



Nano-emulsions as imprints for the design of hierarchical porous silica through a dual templating mechanism



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ABSTRACT

Due to their properties nano-emulsions are excellent candidates to be used as imprints to create a macropore network. In this study nano-emulsions have been formulated from the Remcopal 4/decane/water system and mineralized by a dual templating mechanism in the presence of Pluronic P123 micelles. After removing the organic matter, macro-mesostructured silica materials are obtained. Small angle X-ray scattering patterns of the materials and transmission electronic microscopy experiments show that the mesoporous network (mesopore size around 9 nm) adopts a hexagonal arrangement.

Macropores have been characterized by transmission electron microscopy, scanning electron microscopy and mercury porosity. As determined by mercury porosimetry, the size of the macropores imprinted by the nano-emulsions is of about 240 nm. A second macroporosity is also detected in the micrometer range and could be related to the further fusion of nano-emulsions during the hydrothermal process and to interparticular porosity. To better address the formation mechanism of the hierarchical structure of the silica material, the stability of nano-emulsions in the presence of methanol, P123 and both of them has been investigated.

We have also evidenced the dual role played by the Pluronic micelles. They do not only induce the mesopore network through the cooperative templating mechanism, but their presence also avoids the total destruction of the nano-emulsion by methanol, released during the hydrolysis of the silica precursor.

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1. Introduction

One way to design porous materials consists of combining the sol–gel chemistry and the use of surfactant molecules assemblies as framework templates. Depending on the structure of the initial system either mesostructures, i.e. materials having a pore diameter between 2 and 50 nm or macroporous materials, i.e. compounds with pore size larger than 50 nm are recovered. By this way mesoporous and macroporous materials can be synthesized from micelles and emulsions, respectively. However, practical applications require porous materials having hierarchical pore structures at different length scales, since the limited diffusion of substrates through confined nano-channels can be a problem [1–3]. In

catalysis [4,5] for example, the hierarchical combination of pores reduces transport limitations resulting in higher activities and better control over selectivity [5]. Therefore, over the past few years the development of these hierarchically ordered structures at multiple length scales has attracted much attention and many papers are focused on the synthesis of meso-macro, micro-macro or micro-mesoporous materials [6–11]. Materials with a macroporous structure have been synthesized using multiple templates, such as latex spheres [12,13], solid lipid nanoparticles [14] and emulsions [15–20] using either soft or hard templating methods. For example, these techniques were employed to design a new class of three-dimensional ordered macrostructures (3DOM) [21–23], which have applications in catalysis [22] or photonics [23]. However, emulsions templating is perhaps most general and has been used to produce macroporous silica, titania and zirconia [15]. Although systems having two types of mesopores are rarely investigated, some interesting strategies have been developed to prepare this

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kind of hierarchical materials. One of them consists of using mixture of surfactants [24–27]. For example Morris et al. employed mixtures of micellar solutions of nonionic surfactants, including Pluronic, Brij and Tetronic types, as templates for synthesizing porous silica materials having several pore sizes [26]. Depending on the surfactant mixture, ordered uniform pore size arrangements, partially ordered complex bimodal structures or totally disordered non-mesoporous structures were obtained. As mentioned above various building blocks such as micelles, liquid crystals, micro-emulsions or emulsions can be used to induce and to tune the porosity to the targeted application. Due to their unique properties, nano-emulsions [28–30] make excellent candidates for the design of such materials. Indeed, nano-emulsions are emulsions consisting of small mono-disperse droplets, typically in the 20–200 nm size range, which are often referred to in the literature also as mini-emulsions, ultrafine emulsions, submicron emulsions [31–33]. Although they could have similar size like microemulsion droplets and appear transparent or translucent, they are in fact quite different [34]. Nano-emulsions are thermodynamically unstable and their formation generally requires energy input. The properties of nano-emulsions depend not only on thermodynamic conditions (i.e., composition, temperature and pressure), but also on the preparation method and crucially, on the order of component addition. Among the different preparation methods low-energy ones constitutes a field of growing interest [35–38]. These methods make use of accessible phase transitions occurring during the emulsification process as a result of changes in surfactant film spontaneous curvature. According to this process the formation of nano-emulsions is obtained by the phase inversion temperature method (PIT) [39–41], phase inversion composition method (PIC) [38,42], or self-emulsification method [36,37,43]. Due to their properties these systems are used for different kinds of applications [36,43–46]. For example in the pharmaceuticals field, nano-emulsions emerge as a promising drug delivery technique [43,44,47,48]. Recently, nano-emulsions have been employed as templates for the preparation of porous silica [49,50]. However, to the best of our knowledge only very few papers address this topic. For example Prouzet et al. have reported the synthesis of porous silica from phase inversion composition O/W nano-emulsions [49]. Authors have used the oil phase of the nanoemulsion as a nano-reactor for the preparation of magnetic gamma-Fe₂O₃ nanoparticles. Mou et al. have also used the nanoemulsion-templating approach for the synthesis of silica nanoparticles with compartmentalized hollow structure *via* ultrasound-assisted sol–gel method [50].

