Morphology Control of Mesoporous Silica Particles

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We demonstrate morphology dependence of mesoporous silica synthesized in acidic condition via the control of silica hydrolysis and condensation at 4 °C under quiescent acidic condition, and without using any organic cosolvents. Tetramethyl orthosilicates (TMOS) is used as a silica source and cetyltrimethylammonium chloride (CTAC) as the structure directing agent (SDA). Straight fibers of different aspect ratio with pore channels aligned parallel to the fiber axis are synthesized by varying TMOS from the sols of molar compositions 0.17–0.32TMOS:0.22CTAC:9HCl:100H2O. Curved morphologies such as discoids and spheres are prepared by controlling acidity in the sols of molar compositions 0.17TMOS:0.22CTAC:14–16HCl:100H2O. The mesoporous silica particles show BET surface area of 1100–1400 cm²/g, and the mesopore diameter and mesopore volume are in the range of 2.2–2.6 nm and 0.6–0.8 cm³/g, respectively.

1. Introduction

In the burgeoning field of mesostructured materials, synthesized through the self-assembly of inorganic polymeric species and structure directing agent (SDA), a precise control over the morphology and orientation of the pore channels is needed to realize the promising applications of these materials. For example, mesoporous silica fibers with open-ended straight channels could be used as nanofluidic material for applications in electrophoresis, so also for biologically sensitive transistor, optics, and polymer incorporation and their alignment.1–6

The basic interest in mesoporous silica stems from the presence of well-ordered structure that provides high surface area and accessibility to molecular species through the channels. In addition, the possibility of synthesizing different types of mesostructures with multiple pore architecture further enhances its versatility for different applications.

It is possible to synthesize mesoporous silica via the alkaline or the acidic routes using surfactants as SDAs with the properties of mesoporous silica strongly dependent on the maintained synthesis conditions as hydrolysis/condensation of silica is strongly influenced by the pH of the synthesis sol. Even though better condensation of the silanol groups occurs in mesoporous silica obtained under alkaline conditions,1–3 a rich morphology in shapes is achievable in acidic conditions.9–13

During acid synthesis (with pH <2), the silica species in solution are positively charged as SiO⁻H₃⁺ (I⁺). The surfactant (S⁻) and silica interaction as mediated by the counterion X⁻ becomes S⁺X⁻I⁺, and this micelle—counterion interaction is in thermodynamic equilibrium.7 There are various factors such as ion exchange equilibrium of X⁻ on micellar surface, surface-enhanced concentration of I⁺, and proton-catalyzed silica condensation near micellar surface, phase separation, colloid stability, and micelle aggregation, responsible for directing the shapes of mesoporous silica.9–13 The growth of a mesoporous silica particle in specific shape is believed to be through the firstly formed precursor silica—surfactant nanoparticles which grow through accretion and aggregation of silica/surfactant micelle.9 Small changes in acidity and specific kind of dislocations defects10 are responsible for the production of characteristic shapes such as curved morphologies, etc. Another approach to explain the shape formation was proposed by Sokolov et al.,14 wherein the authors suggested that the shape of the final particles was decided during the liquid-crystal stage by equilibration of free energy with entropic energy. The mechanism was confirmed later by the same authors.15,16

Mesoporous silica have been synthesized in the form of short and long fibers,9,10,16–17 gyroids and discoids,9 hollow and solid spheres,18–22 films,23 or hierarchical spheres24 using tetraethyl orthosilicates (TEOS) and ionic surfactants or block copolymers, in the presence or absence of cosolvents, under various processing conditions. Although a few studies have been reported on the synthesis of short and straight fibers,16,17 the actual control of aspect ratio of such straight fibers with the pore channels aligned parallel to the fiber axis has not been demonstrated so far.

In this work, we will demonstrate morphology dependence of mesoporous silica particles that are synthesized using tetramethyl orthosilicates (TMOS) as the silica source and cetyltrimethylammonium chloride (CTAC) as the structure directing agent (SDA) in acidic condition via the control of silica hydrolysis and condensation processes at 4 °C under quiescent condition. Straight fibers of different aspect ratio with pore channels parallel to the fiber axis are synthesized by varying TMOS in the sols, whereas curved morphologies such as discoids and spheres are prepared by controlling silica hydrolysis and condensation through the adjustment of the acidity of the sols.

