Microporous and Mesoporous Materials 208 (2015) 140–151

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Tunable hierarchical porous silica materials using hydrothermal sedimentation-aggregation technique

Abdelali Zaki [a], Jing Xu [a], Gregory Stoclet [b], Sandra Casale [c], Jean-Philippe Dacquin [a, *], Pascal Granger [a]

[a] Unité de Catalyse et Chimie du Solide (UCCS), CNRS UMR 8181, Université Lille I, Sciences et Technologies, 59655 Villeneuve d'Ascq, France
[b] Unité Matériaux et Transformations (UMET), CNRS UMR 8207, Université Lille I, Sciences et Technologies, 59655 Villeneuve d'Ascq, France
[c] Laboratoire de Réactivité de Surface-CNRS UMR 7197, Université Pierre et Marie Curie, France

ARTICLE INFO

Article history:
Received 6 June 2014
Received in revised form
21 October 2014
Accepted 26 January 2015
Available online 3 February 2015

Keywords:
Hierarchical porous silicas
SBA-15
Polymer spheres
Hydrothermal sedimentaion-aggregation technique

ABSTRACT

Herein, a simple and efficient synthesis based on a dual templating approach allow the preparation of tunable macroporous mesoporous silica materials. Macropores incorporation has been obtained using polymer spheres of well-defined size and their subsequent removal by thermal treatment allowed the independent control of the macropore size entrance between 200 nm and 50 nm. The addition of the block copolymer drives the formation of a second mesostructured skeleton, with a pore size centered around 4 nm, throughout the material framework. By a fine tuning of the sol–gel synthesis parameters (Polymer:TEOS ratio, aging conditions), we succeeded in guiding the SBA-15 rod-like morphology having randomly packed macropores to a derived SBA-15 with a homogeneous honeycomb macrostructure. Moreover, large mesoporous windows are generated between adjacent macropores. Hence, this simple one-pot synthesis approach, allowing scaling-up, offers fine tuning porosity at the macropore scale.

1. Introduction

Porous silica materials are widely used as supports for heterogeneous catalysis and separation applications since they offer various pore morphologies and high specific surface areas [1–5]. Moreover, with the emergence of alternative sources of energy, fuels and raw materials, the need for hierarchical architectures to prevent slow in-pore diffusion and poor atom efficiency of the reaction is highly desirable [6,7]. As a consequence, extensive researches on the design of heterogeneous solid supports have been developed since the end of the nineties [8–10] for maximizing the catalytic activity and reaching more sustainable technologies. In this line, templating strategies i.e. cooperative self-assembly [11], hard templates [12], biotemplates [13], phase separation [14] provide various possibilities for the synthesis of novel ordered mesostructures of tailored porosity and morphology. Various hierarchically structured silica materials can be obtained from the appropriate combination of such templating agents, including spray dried powders [15] and monoliths [16–18]. In these last cases, surfactants such as cetylammonium salts or block copolymers can be added to induce a trimodal pore structure with micrometer-sized macropores. Dual-templating approach is as well an established technique and offers well-defined structural macroporosity and mesoporosity. Most often polymer spheres [19] exhibiting diameters of several hundred nanometers are used, and successful preparation of the macrostructured skeleton is crucially depending on the synthetic procedure usually based on the hard template pre-arrangement before infiltration by the surfactant-containing precursor [12,20]. This approach leads to the synthesis of hierarchical silica materials with an interconnected macropore network and mesopore network known as three-dimensionally ordered macroporous materials with mesoporous walls (3 DOM/m materials) [21]. Research groups have also developed similar routes using polystyrene (PS) or polymethylmethacrylate (PMMA) spheres to produce 3 DOM/m transition metal oxides [22,23]. However, while the generation of smart and highly organized 3DOM structures can be obtained following this synthetic procedure, there is still restricted applications due to depth limitation in scaling-up [5]. Nevertheless, Ihm et al. proposed an alternative synthesis allowing feasible scaling-up with respect to the above described technique by using a sol–gel deposition of the silicate precursor on the polymer spheres

---

* Corresponding author. Tel.: +33 (0)320434795.
E-mail address: jean-philippe.dacquin@univ-lille1.fr (J.-P. Dacquin).

http://dx.doi.org/10.1016/j.micromeso.2015.01.041
1387-1811/

following hydrothermal sedimentation-aggregation technique [24] to generate a macroporous mesoporous MCM-41 [25]. This one-pot synthesis leads to a well-ordered macroporous skeleton with a mesoporous phase located between the walls of the macropores and having the same structure and arrangement of MCM-41. However, the direct application of this one pot synthesis to SBA-15 materials, possessing better hydrothermal stability, led to a limited ordering of the macropores [26]. It has been found that the difference in the macrostructures between MCM-41 and SBA-15 originated from the difference in textural morphology of the parent mesoporous MCM-41 and SBA-15. Nevertheless, the incorporation of macropores (300 nm) in the mesoporous framework of the SBA-15 (5 nm) has been found to boost the catalytic activity for various relevant catalytic reactions [27–29]. Thus, the application of such macroporous mesoporous silica materials derived from SBA-15 demonstrated that an additional macroporous network could alleviate mass-transport limitations encountered in liquid-phase reactions. Unfortunately, all those works [24–30] are reporting hierarchical porous silica materials with only one and large macropore size (300 nm). To our knowledge, hierarchical siliceous materials with sub<100 nm macropore size have been rarely reported in literature and are characterized by poorly ordered macrostructure with a broad macropore size distribution [31]. Herein, we report in a detailed study a simple and efficient one-pot synthesis allowing the preparation of hierarchical porous silica materials with sub-100 nm macropore size and bimodal mesoporosity. Our efforts were first devoted to the decrease of the polymer microsphere size (from 200 nm to 65 nm) and the research of right conditions to succeed in guiding the SBA-15 rod-like morphology having randomly packed macropores to a derived SBA-15 having a well-organized honeycomb macrostructure with a mesoporous phase. Hence, improved textural properties have been found and could be highly desirable for liquid phase catalysis or adsorption of practical as well as fundamental interest.

