



Decoupling particle formation from intraparticle ordering in mesostructured silica colloids

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ARTICLE INFO

Article history:

Received 8 November 2010

Received in revised form 12 April 2011

Accepted 20 April 2011

Available online 27 April 2011

Keywords:

Mesoporous silica

SBA-15

Formation mechanism

Inorganic silica source

Colloidal particles

ABSTRACT

A synthesis methodology that decouples the formation of silica particles from their internal mesoordering has been developed. This was possible by employing synthesis conditions that combine fast nucleation and growth of particles with slow silica condensation. The synthesis developed is based on an inorganic silica source and the nonionic block copolymer Pluronic P123 using a synthesis pH of 3 and conditions that result in a stable colloidal suspension. Using a two-step procedure the particles can be first formed and then triggered into developing an ordered internal mesostructure by subsequent addition of silica or Pluronic. This is possible because under the conditions employed the particles are stabilized by relatively weak interactions before the formation of a stable silica network.

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1. Introduction

Mesostructured silica has received enormous interest since its announcement in the early 1990's. This has led to the development of a large variety of synthesis routes for its preparation. In order to optimize the material for different applications it is important to be able to control properties such as pore size, mesoorder and particle morphology. To do this it is essential to understand the formation mechanism of these materials. One of the synthesis routes that have gained the most attention is the synthesis of SBA-15 in which non-ionic block copolymers are used as structure directing agent [1,2]. The mechanism of this synthesis has been discussed since the first publication but is still not fully understood. One of the main discrepancies between different proposed mechanisms concerns when mesoorder is achieved internally in the formed particles and whether or not a mesoordered structure is obtained directly upon particle formation or if it is a result of a separate subsequent reorganization step following particle formation.

A mechanism based on floc formation and precipitation, followed by an internal rearrangement has been proposed [3,4]. Several other studies also support a mechanism where the silica

and Pluronic aggregate before the generation of an ordered structure takes place [5–8]. However, others have suggested mechanisms, where the interaction between silica and Pluronic leads to elongated cylindrical hybrid organic–inorganic micelles. These micelles then aggregate directly into an ordered structure [9–11].

Recently, a modified synthesis of SBA-15 was presented differing from the conventional synthesis through the silica source used, the synthesis temperature and the pH employed [12,13]. While SBA-15 most often is prepared from tetraethylorthosilicate (TEOS) at pH < 1 at temperatures of 35–60 °C, the modified synthesis is prepared from ion-exchanged water glass at pH 3 and room temperature. All these differences are attractive from an industrial perspective. The final product of the modified synthesis shows some interesting characteristics; the obtained particles are much smaller than the conventional product and the particles can be made colloidally stable. Furthermore, the final particle size can be controlled by the electrolyte concentration of the reaction solution [13]. In this paper attention is directed to the development of mesoorder in the formed particles to further improve the understanding of this exciting and versatile material. The aim with this study is to illustrate whether or not the particle formation and the ordering of the internal structure can be regarded as two separate processes allowing for tuning of particle properties. The internal structure here refers to the organization of the surfactant and silica inside the particle. The results are discussed within the general context of formation mechanisms for block copolymer-templated syntheses and the influence of differences in silica source and pH used is explained.

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2. Experimental methods

2.1. Synthesis

The syntheses of mesostructured silica were performed at room temperature (20 °C) using the nonionic block copolymer Pluronic P123 as structure-directing agent. The silica source used was water glass (SiO₂:Na₂O molar ratio 3.4 obtained from Eka Chemicals). The water glass was diluted, using MilliQ water, to a solution with 5 wt.% SiO₂. The pH of this solution was lowered to pH 3 using a strong ion-exchange resin (Amberjet 1500H).

Synthesis S1 was prepared by adding the acid silica solution to an aqueous solution containing dissolved Pluronic while stirring. The composition of the final reaction solution was 1:1.75:100 (SiO₂:P123:H₂O) based on mass. After about 30 s the stirring was stopped and the synthesis solution was then left at static conditions at room temperature. In order to follow the formation of the mesostructured material, samples of the reaction solution were collected at different times and examined by DLS and TEM.

Syntheses S2–S5 were prepared in the same manner as S1 but with differences outlined in the following in order to illustrate details of the formation mechanism. First S2 and S4 were prepared with the compositions 1:3.5:173 and 1:0.88:92 (SiO₂:P123:H₂O) respectively, based on mass. After 1 h both samples were divided into two equal parts, where one part was kept as prepared. An extra amount of acid silica solution was added to the second part of the S2, while to the second part of S4 an extra addition of Pluronic solution was added, forming reaction solutions S3 and S5, respectively. Stirring was used for about 30 s during the additions. Both S3 and S5 had the same composition as S1, 1:1.75:100 (SiO₂:P123:H₂O) based on mass. The syntheses were then left at static conditions at room temperature.

