Seed polymerization of tetraethyl orthosilicate in the presence of colloidal silica spheres

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Abstract

Kinetic analyses were made for the seed polymerization of tetraethyl orthosilicate (TEOS) in the presence of colloidal silica sphere seeds by turbidity and dynamic light scattering (DLS) measurements. Transmission electron microscopy (TEM) of the spheres formed was also used. TEOS is polymerized exclusively on the surfaces of the seed spheres, their sizes ranging from 29 to 184 nm in diameter. The sphere size versus time and the cube root of the absorbance versus time from DLS and turbidity measurements agree well, especially in the beginning of the reaction. The seed polymerization starts immediately on the addition of seed spheres, though the polymerization in the absence of the seeds proceeds after a certain induction time ranging several tens of seconds to several minutes. The polymerization rates of the reaction increase when the size and/or the concentration of the seed spheres increases. The thickness of the TEOS layers formed on the seed surfaces increases as the seed size increases; this is confirmed by the TEM pictures. These results are consistent with the polymerization mechanism of the formation of small preliminary particles followed by their coalescence on the surfaces of seeds to the final large spheres coated with silica layers.

Key words: Seed polymerization · Turbidity · Dynamic light scattering · Transmission electron microscope

Introduction

Monodisperse colloidal particles of any size and any shape have provided most of the exciting and essential samples for studies in the field of colloidal science. The main purpose of this work was to synthesize hydrophilic and stable colloidal particles of any size and shape. As is well known, colloidal silica spheres are highly hydrophilic and disperse nicely without coagulation in water, especially in the deionized state with the coexistence of mixed beds of cation- and anion-exchange resins. However, syntheses of the monodispersed and non-spherical particles of silica are extremely difficult. The reaction mechanism of the monodispersed, non-spherical and stable colloidal particles was studied in our laboratory by coating the seed particles with silica layers. In this report, the detailed investigation of seed polymerization of tetraethyl orthosilicate (TEOS) on the surfaces of colloidal silica spheres is reported.

There have been significant developments in techniques for colloidal silica synthesis and this have been accompanied by recent advances in the sol-gel method in the field of fine ceramics [1–3]. The synthesis of colloidal silica was first reported by Stober et al. [4] in 1968 and was studied further by several researchers [5–18]. The polymerization reaction is composed of the hydrolysis of silicate, Eq. (1), and then the dehydration is accompanied by three-dimensional cross-linking, Eq. (2).

\[
\begin{align*}
\text{Si(OCH}_3)_4 + 4\text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 + 4\text{C}_3\text{H}_7\text{OH} & \text{(1)} \\
\equiv \text{SiOH} + \text{HO} & \equiv \text{Si} & \equiv \rightarrow \equiv \text{Si} & \equiv \text{O} & \equiv \text{Si} & \equiv +\text{H}_2\text{O} & \text{(2)}
\end{align*}
\]
According to Shimohira and coworkers [7, 19] the primary small particles are formed during an induction period, \( t_i \), at the beginning of the reaction. Their critical size was estimated to be 10–20 nm [7]. The growing process with the coalescence of the primary particles then follows, and the final silica spheres are formed. Shimohira and coworkers proposed that the sixth order of the sphere size increases linearly with the reaction time, Eq. (3),

\[
r^6 \propto t
\]

where \( r \) is the radius of the spheres. It should be recalled that the Lifshitz–Slyozov–Wagner theory supports the second- and third-order relations for the surface reaction-controlled and diffusion-controlled mechanisms, respectively [20]. Furthermore, fourth- and fifth-order relations were proposed for the surface diffusion and the diffusion accompanied by the dislocation in the cases of ceramics and metal formations, respectively [20, 21]. Several experiments, however, supported sixth- or seventh-order relations [22–24], and theoretical explanations for the relationships were not successful. Recently, a small-angle X-ray scattering study [18] revealed that after an induction period the first particles to appear in the solution have a radius of gyration of about 10 nm and are mass fractals characterized by their polymeric open structure. The report did not support the growth model proposed so far by Shimohira and coworkers, for example.

Recent advances in the polymerization reaction of colloidal silica spheres were reviewed by Oghara [25]. We studied the kinetic mechanism of the formation reaction of colloidal silica spheres from TEOS in normal gravity on the Earth [26] and also in microgravity [27].