2. Experimental section

2.1. Materials

2.1.1. Synthesis protocol of large polymer spheres (200 nm)

Polystyrene spheres (PS) with a diameter size of 200 nm were prepared by an emulsifier-free emulsion polymerization technique and carried out in a 500 ml three neck bottom flask [24]. Typically, styrene (St) and divinylbenzene (DVB) are washed three times by an aqueous solution of NaOH (0.1 M) and then three times by distilled water in order to eliminate polymerization inhibitors. Then, 240 mL of distilled water is introduced in a 500 mL batch reactor. Before adding reagents, the aqueous solution is flushed under argon during at least 30 min in order to eliminate dissolved oxygen from the reactional medium. Then, 25.00 mL of St (monomer) and 4.75 mL of DVB (cross linker agent) are introduced in the reactor that is placed in a silicon oil bath under magnetic stirring and heating up to a fixed temperature (between 60 °C and 90 °C). After temperature stabilization, potassium persulfate (KPS) pre-dissolved in 20 mL of distilled water was injected to the reactional medium to initiate polymerization. The aqueous suspension of PS spheres was recovered after reaction by centrifugation or filtration and washed out with distilled water and dried at 80 °C for 24 h.

2.1.2. Synthesis protocol of small polymer spheres (65 nm < PMMA < 100 nm)

Polymethylmethacrylate spheres (PMMA) of diameter sizes between 65 nm and 100 nm were prepared by the surfactant-assisted emulsion anionic polymerization technique [30] and carried out in a 500 mL three neck bottom flask. Typically, 330 mL of distilled water is used as solvent and poured in a 500 mL three neck round bottom flask. Sodium dodecyl sulfate (SDS) surfactant and methyl methacrylate (MMA) monomers are added to the aqueous solution following 30 min of argon bubbling. Vigorous stirring is generally applied in order to have a good dispersion of MMA droplets and SDS. Then, the reactional medium is heated in a silicon oil bath at a desired temperature. After temperature stabilization, KPS pre-dissolved in 20 mL of distilled water was injected to the reactional medium to initiate polymerization. Argon bubbling is maintained during the experiment in order to limit undesired reactions which inhibit the polymer nodules growth. After 2 h reaction, the aqueous suspension of PMMA spheres is recovered by centrifugation and washed out with distilled water and dried at 80 °C for 24 h.

2.1.3. Synthesis protocol of hierarchical porous silica materials (HS)

Siliceous materials were synthesized following a similar dual-templating route reported by Ihm et al. [26] Typically, 3.0 g of Pluronic P123 triblock copolymer was dissolved in 22.50 mL of water and 75.00 mL of 2 M HCl solution while stirring at 35 °C. The required amount of polymer beads were then added to the solution and stirred for 1 h. Once a good dispersion of polymer beads was achieved, 6.90 mL of TEOS was added to the solution at 35 °C and maintained for 24 h while stirring. The mixture was then transferred to the oven ($T = 80$ °C or 100 °C) and maintained in a sealed polypropylene bottle under autogeneous pressure for a period of time ranging from 24 h to 96 h under static conditions. The solid product obtained is filtered, washed 3 times with deionised water and calcined in air at 550 °C (ramp rate of 0.5 °C min^{-1}) for 6 h. The final solids were labeled HS-X, where X = polymer bead size.

2.1.4. Synthesis protocol of SBA-15

Pure mesoporous SBA-15 silica was synthesized following the approach of Zhao et al. [3] Typically, 3.0 g of Pluronic P123 triblock copolymer was dissolved in 22.50 mL of water and 75 mL of 2 M HCl solution while stirring at 35 °C. 6.90 mL of TEOS (TEOS:P123 M ratio of 40) were added to the solution, which was maintained at 35 °C for 24 h while stirring. The mixture was then aged at 80 °C for 24 h and the solid product filtered, washed 3 times with deionised water, and calcined in air at 550 °C (ramp rate of 0.5 °C min^{-1}) for 6 h.

2.2. Characterisation techniques

The average hydrodynamic diameters of PS and PMMA spheres were determined by dynamic light scattering (DLS, Nano ZS, Malvern Instruments). DLS was applied with an angle of 173° by using He–Ne laser (4 mW) operated at 633 nm. Average hydrodynamic diameters of nanoparticles were measured in aqueous solutions. Thermo-gravimetric analysis (TGA) was performed to study the thermal decomposition of polymer spheres. A SDT-2960 TA instrument was used. 20 mg of sample were placed in an alumina crucible with a volume of 100 μl. The thermal analyzes were performed under air. The sample heated with a ramp in temperature of 5 °C min^{-1}, from 25 to 700 °C. Textural properties were carried out on an automated gas adsorption analyzer (Tristar 3020). Nitrogen sorption isotherms of the calcined samples were measured after outgassing at 200 °C in vacuum for 3 h. The multipoint surface area was evaluated with the Brunauer–Emmett–-Teller (BET) method over the range $P/P_0 = 0.075–0.35$ and pore size distribution was obtained using Barrett–Joyner–Halenda (BJH) model applied to the desorption isotherm branch. Total pore volume was determined from the volume adsorbed at $P/P_0 = 0.98$. Transmission Electron micrographs were collected on a JEOL JEM 2011 (LaB_6) operating at 200 kV while scanning emission