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Tailoring of ordered mesoporous silica COK-12: Room temperature synthesis of mesocellular foam and multilamellar vesicles

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ABSTRACT

Ordered mesoporous silica materials are known for their high surface area and highly ordered structure. One of the main advantages of the synthesis of ordered mesoporous silica by soft-templating with amphiphilic molecules is the ability to tailor the mesostructure by using micellar swelling agents. In this context, the addition of hexane and polypropylene glycol (PPG) as micellar swelling agents in the facile room-temperature synthesis of COK-12 was studied to tailor the mesoporous structure of the system. Hexane was used as a micelle expander and as an agent to produce silica mesocellular foams (MCF), resulting in a material with “ink-bottle” pores with a larger diameter than that of the original COK-12, with up to 8.5 nm in cell diameter and 5.3 nm in window diameter. By adding PPG into the synthesis, a shift of the mesostructure of COK-12 from 2D hexagonal to a multilamellar vesicular (MLV) configuration was observed, resulting in the progressive formation of this type of material with increasing concentration of PPG.

1. Introduction

Ordered mesoporous silica materials (OMS) possess attractive characteristics such as large surface areas and well-defined ordered pores of controlled size that are the result of templating with organic molecules [1–3]. Given their particular properties, OMS materials have found application in fields such as catalysis [4], separation [5], adsorption [6], sensors [7] and drug delivery [8], among others. An attractive characteristic of the synthesis of ordered mesoporous silica materials prepared by soft templating with amphiphilic molecules is the ability to tailor the mesostructure for specific applications with the use of micellar swelling agents. Depending on the templating agent selected for OMS synthesis, micellar swelling agents that solubilize within the micelle cores can be used to expand the size of the micelles and produce micellar phase transitions, resulting in materials with larger pores and different pore shapes. This versatility expands the potential application of OMS materials, e.g. for use in adsorption of bulky molecules [9,10] or immobilization of enzymes [11].

One of the phases that have been observed in previous studies regarding the use of micellar swelling agents in the synthesis of OMS is silica mesocellular foams (MCF). MCF materials are composed of uniformly sized large spherical cells that are connected by uniform windows, creating an interconnected 3-D pore system. The synthesis of MCFs based on the synthesis of OMS requires the typical synthesis conditions of the OMS, namely high temperatures and prolonged reaction time [12,13]. MCFs synthesis was first reported by Stucky et al. using P123 as a structure-directing agent and 1,3,5-trimethylbenzene (TMB) as a micellar swelling agent [14]. A study by Lettow et al. reports that the MCF structure results from a phase transition from hexagonal cylindrical pores to “ink-bottle” pores upon increasing concentration of TMB. This is due to the formation of a noded structure that separates into spherical micelles which aggregate to form the foam structure [15]. Recently, the synthesis of MCFs via partitioned cooperative self-assembly using sodium silicate as the silica precursor and P123 as the structure-directing agent has been reported, in which both the hydrophobic and hydrophilic micellar blocks are manipulated, resulting in materials with a bimodal pore structure [12,13].

Another phase that has been observed in the synthesis of OMS with micellar swelling agents is multilamellar vesicular silica (MLV). MLV structures consist of concentric silica shells and voids in alternation. Initial reports on multilamellar vesicular silica synthesis appeared shortly after the discovery of MCM-41 [16–20]. After these initial

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studies, numerous reports regarding the synthesis of siliceous MLVs with P123 as a structure directing, TEOS as a silica source and various co-templates and co-surfactants have been published. Additives commonly used as micellar swelling agents such as hexane [21], 1,3,5 triisopropylbenzene (TIPB) [22], perfluorooctanoic acid (PFOA) [23], 1,3,5 trimethylbenzene (TMB) [24] and more recently, the amphiphilic comb-like polymer with a siloxane skeleton PSPE [25] have been useful in the preparation of MLVs.

Studies regarding the tailoring of OMS materials using micellar swelling agents have thus far been focused on syntheses based on OMS materials such as SBA-15 and FDU-12, which normally require high temperatures, harsh synthesis environments and more expensive silica precursors. In contrast, the present study presents the mesoscale tailoring of the OMS material COK-12 using micellar swelling agents, which has not been reported to date. COK-12 is an OMS produced by soft-templating with the triblock copolymer P123 [26]. The synthesis takes place at room temperature under mild reaction conditions, using an inexpensive silica precursor. In comparison with the most widely known OMS, the synthesis of COK-12 is more time efficient, inexpensive and environmentally friendly, yielding a material analogous to SBA-15 [1]. Furthermore, given the ease of the synthesis, upscaling to yield large amounts of material with little temperature and mixing control can be carried out, making COK-12 an attractive candidate for industrial production and application.

COK-12 has been used in our research group as a catalyst support for the oxidative coupling of methane [4]. The ability to control the size of the active components given the size of the OMS pore is of value when comparative studies are required. In this context, the aim of this work is the study of pore enlargement and mesoscale transformations of COK-12 by incorporation of micellar swelling agents. Based on previous reports of P123-templated ordered mesoporous silica syntheses, hexane [12,24] and polypropylene glycol (PPG) [27] were selected as micellar swelling agents. In contrast to the most recent reports regarding silica MCF and MLV production, the synthesis based on COK-12 is more economically viable and energy efficient, and the facile nature of these syntheses makes them a viable candidate for large-scale production. Potential applications in adsorption/separation of biomolecules [28], catalysis [29] and drug delivery [30] make it an important contribution to the field of OMS material research.

