrich with a purity higher than 99%.

Preparation of Mesoporous/Macroporous Dual Silica. Highly concentrated emulsions were prepared in the system C₁₂(EO)₈/aqueous solution/decan⁵⁴ by slow addition of decane to the mixture of surfactant and hydrochloric acid aqueous solution. The decane mass fraction was 0.8, and the surfactant:HCl(aq) mass ratio was 4:6. Rigorous stirring was required, since cubic liquid crystalline phases are very viscous. TEOS was added to the highly concentrated emulsions, and the samples were left either at 25 or 35 °C, for 48 h, in open dishes to let solvents evaporate. In a typical synthesis, the composition was 7.4 wt % surfactant, 11.1 wt % HCl(aq) 0.5 M, 74.4 wt % decane, and 7.0% TEOS. At the end, white powders were obtained, which were washed for 24 h in ethanol and dried at 80 °C, until weight was constant. Samples were calcined at 500 °C for 6 h in the presence of air, increasing the temperature at 2 °C/min.

Characterization of the Materials. Small-angle X-ray scattering (SAXS) spectra were obtained in a Nanoviewer Instrument, from Rigaku Corp. (Japan), equipped with point collimation and a CCD camera as detector, operated at 40 kV and 20 mA power beam. The silica samples were placed in a sample holder 1 mm thick and sealed by

Mylar film. In typical experiments, X-ray irradiation was carried out for 3 min. The SAXS measurements were performed on dried as well as calcined samples.

Nitrogen adsorption–desorption isotherms were determined using an adsorption porosimeter (AUTOSORB-1, manufactured by QUANTACHROME). Samples were outgassed at 200 °C and weighed prior to sorption experiments. The specific surface area (S_{BET}) was determined by applying the multipoint BET model⁶⁵ to the adsorption isotherm, in a relative pressure range (p/p_0) from 0.05 to 0.3. The mesopore size distribution was calculated from the desorption curve using the BJH model.⁶⁶

The macroporous structure of the calcined materials was investigated by scanning electron microscopy (SEM), with two instruments: a Hitachi S-4100 operated at 20 kV and a HitachiTM 1000 tabletop at 15 kV.

The mesoporous structure was investigated by transmission electron microscopy (TEM) using a Philips CM30 microscope, equipped with a CCD Multiscan Gatan camera. Samples were prepared by allowing ethanol suspensions of finely divided silicas to evaporate on holey copper grids coated with a carbon film. Observations were carried out at 200 kV.

RESULTS AND DISCUSSION

Preparation and Properties of Highly Concentrated Emulsions in the C₁₂EO₈/Water/Decane System. Highly concentrated emulsions were prepared in the surfactant system studied by Kunieda et al.⁶² consisting of C₁₂(EO)₈/water/decane. Figure 1 shows the phase diagram of such system, at 25 °C.

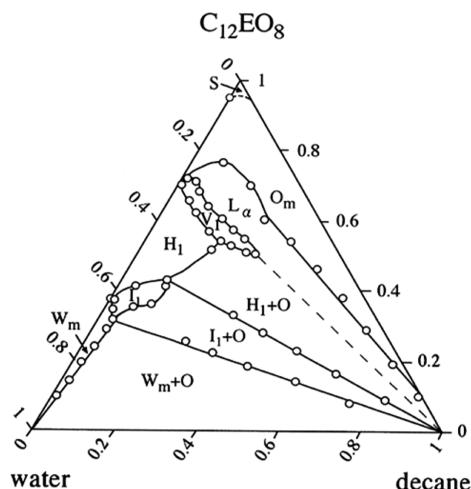


Figure 1. Phase diagram of water/C₁₂(EO)₈/decane ternary system at 25 °C. W_m is an aqueous micellar solution phase. I₁, H₁, V₁, and L_α indicate respectively discontinuous micellar cubic phase, normal hexagonal phase, normal bicontinuous cubic phase, and lamellar phase. O_m is a surfactant liquid or reverse micellar solution phase, O is an excess-oil phase, and S is a solid phase. Reproduced with permission from ref 62. Copyright 2001 Japan Oil Chemists' Society.

