Microporous and Mesoporous Materials 221 (2016) 150–158

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Enlarged pore size in nanoparticulated bimodal porous silicas: Improving accessibility

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ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form
30 July 2015
Accepted 22 September 2015
Available online 3 October 2015

Keywords:
Mesoporous materials
Silica nanoparticles
Bimodal porosity
Swelling agents
Template synthesis

ABSTRACT

Mass-transfer kinetics seems to be highly favored in siliceous materials constructed from the aggregation of mesoporous nanoparticles. Besides intra-particle mesopores, over the course of the aggregation process an inter-particle (textural) large pore system is generated. Diffusion constrains through the resulting hierarchically structured pore systems mainly depend on the characteristics of the intra-particle mesopores. By using alkanes as swelling agents, we have been able to significantly increase the intra-particle mesopore size in previously well characterized UVM-7 materials. The Winsor-III-like behavior associated with the presence of alkanes in the hydro-alcoholic reaction media used in the surfactant-assisted preparative procedure allows explaining the existence of limits to the mesopore size expansion. A preliminary study on enzyme adsorption by these UVM-7-modified solids offers promising results about their capabilities as supports for processing a variety of biomolecules.

1. Introduction

One of the most attractive aspects linked with the discovery of the surfactant-templated M41S silicas was the theoretical possibility of tuning their mesopore size over a wide range [1]. In fact, the controlled expansion of the pores was already subject of interest in the first full-paper published by Mobil's researchers on the matter [2]. In this seminal publication, the authors referred to a significant variation of the mesopore size in MCM-41 silicas by using TMB as organic expander under hydrothermal conditions [2]. Afterwards, with the explosive growth of work on porous materials chemistry, pore-expanding strategies were relegated for a while until expectations of new applications raised again the need for increasing the sizes of pores in order to process relatively large substrates or biomolecules [3–5]. In this context, the use of different swelling agents together with the utilization of bulkier surfactants as templates entailed a breakthrough in the pore size engineering [6–8]. While conceptually the expansion mechanism looks simple (the swelling agent is solubilized in the presence of micelles and makes them more voluminous, which subsequently leads to larger pores after template removal), things are not so straightforward. In practice, the process depends on variables such as, among others, the surfactant nature and its features, the character of the interaction of the surfactant with the silica counterpart (ionic, no ionic) or how the swelling molecules change the preexisting phase diagram of the surfactant [7]. The SBA-15 and FDU-12 solids are archetypal examples of success in expanding the size of pores. For these silicas, isolated by using non-ionic Pluronic surfactants under mild temperature conditions, there have been achieved pore sizes up to 30–40 nm [6–12].

Among the diversity of mesoporous silicas accessible today, those consisting of particles with sizes smaller than ca. 200–300 nm have attracted interest as supports to construct new theranostic agents [13]. This prerequisite practically excludes the SBA-15-related materials because, in the acidic conditions necessary for their syntheses, is problematic prevent the particle growth processes that typically lead to micrometric solids. In fact, it has only been described one example of a SBA-15 nanometric silica (synthesized by using a fluorocarbon surfactant as template) [14]. Therefore, the search scope of nanoparticulated silicas has been necessarily limited and focused on MCM-41-related materials synthesized in basic media and using different alkyltrimethylammonium surfactants as templates [13] (which is, somehow, return to the Mobil's original work) [2]. However, these templates, for themselves, produce only small increases in the pore

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http://dx.doi.org/10.1016/j.micromeso.2015.09.037
1387-1811/

sizes [15,16]. To overcome this restriction, there has made use of a large variety of swelling agents (aromatic hydrocarbons, alkanes, alkylamines and co-surfactants) [2,17–25], although the particle size in the final solids very often exceeds the nanometric range. In general, the maximum expansion achieved (preserving cylindrical mesopores with narrow pore size distributions) corresponds to pores of around 5–6 nm. Furthermore, it has been observed that increasing the amount of swelling agent beyond a certain limit leads to only slight additional expansions and, in all cases, to wide pore size distributions. As suggested above, as far as we know, siliceous materials combining particle sizes in the nanometric range and expanded mesopores are uncommon [13]. Different authors have reported on the use of TMB plus a second swelling agent (or hydrothermal conditions) for obtaining solids with such a combination [26–28]. In any case, all these mesopore-expanded nanoparticulated silicas show highly disordered pore systems with worm-hole like organizations and a certain radial growth. Therefore, it is difficult to relate the resulting pores with the template effect of cylindrical swelled micelles. More recently, Kao and Mou [29] have introduced alkanes and ethanol as swelling agents, what has resulted in isolated silica nanoparticles including somewhat more symmetric unimodal mesopore arrays (similar to those in hexagonal disordered MCM-41 solids).

Our group was successful in synthesizing a new family of nanoparticulated silicas with bimodal porosity (NBS) through a one-pot procedure by using a simple template agent and starting from silicon atrane complexes as inorganic precursors [15,16,30]. The most outstanding feature concerning these materials, denoted UVM-7, is their very open architecture. This last is based on a continuous network constructed from covalently bonded pseudo-spherical mesoporous primary nanoparticles whose aggregation defines a non-ordered secondary system of large textural pores. Likewise, all our results indicated that mass-transfer processes inside UVM-7-based materials are favored by the good pore connectivity in the siliceous skeleton, which is related to the availability of (hierarchically structured) pore sets whose length is limited at the nanometric scale [31].

