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Vapor-phase synthesis of uniform silica spheres through two-stage hydrolysis of SiCl₄

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Abstract

We report, for the first time, a vapor-phase synthesis of nearly monodispersed silica spheres 250–300 nm in size through a twostage hydrolysis of SiCl₄. In the first stage, SiCl₄ vapor was partially hydrolyzed with water vapor in a batch reactor at 150 °C to form silicon oxychloride particles, nearly monodispersed and spherical. In the second stage, these oxychloride particles were converted into silica particles through further hydrolysis at 1000 °C in a tubular reactor, while the morphology and size after the first-stage reaction remained virtually unchanged.

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1. Introduction

Submicron silicas of varying morphology and size are used in many applications, such as fillers for paints and rubbers, for manufacturing nanocomposite materials, and as adsorbents. The preparation of monodispersed spherical silica has received considerable attention since Stober et al. [1] reported that a hydrolysis of tetraethoxysilane in a basic solution of water and alcohol led to the formation of monodispersed silica spheres. A number of studies followed to investigate the particle growth mechanisms, to improve the productivity, and to control the particle size [2–5].

Another applicable method for the preparation of monodispersed spherical silica is the spray hydrolysis of SiCl₄ droplets of uniform size distribution with water vapor [6]. A crucial step is to obtain uniform SiCl₄ droplets. The SiCl₄ droplets formed initially by nebulization are broadly distributed in size, and pass through evaporation and condensation to make the distribution uniform in the presence of AgCl nuclei introduced with the carrier gas. An attempt to hydrolyze tetraethoxysilane (TEOS) droplets was made in a way similar as for the SiCl₄ droplets, but failed due to the slow hydrolysis rate [7].

The vapor-phase synthesis with all reactants as vapor is among the popular routes to nanoparticles of various oxides, including silica. The flame oxidation of $SiCl_4$ vapor is an example. The silica from the flame oxidation, which is called fumed silica, is not spherical; rather, it is highly aggregated and exhibits chain-like structures [8]. Lee and Choi [9] showed that the silica aggregates could be made spherical through a laser beam irradiation; however, those

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Fig. 1. Illustration of the proposed method in comparison with the existing flame oxidation method.

spheres were not uniform in size distribution. TEOS, which is easier to handle than $SiCl_4$, has been used in many studies as a precursor for silica particles through the vapor-phase route [10–13]. None of these silicas was reported to be monodispersed and spherical.

We report a vapor-phase synthesis of nearly monodispersed silica spheres through a two-stage hydrolysis of SiCl₄. The overall reaction of the hydrolysis is represented by SiCl₄ + 2H₂O = SiO₂ + 4HCl. Fig. 1 shows the concept of the proposed method in comparison with flame oxidation. In the first stage, the SiCl₄ vapor is partially hydrolyzed with water vapor at 150 °C to form intermediate oxychlorides, represented by SiO_xCl_y(OH)_z. In the second stage, the intermediates are completely hydrolyzed to silica at a higher temperature. The reactor used in the first stage is of batch type to allow for uniform particle growth; in the second stage, the reactor is tubular for operational convenience. Compared to the Stober method, an advantage of the present method is that dry silica of comparable grade could be produced directly, eliminating the filtration, washing, drying, and calcination. This advantage would be particularly appreciable in ceramics and composites applications that require dry silica as starting material.

2. Experimental

Fig. 2 shows a schematic drawing of the experimental setup, which consists of a precursor evaporator, a tubular furnace and a particle collector. The evaporator, made of stainless steel, is 0.5 cm in diameter and 5 cm in length, and equipped with a septum in the center, a thermocouple, a pressure sensor, and a valve at each end. It is immersed in a cylinder through which hot oil is circulated. A small glove box is located over the septum to protect the moisture-sensitive precursor from being exposed to air during the injection of the precursor with a syringe into the evaporator. More details on the apparatus are available elsewhere [14]. A predetermined volume (less than 1 μ l) of liquid SiCl₄ was injected into the evaporator at 150 °C. The pressure in the evaporator rose with the vaporization and leveled off at the completion of vaporization. A volume of water was then injected into the evaporator. The volume was so small that, upon injection, the water hung as a drop on the syringe tip. The vaporization of the water drop finished within a few seconds, which was confirmed with the pressure sensor.