°C.⁶² In the water-binary axis, W_m and H₁ phases are observed. The I₁ cubic phase appears after the addition of small amounts of decane, at C₁₂(EO)₈/water ratios close to 4/6.⁶² The phase diagram shows that this cubic phase appears between the W_m aqueous micellar phase and the H₁ direct hexagonal phase. Consequently, the cubic phase is considered to have the structure of a discontinuous micellar cubic phase (I₁) as confirmed by simple dye diffusion tests. At higher decane concentrations this cubic phase coexists with the excess of decane (I₁ + O). Near the decane vertex, “decane-in-cubic phase” highly concentrated emulsions can be formed.

In the present work, highly concentrated emulsions were prepared, by slow addition of decane to the mixture of surfactant and water. Figure 2 shows the appearance of an emulsion, which contains a decane mass fraction of 0.8.

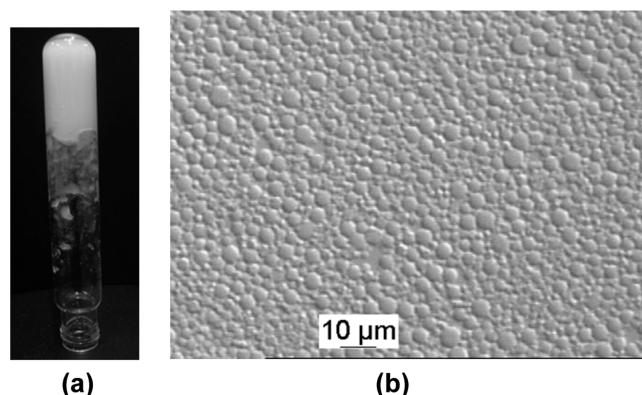


Figure 2. Highly concentrated emulsion, with a decane mass fraction of 0.8 and a C₁₂(EO)₈/water mass ratio of 4/6. (a) Aspect to the naked eye. (b) Image obtained by optical microscopy of the same emulsion.

A highly concentrated emulsion was prepared with the composition 8 wt % C₁₂(EO)₈, 12 wt % of aqueous solution containing HCl 0.2 mol dm⁻³ and 80 wt % decane. This emulsion was very viscous due to the high content of decane (dispersed phase) and the presence of the I₁ cubic liquid crystal in the continuous phase. The structure of the I₁ cubic crystal was confirmed by small-angle X-ray scattering (SAXS). The spectra of the final emulsion showed four Bragg peaks or bands (Figure 3a), which appeared at ratios (q values) approximately

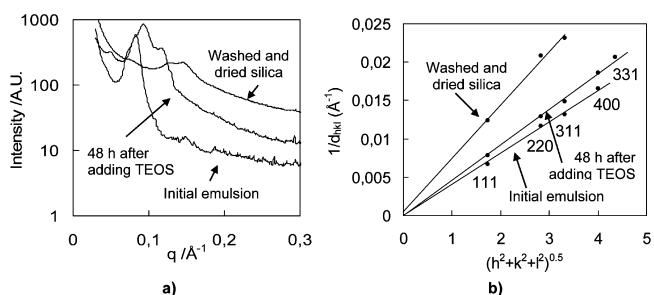


Figure 3. Results obtained by small-angle X-ray scattering (SAXS) of samples prepared in the C₁₂(EO)₈/HCl(aq) 0.5 mol dm⁻³/decane/TEOS system. (a) SAXS spectra; (b) crystallographic assignation of the peaks and bands observed in the spectra. The mass ratio of surfactant/aqueous solution was 4/6 and the percentage of decane, before adding TEOS, was 80 wt %. The overall composition was 7.4 wt % surfactant, 11.1 wt % HCl(aq) 0.5 mol dm⁻³, 74.4 wt % decane, and 7.0% TEOS.

equal to $\sqrt{3}/\sqrt{3}$, $\sqrt{8}/\sqrt{3}$, $\sqrt{11}/\sqrt{3}$, and $\sqrt{16}/\sqrt{3}$. These ratios can be associated with the Miller indices (111), (220), (311), and (400), respectively, corresponding to a discontinuous cubic liquid crystal with Fd3m (face-centered) space group (Figure 3b). The distance parameter of cubic cell, 23 nm, was calculated as the inverse of the slope when plotting $1/d$ as a function of $(h^2 + k^2 + l^2)^{0.5}$, where d is the d -spacing and h , k , l are the Miller indices (Figure 3b).