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2 Experimental

2.1 Synthesis. Mesoporous silica straight fibers, discoids, and spheres were synthesized using TMOS (98%, Aldrich) as the silica source and CTAC (25% aqueous, Aldrich) as the SDA in the presence of HCl (36% aqueous, J T Baker) at 4 °C, under quiescent condition. The molar sol compositions required for the selective synthesis of fibers and curved shapes are shown in Table 1. Prior to the synthesis, chemicals and deionized water (resistance 18 MΩ cm, MilliQ ultrapure) were precooled to 4 °C for 2 h. Concentrated HCl was added to CTAC/H₂O solution taken in a high-density polypropylene (HDPP) bottle, and the mixture was stirred at 500 rpm on a magnetic stirrer for 10 min; thereafter, it was cooled to 4 °C in a freezer for 30 min under static condition. Precooled TMOS was then added slowly to the above sol under stirring at ambient conditions in 1 min. The clear sol was then allowed to react at 4 °C under quiescent condition for 3 h. The white product formed was recovered by vacuum filtration using a Buckner funnel, washed several times with distilled water and subsequently dried at 70 °C for 2 h. Calcination of the material was performed at 500 °C for 5 h, in flowing air atmosphere. The heating rate of the furnace was maintained at 5 °C/min.

2.2 Characterization. The powder X-ray diffraction (XRD) patterns on the particles were collected on an M03X-HF, Bruker AXS, instrument using Cu Kα radiation (40 kV, 40 mA) and in the range of 1.5—8° 2θ, 26. The scanning electron microscopy (SEM) images were recorded by using a JEOL 6300 instrument operating at 15 kV. Prior to the measurements, the samples were coated with gold for 1 min in an Anatech hummer 6.2 sputtering system operating at 40 millitorr. The transmission electron microscopic (TEM) images of the calcined particles were recorded by using a JEM 2010, JEOL, electron microscope, at an acceleration voltage of 200 kV. The samples were prepared by dispersing the calcined material in water at room temperature. A few drops of this dispersion were placed on a holey carbon-coated copper mesh and dried at room temperature. The N₂ adsorption/desorption isotherms of the calcined mesoporous silica samples were measured at 77 K on Autosorb-1, Quantachrome, instrument. Before the measurement, samples were degassed at 200 °C and 10 Pa for at least 12 h.

3. Results

It is evident from Table 1 that the morphology and the mesoporous order [expressed in terms of the normalized intensity of d(100), p6mm, hexagonal, peak in XRD] of the synthesized particles is strongly dependent on the molar composition of the synthesis sol. The morphology of the particles was monitored using an optical microscope (Polarm-L 213-TR) and confirmed from SEM.

### Table 1: Molar Sol Compositions, Morphology, and Mesoporous Order Estimation from XRD for Silica Particles Synthesized at 4 °C, 3h