The mixture of the two vapors was held in the evaporator for a while to induce a partial hydrolysis or the first-stage hydrolysis leading to the formation of an intermediate product. Thus, the evaporator also worked as the reactor for the first-stage hydrolysis. By opening the valves at both ends, the intermediate product was transported by nitrogen gas to a quartz tube, 4 mm in diameter and 35 cm in length, for the second-stage hydrolysis at 1000 °C. After the second-stage reactor, a 250 ml flask containing 1 N NaOH solution was installed for removal of the HCl gas formed due to the hydrolysis.

At the reactor exit, the produced particles were collected in situ on a carbon film that coated a 200 mesh nickel grid (Electron Microscopy Science, Model CF200-Ni) and examined by transmission electron microscopy (TEM) (JEOL,



Fig. 2. Schematic drawing of the experimental apparatus.

Model JEM-2010) and scanning electron microscopy (JEOL, Model JSM-6335F). The crystalline structure was identified by analyzing the electron diffraction pattern obtained from TEM. The chlorine content of the particles was determined with the energy dispersive X-ray of TEM.

3. Results and discussion

3.1. Particle formation in the 1st reactor

Fig. 3 shows the TEM images of the deposits on the grid after the first-stage hydrolysis for 60 s, with the 1st reactor temperature varied from 90 to 150 °C. The volumes of SiCl₄ and water injected into the evaporator were 0.5 and 0.3 μ l, respectively, which were determined to have a SiCl₄ vapor concentration of 10 mol% with the molar ratio of water to SiCl₄ at the stoichiometric value of 2. No distinguishable particles were obtained at 90 and 120 °C. As the temperature was increased to 150 °C, spherical particles, approximately 250 nm in diameter, emerged. By energy dispersive X-ray analysis of the particles, the atomic ratio of Si:O:Cl was determined to be 32:32:36, suggesting that the obtained spheres were not silica, but rather oxychlorides. Ignatov et al. [15]



Fig. 3. Transmission electron microscopic images of the particles collected at the 1st reactor outlets with the reactor temperature varying from 90 to 150 °C; (a) 90 °C; (b) 120 °C; (c) 150 °C. The white scale bar represents 100 nm. The 2nd reactor temperature was held constant at 1000 °C. The initial concentration of SiCl₄ vapor in the 1st reactor was 10 mol%, and the molar ratio of H₂O to SiCl₄ was at the stoichiometric ratio of 2.0. The residence times were 60 s in the 1st reactor and 0.7 s in the 2nd reactor. The reactor pressures were atmospheric.



Fig. 4. Scanning electron microscopic image, at a higher magnification, of a particle of rough surface shown in Fig. 3. The white scale bar represents 100 nm.

proposed the following mechanism for the gas-phase hydrolysis of SiCl₄, showing potential evolution of the intermediate silicon oxychlorides:

$$\begin{split} & SiCl_4 + H_2O \rightarrow SiCl_3OH + HCl \\ & Cl_3SiOH + HOSiCl_3 \rightarrow Cl_3Si - O - SiCl_3 + H_2O \\ & Cl_3Si - O - SiCl_3 + H_2O \rightarrow Cl_3Si - O - SiCl_2 - OH + HCl \end{split}$$

followed by further branching, chain growth and cyclization.

Two groups of spheres can be seen in Fig. 3(c): one with a smooth surface and the other with a rough surface. A sphere of rough surface was further investigated by scanning electron microscopy at higher magnification. As shown in Fig. 4, that sphere was composed of numerous smaller objects of irregular shape. By EDS analysis, the chlorine content was 13.8 at.% in the spheres of smooth surface and 54.0 at.% in those of rough surface. The spheres of rough surface disappeared as the hydrolysis reaction time was increased from 60 to 180 s or as the molar ratio of water to SiCl₄ was increased to 6.0 by three times the stoichiometric ratio. From these experimental observations, the spheres of rough surface were probably in the transition toward the spheres of smooth surface.

3.2. Comparison of particles between the first and the second stage reactors

Fig. 5 compares the TEM images of the particles collected at the exits of the 1st and 2nd reactors, respectively. The operating condition was the same as for Fig. 3. The morphology and the particle size are similar between the two images. The primary particles after the second-stage reactor are spherical and nearly uniform in size distribution. The standard



Fig. 5. Transmission electron microscopic images of the particles collected at the 1st and 2nd reactor outlets: (a) 1st reactor outlet; (b) 2nd reactor outlet. The 1st reactor temperature was 150 °C. The other operating conditions were the same as for Fig. 3. The white scale bar represents 100 nm.