2. Experimental

2.1. Chemicals

The templating agent Pluronics P123 (MW ~ 5800 g/mol) and the swelling agent polypropylene glycol (PPG, MW ~2000 g/mol) were obtained from Sigma-Aldrich. Citric acid (≥99,5%, p.a., ACS, anhydrous), trisodium citrate dihydrate (CELLPURE® ≥99%), sodium silicate (7.8–8.5%wt Na_2O, 25.8–28.5%wt SiO_2) and n-hexane (≥99%, for synthesis) were obtained from Carl Roth GmbH + Co. KG. Distilled water (DIW) was used for all syntheses.

2.2. Materials synthesis

2.2.1. COK-12 synthesis

Powder COK-12 (P-COK-12) was synthesized according to previous reports [4,26]. The synthesis takes place at room temperature. In a typical synthesis, 4.0 g of P123 were dissolved in 107.5 ml DIW. After complete P123 dissolution, 3.684 g anhydrous citric acid and 2.540 g trisodium citrate dehydrate were added to control the synthesis pH between 4 and 5. The buffered surfactant solution was then stirred for 24 h. A solution of 10.4 g sodium silicate and 30 ml DIW was prepared and incorporated into the buffered micellar solution. Immediate solid formation was observed, and stirring was maintained for 5 min after which the slurry was kept for 24 h without stirring. The solid was separated from the mother liquor by vacuum filtration and thoroughly washed with DIW, and then dried at 60 °C overnight. The dry solid was then calcined at 500 °C for 8 h, with a 1 °C/min heating ramp to remove the organic templating agent.

2.2.2. Mesocellular foam and multilamellar vesicular silica synthesis

The synthesis of mesocellular foam (MCF) and multilamellar vesicular (MLV) silica materials was based on the synthesis of COK-12, with the additional step of swelling agent incorporation. Initially the templating agent was dissolved in water at room temperature. After complete P123 dissolution and before incorporation of the buffer, a certain amount of n-hexane (for MCF synthesis) or polypropylene glycol (PPG, for MLV synthesis) was added after which the buffer was incorporated. Then the sodium silicate solution was added and immediate precipitation was observed. After aging for 24 h the materials were washed with water, filtered, dried and calcined at 500 °C to remove organics, in the same way as for P-COK-12. The last number in each sample name corresponds to the amount of swelling agent in ml per gram of P123, e.g. MCF-COK-12-2.0 was prepared with 2.0 ml hexane/g P123 and MLV-COK-12-0.10 was prepared with 0.10 ml PPG/g P123.

2.3. Characterization

The morphology of all synthesized materials was studied via scanning electron microscopy (SEM) in a Zeiss Gemini Leo 1530 (Zeiss, Germany). Samples were placed on conducting carbon pads and then sputtered with a thin layer of gold to prevent sample charging. The mesostructure of the samples was studied via transmission electron microscopy (TEM) in a FEI Tecnai G2 20 S-TWIN equipped with a LaB_6-source at 200 keV acceleration voltage (FEI, USA), images were recorded with a GATAN MS794 P CCD-camera. Long-range ordering was studied by small-angle X-ray diffraction (SAXRD) in a Bruker AXS D8 ADVANCE with a Bragg–Brentano geometry and a Lynx Eye 1D detector with a $CuK_{\alpha1}$ radiation wavelength of 0.154 nm (Bruker, Germany). Measurements were carried out between 0.5 and 6.0° 2θ value, with a step time of 1 s/0.0003° at 35 kV and 40 mA and with a 280 mm sample-detector distance. The patterns were analyzed using the Diffrac-Plus/EVA software from Bruker AXS. The pore structure, pore size and specific surface area were studied with nitrogen sorption analysis in a QuadraSorb Station 4 apparatus (Quantachrome, USA). Isotherms were recorded at 77 K on after degassing for 10 h at 200 °C under vacuum. Surface area was determined using the Brunauer, Emmet and Teller (BET) method. The estimation of the cell and window size of MCF materials was based on NLDFT calculations for adsorption on silica at 77 K, using the adsorption branch of the isotherm to estimate the diameter of the cell and the desorption (equilibrium) branch of the isotherm to determine the diameter of the pore window. All nitrogen sorption data was analyzed using the Quantachrome/QuadraWin software. The packing parameter g is used to correlate the mesophase transformation to the addition of swelling agents and is defined by $g = V_H/a_0 l$, where V_H is the total volume of the hydrophobic chains plus any organic molecules between the chains, a_0 is the effective hydrophilic headgroup area at the aqueous/micelle surface and l is the kinetic hydrophobic tail length [31]. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out for elemental analysis in a Horiba Scientific ICP Ultima2 (Horiba, Japan). Samples were digested in an aqueous suspension with the addition of HNO_3 and HF at 200 °C for 5 h in an autoclave.

3. Results and discussion

3.1. Silica mesocellular foam

In this section, studies regarding the synthesis of silica mesocellular foam (MCF) based on the synthesis of COK-12 using hexane as a micellar swelling agent are presented. COK-12 is considered a reference material and is used as a basis for comparison; the characterization of