### Experimental

**Materials**

Six kinds of colloidal silica spheres were kindly donated by Catalyst & Chemicals Co. (Tokyo). The characteristics of the spheres are compiled in Table 1. Their diameters and the polydispersity indices range from 29 to 184 nm, and from 0.04 to 0.21, respectively. The colloidal samples were first purified several times using an ultrafiltration cell (model 202, Diaflo-XM300 membrane, Amicon Co.), and then deionized by a mixed bed of cation- and anion-exchange resins more than 3 years before use. They released an amount of alkali from their surfaces. Thus, it takes a long time for complete deionization, since the deionization proceeds between the two solid–liquid phases stepwise, i.e., between colloidal spheres and water and then between water and the resins. Their diameters (\( d \)) were determined through the courtesy of Nippon Synthetic Rubber Co. (Tokyo) by electron microscopy. The standard deviation (\( \delta \)) of the diameter of each sphere from the mean diameter was determined from the electron microscope pictures of more than 500 spheres. The surface density of strongly acidic groups of these spheres was determined by conductometric titration with a Horiba model DS-14 conductivity meter (Kyoto). Strongly acidic and weakly acidic groups coexisted at the surface of the colloidal silica spheres.

**Table 1 Properties of the colloidal silica spheres used as seeds**

<table>
<thead>
<tr>
<th>Spheres</th>
<th>Diameter (d) (nm)</th>
<th>( \delta ) (nm)</th>
<th>( \delta/d )</th>
<th>Charge density (( \mu )C/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-22</td>
<td>29</td>
<td>6</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>CS-45</td>
<td>56.3</td>
<td>7.6</td>
<td>0.13</td>
<td>0.30</td>
</tr>
<tr>
<td>CS-82</td>
<td>103</td>
<td>13.2</td>
<td>0.13</td>
<td>0.38</td>
</tr>
<tr>
<td>CS-91</td>
<td>110</td>
<td>4.5</td>
<td>0.040</td>
<td>0.48</td>
</tr>
<tr>
<td>CS-121</td>
<td>136</td>
<td>10.9</td>
<td>0.080</td>
<td>0.40</td>
</tr>
<tr>
<td>CS-161</td>
<td>184</td>
<td>18.6</td>
<td>0.10</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**TEOS** was purchased from Wako Pure Chemicals (Osaka). Ethanol (99.5%) and ammonia (N25%) were commercially available purified grade reagents and were obtained from Wako Chemicals. The water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, Mass.).

**Turbidity and dynamic light scattering measurements**

The turbidity, i.e., absorbance at 600 nm, was recorded using a spectrophotometer ( Beckmann, DU650). Quartz optical cells (10 mm x 10 mm x 70 mm high) with long necks and screw caps were used for the kinetic turbidity measurements. The seed polymerization was started by adding 1 ml TEOS in ethanol to the mixtures of ammonia and the seed spheres in ethanol. Then, the increase in absorbance at 680 nm was measured. The change in the effective radii of the colloidal silica spheres including the thickness of the polymerized layers was also determined using a dynamic light scattering (DLS) spectrophotometer (DLS-7000, Osaka), The reaction mixture of 5 mL was prepared in a Pyrex cuvette (12-mm outside diameter and 130-mm length) with a screw cap. These cuvette cells were ground to a spectroscopic guaranteed level and were very clear.

**Transmission electron microscopy**

The suspension (0.1 ml) was dried on a collodion mesh at room temperature before the transmission microscopy (Hitachi, H8100).

**Results and discussion**

**Size, induction periods, and polymerization rates from turbidity measurements**

A typical example of the turbidity measurements is shown in Fig. 1. The volume fraction of the seed spheres ranges from 0 to 0.001. The total absorbance (\( A \)) consists of the solvent absorption (\( A_s \)), the absorption from the particle formed (\( A_p \)), and the light scattering at \( \theta \) (scattering angle) = 0 (\( A_s \)), i.e., Eq. (4) [4].

\[
A = A_s + A_p - A_s
\]

The \( A_p \) term arising from the colloidal spheres formed in the seed polymerization should increase linearly with increasing volume of the sphere as

\[
A_p \propto N r^3
\]

(5)