Taking advantage of the monodispersity of nano-emulsions in this paper we are interested in combining the cooperative templating mechanism (CTM) with the nano-emulsions templating to design hierarchical porous silica using tetramethoxysilane (TMOS) as the silica precursor. Nano-emulsions have been prepared from the Remcopal 4/decane/water system according to the PIT method. Since both the methanol, released during the hydrolysis of TMOS, and the presence of micelles, required for the CTM mechanism, can modify the Remcopal 4/decane/water phase behavior and thus disturb the domain of nano-emulsions we have also investigated the effect of the presence of these two additives on the stability of the nano-emulsions. This allows to shed some lights on the formation of the hierarchical porous silica.

2. Materials and methods

Remcopal 4 (commercial name) was provided by CECA. It is a technical grade surfactant, which formula mainly consists of a hydrogenated carbon chain with 12 carbons and the average number of oxyethylene is 4. It is noted as C₁₂(EO)₄. The triblock copolymer

P123 (EO)₂₀(PPO)₇₀(EO)₂₀ and decane were purchased from Aldrich. Deionized water was used to prepare the various samples.

Preparation and stability of the nano-emulsions: Nano-emulsions have been formulated from the Remcopal 4/decane/water system using the PIT method, according to a procedure previously reported [51]. Here the oil to surfactant ratio and the weight fraction of water have been fixed to 3 and 0.74, respectively. These conditions lead to formation of nano-emulsions with a size, determined by SAXS and DLS, of around 100 nm in diameter [51]. The stability of the nano-emulsions in the presence of methanol, P123 micelles and both of them has been investigated by visual observations and by DLS. The quantity of methanol has been varied from 0 to 40%, this corresponds to the maximum amount of methanol released during the hydrolysis of the silica precursor. The concentration of the P123 micellar solution has been changed from 0 to 10 wt.%.

Porous materials preparation: First a solution of nano-emulsions and a micellar solution of Pluronic P123, at various concentrations, are separately prepared. Then 50% in volume of each solution are mixed and in the final mixture the content of the Pluronic P123 varied between 0 and 10 wt.%. The pH of the mixture was kept at value of 0.3. After that tetramethoxysilane (TMOS), used as the silica source was added. The quantity of TMOS is calculated according to the P123/TMOS molar ratio (R), which was varied between 0.0075 and 0.0015. The mixture was stirred at ambient temperature for 1 h using a magnetic stirrer. Then it was transferred and sealed in a Teflon autoclave. The autoclave was heated at 40 °C for 24 h, afterward at 100 °C for 24 h. The final products were recovered after ethanol extraction with a Soxhlet apparatus for 48 h. Before characterization samples are dried at room temperature.

Characterization: A Malvern zetasizer 3000HSA instrument was used to measure the size of the nano-emulsions in water by dynamic light scattering. The Helium–Neon laser, 5 mW operates at 633 nm, with the scatter angle fixed at 90°. The sample is contained in a flow-through cell kept at 25 °C. All the measurements were performed in the suitable conditions by systematically diluting three time the samples with water to validate the results. Water was first filtered with a mixed cellulose ester (surfactant free) filter (0.45 μm). The attenuator (diaphragm) of the photomultiplier was automatically adapted for each sample in order not to saturate the detector. The data were analyzed by the CONTIN method and the size was provided by an intensity distribution.

SAXS measurements were carried out using a SAXSess mc2 (Anton Paar) apparatus. It is attached to a ID 3003 laboratory X-Ray generator (General Electric), equipped with a sealed X-ray tube (PANalytical, λ_{Cu (Kα)} = 0.1542 nm, V = 40 kV, I = 50 mA). A multilayer mirror and a block collimator provide a monochromatic primary beam. A translucent beam stop allows the measurement of an attenuated primary beam at q = 0. Porous materials are introduced into a powder cell before being placed inside an evacuated chamber equipped with a temperature controlled sample holder unit. Acquisition times are typically in the range of 1–5 min. Scattering of X-ray beam is recorded by a CCD detector (Princeton Instruments, 2084 × 2084 pixels array with 24 × 24 μm² pixel size) in the q range 0.3–5 nm⁻¹. The detector is placed at 309 mm from the sample holder.

N₂ adsorption and desorption isotherms were determined on a Micromeritics TRISTAR 3000 sorptometer at –196 °C. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method applied to the adsorption branch of the isotherm [52].

Macropores were detected using mercury porosimetry on a Micromeritics Autopore IV 9500. The penetrometer (stem volume = 0.412 ml, penetrometer volume = 1 ml) was filled with 0.1 g of the sample. A low pressure (0.1–15 psia) followed by a high

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