<table>
<thead>
<tr>
<th>sample</th>
<th>morphology</th>
<th>average particle size (µm)</th>
<th>TMOS</th>
<th>HCl</th>
<th>CTAC</th>
<th>H₂O</th>
<th>molar sol composition</th>
<th>normalized intensity of the p6mm d(100) XRD peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>fiber</td>
<td>4 × 1.8</td>
<td>0.17</td>
<td>9</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>1</td>
</tr>
<tr>
<td>F-2</td>
<td>fiber</td>
<td>8 × 1.6</td>
<td>0.22</td>
<td>9</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>0.66</td>
</tr>
<tr>
<td>F-3</td>
<td>fiber</td>
<td>18 × 8</td>
<td>0.32</td>
<td>9</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>0.55</td>
</tr>
<tr>
<td>M-1</td>
<td>mixture (fiber, sphere and discoid)</td>
<td>0.17</td>
<td>12</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>D-1</td>
<td>discoid</td>
<td>3</td>
<td>0.17</td>
<td>14</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>0.46</td>
</tr>
<tr>
<td>S-1</td>
<td>sphere</td>
<td>3</td>
<td>0.17</td>
<td>16</td>
<td>0.22</td>
<td>100</td>
<td>as-prepared</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Straight and mesoporous silica fibers (F-1), Figure 1A, average size 4.0 × 1.8 µm (estimated from SEM images), were obtained from the synthesis sol of composition 0.17TMOS:9HCl:0.22CTAC:100H₂O at 4 °C, 3 h. However, when the TMOS concentration in the sol was increased to 0.22 (0.22TMOS:9HCl:0.22CTAC:100H₂O), longer fibers, F-2, of average size 8.0 × 1.6 µm were obtained, Figure 1B. As can be seen from the figure, there is an increase of length of the fiber by twice that of F-1; the diameter or width of the fiber was found to be slightly decreased. Further increase in the concentration of TMOS to 0.32 (0.32TMOS:0.22CTAC:100H₂O) results in the formation of much thicker and broader fibers, F-3, of average size 18 × 8.0 µm, Figure 1C. Additionally, we also investigated the effect of HCl on the morphology of the particles obtained at 4 °C for 3 h, under quiescent condition. A mixture, M-1, comprising short fibers, discoids, and spheres, was obtained for the sol of molar composition 0.17TMOS:12 HCl:0.22CTAC:100H₂O. Further increasing the concentration of HCl to 14 and 16, resulted in the formation of discoids and spheres, D-1 and S-1, respectively (Table 1). The morphology of the three samples, M-1, D-1 and S-1, was confirmed from the SEM images shown in Figure 1D and Figure 2A,B, respectively.

The presence of hexagonal p6mm hexagonal structure akin to that of SBA-3 in the particles was confirmed from XRD patterns of the as-synthesized samples shown in Figure 3A—F. The XRD patterns for the calcined fibers shown in Figure 4A—F indicate that mesoporous structure was retained even after high-temperature calcination. Apparently, the TMOS concentrations investigated in this study, influenced slightly the mesoporous order in the fibers, as evaluated from the intensities of p6mm, (100) peak in the XRD before and after calcination. Among the three fibers, F-1 had the maximum pore order, followed by F-2 and F-3, respectively.

A partial damage to the mesoporous structure for the spheres, S-1, was observed from the decrease of intensity of the (100) peak in the XRD pattern of the calcined spheres (Figure 3F and Figure 4F). The spherical external morphology was however not affected upon calcination, as checked from SEM (not shown).

The TEM image of F-1, shown in Figure 5A, confirms the p6mm hexagonal structure in the fibers. The pore channels in the fibers run parallel to the horizontal fiber axis, providing pore accessibility from the ends of the fiber as evidenced from the TEM study. The TEM images of discoids and spheres, shown in panels B and C, respectively, of Figure 5 confirm the mesoporous structure further revealing the pore arrangement of the silica mesostructure. In discoids, the pore channels are coiled around the particle axis providing a close-type structure. In contrast, the less-ordered mesostructure in sphere is of open-
type, providing greater molecular accessibility from the surface-air interface.

The N\textsubscript{2} adsorption/desorption measurement on the calcined materials resulted type IV isotherms in all cases as shown in Figure 6. The BET surface area of the materials was 1100–1400 m\textsuperscript{2}/g, the total pore volume and the BJH pore diameter, calculated from the adsorption branch of the isotherm were 0.6–0.8 cm\textsuperscript{3}/g, and 2.2–2.6 nm, respectively. Generally, the mesopore diameter was found to be increasing upon increase of TMOS and HCl concentrations in the sol. The data obtained together with the calculated unit cell parameter, \(a_0\), are shown in Table 2. The porosities, BET surface area, and unit cell parameter are in agreement with the earlier data published for mesoporous silica\textsuperscript{3,18–20}