Fig. 6. Electron diffraction pattern of selected particles in Fig. 5(b).

Table 1

Chlorine content of the particles collected at the 1st and 2nd reactor outlets with the molar ratio of H_2O to SiCl₄ varied from 2 to 6

Molar ratio of H ₂ O to SiCl ₄	Sampling point	Chlorine content (at.%)
2	1st reactor outlet	33.8
2	2nd reactor outlet	8.0
4	1st reactor outlet	10.6
4	2nd reactor outlet	1.07
6	1st reactor outlet	0.54
6	2nd reactor outlet	0.57

deviation for 150 primary particles including those in Fig. 5(b) was calculated to be 9.8% of the number average diameter. Fine dust-like matter is scattered over the particles collected at the exit of the second-stage reactor, the reason for which is not known. One possibility is that some of the SiCl_xO_y(OH)_z particles that passed from the 1st reactor vaporized upon entering the 2nd reactor, which was set at the higher temperature of 1000 °C, and then precipitated through further hydrolysis to form smaller secondary particles or the dust-like material. The crystalline phase of the particles after the 2nd reactor was amorphous by selected area diffraction, as shown in Fig. 6, and their chlorine content was determined to be 0.5 at.%. The chlorine content is expected to be further reduced by replacing the second-stage reactor with a flame reactor; a reaction temperature as high as 1800 °C is usually obtainable with the flame reactor.

Table 1 shows the variation of chlorine content of the particles after the two reactors with the molar ratio of H_2O to SiCl₄ varied from the stoichiometric value of 2–6. At the molar ratio of 2, the chlorine content was 33.8 at.% after the 1st reactor and 8 at.% after the 2nd reactor. As the ratio was further increased, the chlorine content decreased gradually; at the ratio of 6, the chlorine content after the 2nd reactor was reduced to 0.5 at.%. The gap in the chlorine content between the two sampling points narrowed as the ratio was increased, and it became negligible at the ratio of 6.

3.3. Effect of SiCl₄ concentration on particle size

An increase in the SiCl₄ concentration from 10 to 20 mol%, achieved by doubling the volume of SiCl₄ injected into the evaporator, decreased the particle size of the produced silica from 300 to 250 nm, as shown in Fig. 7. In a synthesis



Fig. 7. Comparison of morphology and size between the silica spheres produced at the two $SiCl_4$ concentrations in the 1st reactor: (a) 10 mol% and (b) 20 mol%. The other operating conditions were the same as for Fig. 5. The white scale bar represents 100 nm.

of silica by oxidation of SiCl₄ vapor at 1200 $^{\circ}$ C, the particle size was reported to have increased initially upon increasing the SiCl₄ concentration, showed a maximum, and then decreased with a further increase [16]. In the gasphase synthesis of silica using TEOS as precursor, Okuyama et al. [10] reported an increase in particle size, whereas Smolik and Moravec [13] reported a decrease in the particle size upon increasing the precursor concentration. The effect of the precursor concentration on the particles has thus been controversial. An increase in the precursor concentration would increase or decrease the particle size, depending upon its influences on the nucleation rate and the particle growth rate. In the present hydrolysis, the concentration increase probably increased the nucleation rate predominantly, resulting in a decrease in the silicon source available per nucleus for subsequent growth, yielding smaller particles.

4. Conclusion

The two-stage hydrolysis of SiCl₄ vapor proposed in Fig. 1 was experimentally validated. Compared to the highly agglomerated chain-like silica from the one-step flame oxidation of SiCl₄ vapor, the present silica was nearly uniform in size distribution and was spherical due to the morphology control through the low-temperature partial hydrolysis in the first-stage batch reactor. In the second-stage tubular reactor at the high temperature, the hydrolysis continued toward completion; the chlorine content of the particles after the first stage was reduced, while the particle morphology was nearly retained. The vapor-phase chemical preparation of nearly monodispersed silica was demonstrated for the first time. The characterization of the particles was not sufficient, however, due to the small volume of the particles obtainable from an experimental run. Further studies will follow in order to extensively characterize such silica, for which scaling up may be required to obtain particles in larger quantity.

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