Colloids and Surfaces A: Physicochem. Eng. Aspects xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Nanostuctured mesoporous materials from different silica sources using fluorinated surfactants as templates

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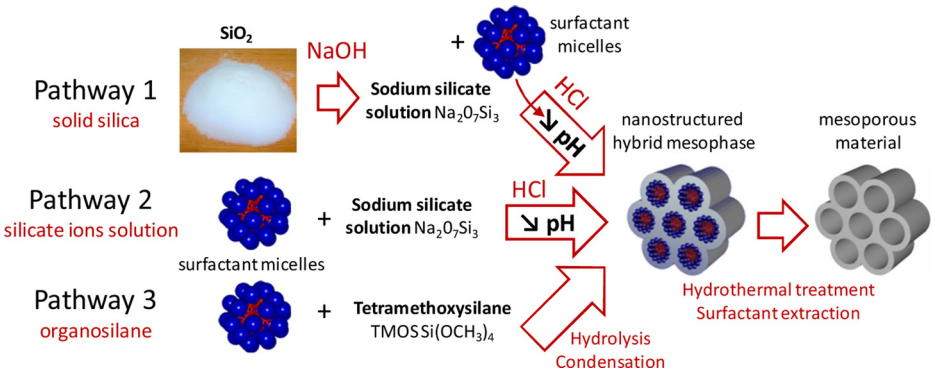
HIGHLIGHTS

- Preparation of mesoporous materials from economical silica sources under acidic pH.
- PH governs the interactions between the surfactant and the inorganic precursor.
- Surfactant-silicate interactions play a key role in the mesophase formation.
- PH range, leading to a mesopore ordering, depends on the silica source.
- Surfactant- silica species self assembly is better control with the alkoxysilane.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 January 2016
Accepted 28 April 2016
Available online xxx

Keywords:
Ordered mesoporous materials
Fluorinated surfactant
Sodium silicate
Silica fumed
Synthesis pathway

ABSTRACT

We report here the synthesis of mesoporous silica materials from various fluorinated-based systems using as the inorganic precursor either sodium silicate solution or silicate ions produced from the dissolution of silica under basic conditions. The properties of the materials are compared with the ones of the mesostructures prepared from tetramethoxysilane as silica source. Results show that whatever the silica source, well-ordered hexagonal materials with a narrow pore size distribution are obtained. Nevertheless, the pH has a great influence on the properties of the recovered materials since it governs the interactions between the surfactant and the inorganic precursor and the pH range for which the hexagonal mesopore ordering is obtained, depends on the silica source. Using sodium silicate, hexagonal mesostructured materials with high specific surface area ($\geq$800 m^2/g) and narrow pore size distribution (4 nm) are recovered for pH from 0.3 to 5. It should be noted that the formation of organized mesoporous silica under acidic conditions with this precursor is barely reported in literature. Replacing sodium silicate by silica fumed, the pH range leading to a hexagonal mesopore ordering is reduced to 0.3–1.5. When the organosilane is used the ordered mesoporous materials are recovered regardless the pH. In addition in that case a better control of the self assembly between the surfactant and the silica species allows tuning the particles' morphology. Under acidic conditions tetramethoxysilane gives rise to gyroids or toroids and favors the formation of submicrometer particles, while irregularly shaped particles

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http://dx.doi.org/10.1016/j.colsurfa.2016.04.067
0927-7757/

are produced with sodium silicate or silica fumed under alkaline conditions. Results also show that neither the specific surface area, nor the cell parameter strongly depend on the silica precursor as long as the hexagonal structure is kept.