Preparation and Characterization of Mesoporous/Macroporous Silica in the C₁₂(EO)₈/Water/Decane Sys-

tem. It has been reported that sol–gel reactions, in the external phase of highly concentrated emulsions, may require long times, as much as periods of 1 week.³⁰ A strategy to obtain meso/macroporous materials, by a simple and faster method, is to increase the reaction kinetics of TEOS hydrolysis and polycondensation, by evaporating the ethanol released during the hydrolysis reaction. Since hydrolysis and polycondensation reactions are simultaneous, the overall kinetics can be accelerated by ethanol removal. Consequently, in the present work 7 wt % TEOS was added to the highly concentrated emulsion, and the samples were left at 25 °C for 48 h, in open dishes to let ethanol evaporate.

After 48 h, a sample was analyzed by SAXS. The pattern indicated the same *Fd3m* face-centered cubic symmetry, as shown in Figure 3a,b. Therefore, this structure was preserved after addition of the TEOS and the evaporation of the solvents. A small contraction of the nanostructure was produced, since the cell parameter of the cubic crystal decreased from 23 to 21 nm. Probably, this shrinkage of the nanostructures occurred during the polycondensation of silica species.

A macroscopic contraction of the sample could be seen by direct visual observations, and cracking occurred. White powders, with particles around few millimeters in size, were recovered, washed with ethanol, and dried at 80 °C until constant weight was reached. Finally, the materials were calcined at 500 °C, increasing the temperature at 2 °C/min.

The microstructure of the final calcined powder was investigated by means of nitrogen sorption, small-angle X-ray scattering, and transmission electron microscopy. The adsorption study showed that the powder has a relatively high specific surface area of 411 m²/g, which can only be attributed to the presence of mesopores. The arrangement of the pores was also studied by SAXS (Figure 3). The patterns exhibit three small peaks, which are too broad to be associated with a cubic structure. The crystallographic assignation of the calcined material (Figure 3b) shows that the relative position of these peaks does not fit the *Fd3m* structure. This result was confirmed by TEM observations (Figure 4b) which show a wormhole-like mesoporous structure.

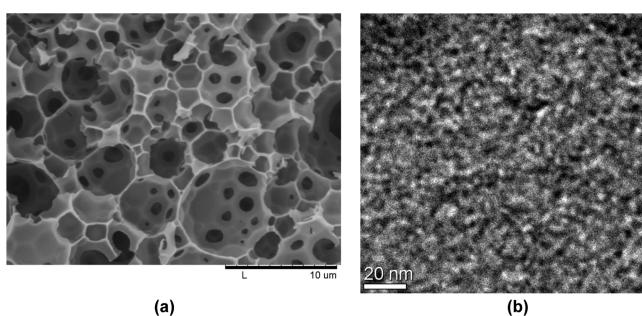


Figure 4. Images obtained by SEM and TEM, of a silica sample prepared with 7.4 wt % surfactant, 11.1 wt % HCl(aq) 0.5 M, 74.4 wt % decane, and 7.0% TEOS. (a) Macropores observed by SEM at low magnification (the scale bar indicates 10 μ m). (b) Mesopores observed by TEM at high magnification (scale bar indicating 20 nm).

Figure 4 shows the dual meso/macroporous nature of the material. The macropores between 0.5 and 5 μ m can be observed in the SEM images (Figures 4a and 5a). These sizes are approximately the same than the droplet size of the initial highly concentrated emulsion (Figure 2b), indicating that the macropores were templated by these emulsion droplets.

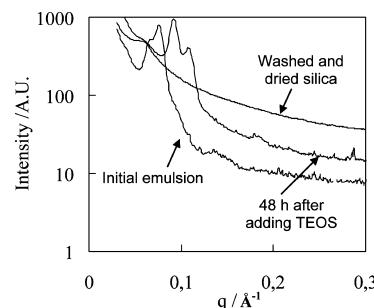


Figure 5. Small-angle X-ray scattering (SAXS) spectra of samples prepared in the $C_{12}(EO)_8$ /Pluronic F127/HCl(aq) 0.5 mol dm⁻³/decane/TEOS system. The overall composition was 7 wt % $C_{12}(EO)_8$, 0.4 wt % Pluronic F127, 11.1 wt % HCl(aq) 0.5 mol dm⁻³, 74.4 wt % decane, and 7.0% TEOS.

TEM image (Figure 4b) confirmed that the mesopores are disordered, as indicated by SAXS, with a pore size around 5 nm. Therefore, the periodic and ordered arrangement of the cubic liquid crystalline phase was lost during drying and/or calcination. The mesopores are densely packed, and the short distance between adjacent mesopores probably produces the appearance of distance-correlation peaks in the SAXS spectra.