4. Discussion

For the formation mechanism of mesoporous materials, two different pathways were proposed first by the Mobil group\textsuperscript{2–3}. According to the first model, inorganic material enters the aqueous region of a pre-existing liquid crystal phase and condenses to form inorganic walls by liquid crystal templating model. Based on the other pathway, called micelle assembly model, the inorganic species interact with micelles in solution and mediate an organization process leading to liquid-crystal-
like structures. The idea was further developed by Chen et al., who suggested that rod-like inorganic/surfactant complexes are first formed, which then spontaneously pack into an ordered arrangement. Variants of both the models have also been proposed. Later on, Stucky and co-workers developed a more general cooperative assembly model, emphasizing the role of specific interactions between surfactant head groups and inorganic species during self-assembly. They considered electrostatic interactions between cationic surfactants and silica species and argued that the first stage of the process was multidentate binding of silica species to surfactant, which was followed by cooperative assembly of a liquid crystal like phase, driven by the necessity for charge density matching between charged silica and surfactant.

For the formation of different shapes and curved morphologies of mesoporous silica, Ozin and co-workers have suggested that morphologies of mesoporous silica depend largely on the degree of curvature and the accretion type induced by various topological defects in the SiO$_2$—CTAC precursor particles that directs the growth of hexagonal mesoporous silica toward specific morphology. Sokolov et al. and Yang et al. also proposed a model of minimization of free energy for the formation of curved shapes that was later corroborated in. Mou and co-workers have highlighted the role of anions and their binding strength with the surfactant to explain the formation of different shapes and curved morphologies.

Figure 3. (A–F) XRD patterns of the as-synthesized mesoporous silica particles, fibers F-1 to F-3, mixture of particles, M-1, discoids, D-1, and spheres, S-1, respectively.

Figure 4. (A–F) XRD patterns of the calcined mesoporous silica particles, fibers F-1 to F-3, mixture of particles, M-1, discoids, D-1, and spheres, S-1, respectively.

Figure 5. (A–C) TEM images of mesoporous silica particles, fiber, discoids, and spheres, F-1, D-1, and S-1, respectively.
rope or gyroid shaped mesoporous silica, while Marlow et al.\textsuperscript{33} have proposed the formation of long, curved fibers through coiling of the growing micellar seeds in liquid state.

In another recent study, Park et al.\textsuperscript{34} have proposed an end-to-end growth between growing silica/surfactant seed and hexagonal micellar rod to explain the formation of long periodic mesoporous organosilica fibers. Side-to-side growth of rod and seed with decrease of surface double layer charge density by agitation at higher temperature was proposed to explain the formation of curved particles.

On the basis of the earlier reports\textsuperscript{9–17,35} and our present experimental results, we believe that the growth of mesoporous silica particles must be involving two stages. The first stage is the self-assembly between polymeric silica species and surfactant molecules to form the precursor species. The second stage involves continuous growth of these precursors into well-formed particles through accretion. The morphology and the internal pore structure of the particles being influenced by the first stage of the cooperative assembly and the associated free energy change. The contribution toward free energy change results from the interactions between polymeric silica and surfactant, conformational energies of surfactant hydrocarbon chain and head group, and the chemical potential of the sol, as has been recently proposed by Wang et al.\textsuperscript{35} Increase of TMOS concentration in the sols F-1–F-3, favors a higher rate of silicification, and hence polymerization induces differential contraction of silicate micelle rods leading to end-to-end or lateral growth\textsuperscript{34} of the particles as in the case of F-2 and F-3, respectively, resulting in the increase of fiber size. In fact for F-3, the thick fibers synthesized from the sol of molar composition 0.32TMOS:9HCl:0.22 CTAC:100 H\(_2\)O, a few glued up together particles were observed in SEM as shown in Figure 8, suggesting that the excess TMOS in the sol must have promoted higher rate of silicification and accretion, hastening the gluing up of some of the growing precursor particles—either end-to-end or laterally.