At this point, the aim of this work is dual. First, we intend to expand the mesopore size characteristic of the UVM-7 silicas for further progress in reducing diffusion constraints in these supports. The intra-particle pore system in UVM-7 (originated by the template effect of the surfactant) has similarities with those present in MCM-41-like solids. It is precisely this cylindrical pore system which we want to expand while maintaining all the remaining features of the UVM-7 architecture. Secondly, we intend to understand why, according to the up to date reported results, the maximum possible pore size expansion in related materials is relatively small, even when using great amounts of swelling agents.

2. Experimental section

2.1. Chemicals

All the synthesis reagents are analytically pure and were used as received from Aldrich (≥98.0% tetraethyl-orthosilicate (TEOS), ≥99.0% triethanolamine [$N(CH_2{-}CH_2{-}OH)_3$, hereinafter TEAH3], ≥98% cetyl-trimethylammonium bromide (CTMABr), (≥99%) alkanes of different chain length (from n-hexane to hexadecane) and absolute ethanol).

2.2. Preparative procedure

The method is an adaptation of the so-called “atrane route”, which is based on the use of (1) a hydroalcoholic reaction medium supporting the formation of silatranes as inorganic precursors and (2) a cationic surfactant as supramolecular template and, consequently, as a porogen agent after template removal. Details of the “atrane route” have been reported elsewhere [15,16,32]. Its application for obtaining the conventional UVM-7 materials was widely discussed in Ref. [16]. In the present case, the use of alkanes as swelling agents requires procedural modifications but enables a certain modulation of the porogen effect of the surfactant. All of the silica samples reported in this publication were prepared by the same general method, and using molar ratios of the reagents in the final reaction mixture according to: 2 Si:7 TEAH3:x CTMABr:y C_nH_{n+2}:180 H_2O ($0.3 \leq x \leq 1.9$; $0 \leq y \leq 4$; $n = 6, 8, 10, 12, 14, 16$). Insofar as one basic objective was to evaluate the influence of the swelling agents (alkanes) by themselves in the expansion of the pore size, we prepared a series of silicas of reference in which x was fixed at 0.5 (i.e., the x value previously optimized for obtaining the conventional UVM-7 materials [16]). The implication of alkanes in the reaction processes forced us to modify the original “one-pot” synthetic procedure by adopting a “two-pot” strategy. Thus, two reagents, A and B, were independently prepared. A was a dissolution containing silatranes and B a colloidal suspension of expanded micelles. The A dissolution was prepared by mixing 11.2 mL of TEOS and 13.3 mL of TEAH3. This mixture was heated at 140 °C for 5 min to favor the formation of silatrane complexes in TEAH3 medium. The resulting clear solution, which contained practically 0.05 mol of silatranes (mainly in the form of Si(TEA) (TEAH2) [15,32], where TEA is the fully deprotonated ligand), was cooled down to room temperature. B was prepared by dissolving 4.56 g of CTMABr ($x = 0.5$ series; the corresponding quantity for other x values) in 10 mL of TEAH3 at 120 °C. When the temperature dropped to ca. 80 °C, 80 mL of water plus the required volume of alkane (according to $0 \leq y \leq 4$) were added to this solution, what immediately provoked some turbidity (except for $y = 0$). The resulting colloidal suspension, B, was stirred for 10 min and then added to A. After a few seconds, we were already beginning to see a white solid in suspension in the reaction mixture (A + B). This as-prepared mixture was allowed to age at room temperature for 12 h under stirring at ca. 700 rpm. The resulting mesostructured powder was separated by filtration, washed with water and ethanol, and air dried (samples denoted as x/yCn-UVM-7(M)). In order to prepare the final porous material, the surfactant was removed from the mesostructure by calcination at 550 °C for 5 h under static air atmosphere (samples denoted as x/yC_n-UVM-7(C)). Alternatively, surfactant removal can be performed by chemical extraction (see Supplementary information). Summarized in Table 1 are the main preparative and physical data for some representative x/yC_n-UVM-7(C) porous silicas (the data for the complete set of silicas prepared in this work can be found in the Supplementary information, Table S1).

2.3. Chemical analysis

A selected set of as-synthesized mesostructured samples (i.e., solids containing both surfactant and alkane) were analyzed by CNH elemental analysis. In all cases, the surfactant content was independently determined spectroscopically. So, 0.025 g of the mesostructured sample were dissolved in 25 mL of 5 M NaOH. Then, the organic portion was extracted with chloroform and methyl orange, and the specific surfactant content was easily calculated from the absorbance value at 508 nm [33]. In turn, the combination of these results with the CNH analyses allowed us to determine the amounts of the swelling agent (alkane) really included in the as-synthesized samples (x/yC_n-UVM-7(M)) (Table 2).