1. Introduction

For the past few years, due to their properties such as high specific surface area and pore volume, surfactants templated silica mesoporous materials have attracted much research attention [1]. The synthesis of these compounds combines the sol-gel chemistry and the use of assemblies of surfactant molecules as framework templates. Depending on the starting block, mainly two mechanisms can lead to the formation of the ordered mesostructures. The first one is the cooperative templating mechanism (CTM) and in this case the building blocks are the micelles [1–6]. The second approach to the preparation of ordered mesostructures uses liquid crystal phase and is labeled as the direct liquid crystal templating (LCT) pathway [7–9]. Several experimental techniques [10–24] such as Raman [10] NMR [11,12], fluorescence probing techniques [13], EPR [14], transmission electron microscopy (TEM) [15,16], IR spectroscopy [17] and small angle X-ray (SAXS) or neutrons (SANS) scattering [6,18–24] have been used to investigate the formation of the mesoporous materials. Nevertheless, whatever the synthesis pathways, the characteristics of the recovered materials, such as the structure and the pore diameter, are strongly related to the properties of the surfactant used for their preparation [25–29]. For example, in a paper dealing with the structural design of mesoporous silica by micelle-packing control using blends of amphiphiles [$C_mH_{2m+1}(OCH_2CH_2)_nOH$, m = 12–18, n = 2–100], Stucky et al. [25] authors have established a correlation between the final structure and the ratio between the volume of the hydrophilic head group (V_A) and the hydrophobic part (V_B) of the surfactant. In another paper, Zhao et al. [26] have reported the synthesis of silica mesostructures by using the triblock copolymer P85 ($EO_{26}PO_{39}EO_{20}$) and P65 ($E_{20}PO_{30}EO_{20}$) as structuring agent and tetraethyloxysilane (TEOS) as silica precursor. These structuring agents, which have a cloud point (CP) value of 82 °C, only allow the formation of ordered mesoporous silicates at a temperature higher than 90 °C. To explain this fact, the authors assume that the high concentration of H^+ and the ethanol released by the hydrolysis of TEOS have increased the CP of the triblock copolymer to a temperature higher than 100 °C. The second partner, i.e. silica, involves in the preparation of the ordered mesoporous materials also plays a key role. The properties of the recovered mesostructures are governed not only by the synthesis conditions such as the pH, the surfactant to silica molar ratio, the hydrothermal temperature and duration, but also by the nature of the silica precursor [30–34]. For example Tang et al. [35] have reported that under static acidic conditions the diameter of mesoporous silica spheres is in the range from 1 to 3.5 μm and from 2 to 10 μm when sodium silicate and tetraethoxisilane are the silica precursor, respectively. In addition, to develop the applications of these materials in catalysis, adsorption and so on, recently must efforts have been devoted to favour their ecodesign [36,37] and to simplify the synthesis procedures [38]. Research studies are focus not only on the templates, but also on the silica precursor. More and more sodium silicate [39–43], silica fumed [44,45], rice husk [46] or even recycling products such as electronic packaging resin [47] or silica waste [48] are preferred to silicon alkoxides. For example, using SiO_2 as precursor Jang et al. [49] have developed a modified alkaline fusion method for the economical synthesis of mesoporous silica materials, which are used as adsorbents for the removal or delivery of ibuprofen.

Among the different surfactant based systems, fluorinated ones are in particular interest. Indeed, thanks to their higher thermal stability [50], the hydrothermal treatment can be performed at higher temperature, involving an enhancement of the silica condensation level. As a consequence, the recovered materials exhibit a higher hydrothermal stability than those obtained from their hydrogenated analogues [51]. However, most of the papers addressing this topic concern mixtures of a fluorocarbon surfactant with a hydrogenated one [52–54]. Only few groups have been interested in using only fluorinated surfactants for the mesostructured silica preparation [27,55–58]. For instance, Esquena and coworkers [57] have investigated the formation of mesostructured silica using $CF_3(CF_2)_7SO_2$-$[CH_3(CH_2)_2]N$-$(C_2H_4O)_nH$ [labeled as $C_8F_{17}(EO)_n$)] as surfactant, the value of n was varied from 6 to 20. Mesoporous silica with a hexagonal channel array are formed only with n = 10; other values of n lead to disordered structure. In addition, the silica precursor used to synthesize the mesoporous compounds is a silicon alkoxides. The preparation of mesoporous materials from fluorinated-based systems using more economical silica sources has not yet been reported. In this paper, we have led such study and in particular we have investigated the effect of the silicon alkoxide substitution by sodium silicate or fumed silica on the structural and textural properties of the recovered mesoporous materials.

2. Materials and methods

The used fluorinated surfactants, which were provided by DuPont, have an average chemical structure of $C_8F_{17}C_2H_4(OC_2H_4)_9OH$, $C_7F_{15}C_2H_4(OC_2H_4)_8OH$ and $C_6F_{13}C_2H_4(OC_2H_4)_{11}OH$. They are labeled as $R^F{}_8(EO)_9$, $R^F{}_7(EO)_8$ and $R^F{}_6(EO)_{11}$, respectively. For each of them, the hydrophilic chain moiety exhibited a Gaussian chain length distribution and the hydrophobic part is composed of well defined mixture of fluorinated tails. Sodium silicate (Na_2SiO_3), fumed silica and tetramethoxysilane (TMOS), used as the inorganic precursors, were purchased from Aldrich.

2.1. Mesoporous preparation

Mesoporous materials have been prepared through the CTM mechanism and whatever the silica precursor the surfactant concentration in the micellar solution has been fixed to 10 wt.%.

2.1.1. Sodium silicate as precursor

After the addition of 0.66 g of sodium silicate (Na_2SiO_3) to the surfactant solution, the mixture was let under stirring until homogenization. Then HCl (37%) was incorporated to adjust the pH to the targeted value from 0.3 to 11. The obtained solution was stirred (300 rpm) at room temperature during 24 h. The obtained gel was sealed in Teflon autoclaves and heated for 1 day at 100 °C.

2.1.2. Silica fumed as precursor

First 0.23 g of the silica fumed was dissolved in 10 mL of a NaOH solution at pH = 14 before the addition of 1 g of $R^F{}_8(EO)_9$. Then HCl (37%) was incorporated to adjust the pH to the targeted value from

Please cite this article in press as: J.L. Blin, et al., Nanostuctured mesoporous materials from different silica sources using fluorinated surfactants as templates, Colloids Surf. A: Physicochem. Eng. Aspects (2016), http://dx.doi.org/10.1016/j.colsurfa.2016.04.067