Increasing the concentration of TMOS also promotes the formation of silicates with a lower degree of protonation to a

<table>
<thead>
<tr>
<th>particle</th>
<th>(d(100) \text{[nm]})</th>
<th>(a_0/\sqrt{\text{a}}) \text{(nm)}</th>
<th>pore \text{diameter} \text{a} \text{(nm)}</th>
<th>pore \text{volume} \text{b} \text{(cm}^3\text{/g)}</th>
<th>BET \text{(m}^2\text{/g)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>2.805</td>
<td>3.225</td>
<td>2.2</td>
<td>0.72</td>
<td>1239</td>
</tr>
<tr>
<td>F-2</td>
<td>2.800</td>
<td>3.220</td>
<td>2.4</td>
<td>0.74</td>
<td>1300</td>
</tr>
<tr>
<td>F-3</td>
<td>2.701</td>
<td>3.107</td>
<td>2.4</td>
<td>0.60</td>
<td>1121</td>
</tr>
<tr>
<td>M-1</td>
<td>3.032</td>
<td>3.487</td>
<td>2.4</td>
<td>0.72</td>
<td>1345</td>
</tr>
<tr>
<td>D-1</td>
<td>3.080</td>
<td>3.542</td>
<td>2.5</td>
<td>0.79</td>
<td>1298</td>
</tr>
<tr>
<td>S-1</td>
<td>3.280</td>
<td>3.772</td>
<td>2.6</td>
<td>0.80</td>
<td>1421</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unit cell \(a_0 = 2\sqrt{3} \times d(100). \textsuperscript{b} Determined from adsorption branch of N\(_2\) adsorption/desorption isotherm according to Barret–Joyner–Halenda (BJH) method).
more weakly bound and progressively less well organized surfactant-silicate co-assembly, as such, the d(100), p(6nm) peak intensity, was found to be slightly decreased upon increase of TMOS concentration in the sol (Table 1).

Increasing the concentration of HCl in the sol strongly influences the shape of particles, as it affects electrostatic interactions between surfactant molecules and charged silica species changing the chemical potential of the solution. Further, silica polymerization of SiO$_2$–CTAC precursors is also increased creating much higher protonated silica in the headgroup region of the micelles. Alterations in pH will tune both the sheath of positive charge on the surface of the SiO$_2$–CTAC precursor particle and the magnitude of the electrical double-layer repulsion between particles, as a result, the cooperative assembly between surfactant molecules and silica species produces nucleation sites with different morphology in order to minimize the overall free energy of the growth system. When TMOS is used as the silica source, the silica condensation rate is faster, resulting in a high local curved energy so that energy penalty for cylindrical channel bending is quite high that the rate is faster, resulting in a high local curved energy so that energy penalty for cylindrical channel bending is quite high that the formation of more curved morphologies, such as discoid that transforms to sphere upon further increase of acidity. Previously, Ogura et al. have reported the mesophase transformation proceeds to follow fiber – discoid – sphere transition with increasing acidity. Previously, Ogura et al. have reported the mesophase structure control through the adjustment of silica condensation and drying of the wet precipitates at room-temperature highlighting the role of silica condensation in mesostructure determination of silica.

It is clear from this study that through the control of silica hydrolysis and condensation, and acidity, one could get a much better handle to control the morphology and the pore architecture in mesoporous silica synthesized under acidic quiescent condition. The aspect ratio of the fibers could be further improved by increasing the reaction temperature as the length of the fiber will increase with higher thermal energy. Replacing TMOS with other alkoxysilanes or further fine-tuning of the synthesis conditions can also provide a plausible approach to the formation of mesoporous particles of desired morphology and internal structure.

5. Conclusion

We have selectively synthesized mesoporous silica straight fibers of different aspect ratio, and curved morphologies such as discoids and spheres using tetramethyl orthosilicates (TMOS) as a silica source and cetyltrimethylammonium chloride (CTAC) as the structure directing agent (SDA) at 4 °C, under acidic quiescent condition and by adjusting silica/surfactant molar composition to control the silica hydrolysis and condensation in the liquid state. The particles showed p(6nm) hexagonal structure, the BET surface area, mesopore diameter, and mesopore volume of the materials were in the range of 1100–1400 m$^2$/g, 2.2–2.6 nm, and 0.6–0.8 cm$^3$/g, respectively.

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References and Notes


(22) Naik, S. P.; Sokolov, I. Private communication.