A block copolymer surfactant, F127, was added to increase the size of the mesopores. Pluronic F127 was chosen as structure directing agent because it is known that it forms a cubic micellar phase in the surfactant–water binary system.⁶⁷ The ratio $C_{12}(EO)_8$:F127 was equal to 95:5. The same procedure, as described in the previous section, was applied to this system. Figure 5 shows the SAXS spectra, for the initial emulsion, the sample obtained 48 h after addition of TEOS and the final calcined powder.

As observed for the system without F127, the initial highly concentrated emulsion has the nanostructure of a cubic liquid crystal, in the external phase. The crystallographic assignation (available as Supporting Information) also indicates the presence of an *Fd3m* face-centered cubic structure. The addition of TEOS did also not affect this cubic structure. However, also in this case, the final calcined powder did not exhibit any ordered mesostructure as indicated by SAXS results. The ordering of nanostructure was also lost during drying and/or calcination. This was confirmed by the TEM observations (Figure 6b).

Figure 6b shows that the mesopores have a remarkably narrow pore size distribution. The specific surface area, determined by applying the BET equation to the nitrogen adsorption isotherm, is 102 m²/g. This is a smaller value than

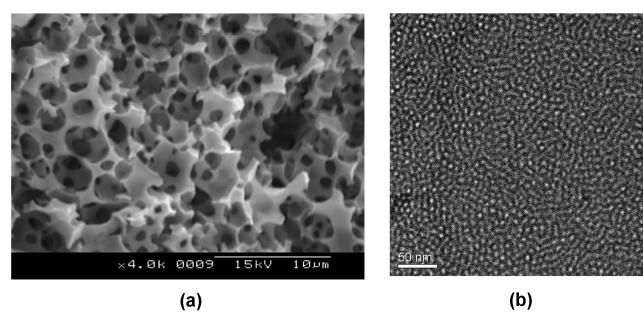


Figure 6. Images obtained by SEM and TEM, of a silica sample prepared with 7 wt % $C_{12}(EO)_8$, 0.4 wt % Pluronic F127, 11.1 wt % HCl(aq) 0.5 mol dm⁻³, 74.4 wt % decane, and 7.0 wt % TEOS.

that obtained when using the $C_{12}(EO)_8$ system without F127 ($411 \text{ m}^2/\text{g}$). It could be partly attributed to the fact that the pore size is bigger in the system obtained with presence of F127, leading to a smaller specific surface area. The pore size distributions are compared in Figure 7.

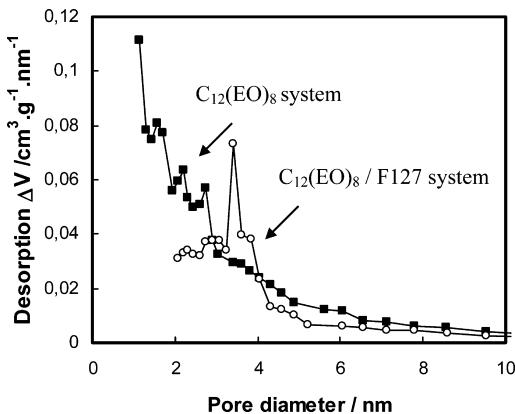


Figure 7. Pore size distributions, calculated by applying the BJH equations to the desorption curves of the nitrogen isotherms. Silica samples prepared with 7.4 wt % surfactant, 11.1 wt % HCl(aq) 0.5 mol dm^{-3} , 74.4 wt % decane, and 7.0% TEOS.

Figure 7 shows the pore size distribution of the material synthesized in the presence and absence of F127. The system without F127 shows a broad distribution of pore sizes with the major fraction of volume in pores smaller than 3 nm. As it can be observed, the addition of Pluronic F127 changes the mesopore size distribution from polydisperse to monomodal, with a maximum at ≈ 3.4 nm pore size. This lower pore polydispersity evidence that mixed surfactant aggregates, composed of $C_{12}(EO)_8$ and F127, are formed and direct the pore formation. Moreover, F127 molecules seem to increase the size of aggregates, producing a swelling effect which results in larger pores. This was expected, since the use of a high molecular weight surfactant can result in materials with larger mesopores.⁶³