2.2. Analytical methods

Transmission electron microscope (TEM) images were obtained with a JEOL JEM-1200 EX II TEM operated at 120 kV. S1 was analyzed by diluting a small amount of reaction solution with MilliQ water after 1, 10 min, 1, 4, and 24 h of reaction, respectively. The samples were prepared by adding a drop of diluted reaction solution on a holey carbon-coated copper grid followed by evaporation. For syntheses S2–S5 only samples of the final stage, several days after the start of the synthesis [13], were prepared using the same sample preparation method.

Dynamic light scattering (DLS) measurements were performed using a Zetasizer nano-ZS from Malvern Instruments. The correlation functions were analyzed using cumulant analysis [14] and CONTIN [15]. The two methods gave similar results and the reported values are intensity averaged hydrodynamic diameter obtained from calculations based on the first cumulant. The quality of the results from the cumulant analysis was evaluated using the residuals obtained in the analysis. These show the deviation between a measurement data point and the fitted curve. For a good fit the values of the residuals should be low and vary with a random behavior. For the measurements performed most of the fits were very good with low residuals (less than ± 0.01) for the entire fit. A few samples showed larger residuals and oscillations at longer correlation times. This indicates a lower quality of the fit in the region corresponding to larger particles and that these samples contain small amounts of larger particles, most probably dust. The influence of these deviations on the calculated Z-average has been tested by reducing the amount of data used in the cumulant analysis. It was found that this only had a minor effect on the calculated Z-average. We therefore decided to use the default

settings, excluding data below 10% of the starting value for the correlation function, for all samples analyzed.

S1 was analyzed after 1, 10 min, 1, 4, and 24 h of reaction both as prepared and by diluting a small amount of reaction solution with MilliQ water. The duration of each measurement was ca 1 min. The main reason for studying both the as-prepared and the diluted samples is that the as-prepared measurements give results for the actual synthesis solution where interparticle interaction and viscosity could influence the results, whereas the diluted sample gives a more accurate particle size since concentration effects are minimized. The diffusion in the concentrated reaction solution may be restricted and the size of the particles may thus be overestimated. For syntheses S2–S5 only the final stage was analyzed. These samples were diluted with MilliQ water prior to the measurement. In order to minimize the influence from the dilution all solutions were analyzed directly after dilution. The particles studied are not always spherical and the values reported should be used for comparing different samples and showing trends of changes, not as measurements of the absolute particle size.

The small-angle X-ray scattering (SAXS) instrument used was the pinhole instrument at the University of Aarhus [16]. It is the prototype of a commercially available small-angle X-ray camera (NanoStar, Bruker AXS). It employs a rotating anode X-ray source (CuK α) (0.1 \times 1.0 mm² source size with a power of 1 kW) and a set of cross-coupled Göbel multilayer mirrors for monochromatizing the radiation and for converting the divergent beam from the source to an essentially parallel beam. The instrument has an integrated vacuum in order to reduce background. The instrument covers a range of scattering vectors q between 0.010 and 0.35 Å⁻¹ ($q = (4\pi/\lambda) \sin\theta$, where 2θ is the scattering angle and $\lambda = 1.542$ Å, the X-ray wavelength). All measurements were made at room temperature. The SAXS data were corrected for variations in detector efficiency, for spatial distortions, and azimuthally averaged. A measurement on water with a small amount of HCl (pH 2.8) was used as background and was subtracted from the data. Finally, the data were converted to an approximate absolute scale using the scattering from pure water as a primary standard. A small amount of each reaction solution was directly transferred to a capillary tube, which was sealed and placed in the sample holder for *in situ* SAXS analysis. The first spectrum was recorded within a few minutes after the mixing of each synthesis solution. The duration of the initial measurements was 30 s. This time was subsequently increased to improve the signal to noise ratio.

Since the DLS and the *in situ* SAXS measurements were performed at different geographical locations, synthesis S1 was performed twice using as similar conditions as possible. The TEM analysis was performed on both samples to confirm that comparable results were obtained. The results shown are from the sample used in the DLS study. The TEM results for the synthesis analyzed with *in situ* SAXS showed the same trends but the final average particle size was somewhat smaller.

3. Results

The results section is divided in two parts, where the first focuses on following the evolution of synthesis S1 with time. The second part concerns the separation of particle formation and ordering of the internal structure by the two-step procedure, employed in syntheses S2–S5.

3.1. Evolution of synthesis S1

For synthesis S1 the development of particles during their formation was studied using DLS on as-prepared samples of the

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