The reduction in polydispersity, with the addition of F127, could be explained as due to stronger interactions with silica species. Previous studies described the cooperative self-assembly process between nonionic surfactants molecules and silica precursor species, for synthesizing mesoporous silica at pH below its isoelectric point ($\text{pH} < 2$).^{48,58,63,64} The proposed mechanism considers that poly(ethylene oxide) chains are positively charged at very low pH, due to interactions with H_3O^+ ions. Silica species (I^+) are also positively charged below the isoelectric point, and these species may interact with the protonated PEO chains (S^0H^+) by the bridging of halide anions (X^-). This binding mechanism was summarized as $\text{S}^0\text{H}^+\text{X}^-\text{I}^+$, where a combination of electrostatic and hydrogen-bonding interactions may cause the cooperative self-assembly, templating the formation of mesopores.^{48,58,63,64}

Accordingly, it could be postulated that these interactions may be stronger in the case of surfactants with long ethoxylated chains, and therefore a higher degree of ordering is obtained in the presence of the polymeric surfactant F127. Moreover, addition of triblock copolymer $(\text{EO})_{100}(\text{PO})_{70}(\text{EO})_{100}$ allows to form mixed micelles, with a more hydrophilic external environment composed of the ethoxylated group of the $C_{12}(EO)_8$ and the large PEO groups of F127. This could

enhance the bonding with silica species, causing the accumulation of silica species around the micelles and thus producing thicker pore walls, as observed in the TEM images. However, the self-aggregation mechanism in the present mixed surfactant, which results in bigger pore sizes, can be more complex than postulated and may require further investigations.

In any case, one should also consider that hydrolysis of one molecule of TEOS releases four ethanol molecules as a byproduct. Ethanol has a strong influence on phase behavior and probably produces a disorganization of the surfactant aggregates.⁵⁴ For instance, it is known that the presence of ethanol decreases the size of micelles and increases the solubility of nonassociated surfactant molecules, increasing the CMC.⁵⁵ Therefore, the presence of ethanol could greatly contribute to the disordering of mesopores, and thus the cubic liquid crystalline phase does not lead to an ordered cubic array of mesopores.

Silicon alkoxides, such as TEOS or TMOS (tetramethyl orthosilicate), have in common that short-chain alcohols are released during its hydrolysis. However, this problem could be overcome by using other silica precursors. In this context, some novel glycol-based silica precursors have been recently described for the synthesis of silica materials, where polyols are released instead of short-chain alcohols.⁶⁹ These precursors could be very promising for the preparation of dual meso/macroporous materials, and this subject will be within the scope of future works.

However, it should be pointed out that the present work described the formation, in a simple single-step method, of a dual meso/macroporous material with controlled size of mesopores. These materials possess both high specific surface area and pore volume. Moreover, the larger mesopore diameter obtained in the presence of Pluronic F127 might be of interest in applications such as adsorption and catalysis in which good dispersion of molecules is required for fast provisioning of reactive species and quick removal of the synthesized molecules.⁶⁸

CONCLUSIONS

A simple single-step method for the preparation of dual meso/macroporous materials has been developed, which consists in using highly concentrated emulsions, with cubic liquid crystals in the continuous phase as templates. The silica materials obtained have bimodal pore size distributions, consisting of macropores formed by the emulsion droplets, and mesopores produced by the presence of surfactant aggregates. The mesopores are located in the walls that separate the macropores. Both mesopores and macropores are randomly disordered because the ordering of the cubic structure is not preserved during the preparation process, probably due to the influence of ethanol. However, relatively high specific surface areas (around $400 \text{ m}^2/\text{g}$) can be obtained, and the size of mesopores can be controlled by tuning the surfactant composition. The addition of a polymeric surfactant (F127) leads to the formation of bigger and more homogeneous mesopores, which could be attributed to formation of larger mixed micelles and stronger interactions between protonated PEO chains and silica species. The resulting materials may have promising applications as adsorbents and supports for catalysts.

■ ASSOCIATED CONTENT

§ Supporting Information

Crystallographic analysis of the SAXS spectra of samples obtained in the system composed of $C_{12}(EO)_8/F127/HCl(aq)$ 0.5 mol dm^{-3} /decane/TEOS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors greatly acknowledge Prof. H. Kunieda (deceased in 2005) since he inspired this work, which was initiated under his guidance and advice. The research was supported by CREST of JST (Japan Science and Technology Corporation). The authors also acknowledge the Spanish Ministry of Economy and Competitiveness for the CTQ2011-2348 project, and Generalitat de Catalunya for the 2009SGR961 grant. Finally, the authors are grateful to Dr. Carlos Rodríguez-Abreu and Dr. Paqui Izquierdo for valuable assistance.

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