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A Method for Preparing New Elongated-Shaped Silica Sols

Akitoshi YOSHIDA,* Yoshitane WATANABE, Mikio ANDOO, and Kenji TANIMOTO
Central Research Institute, Nissan Chemical Industries, Ltd., 722 Tuboi-cho, Funabashi, Chiba 274
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Synopsis. An active silicic acid sol was added to a mixture of a $Ca(NO_3)_2$ aqueous solution and a NaOH aqueous solution, then the mixture was heated for several hours under stirring at 100—150 °C to obtain a silica sol. The silica sol consisted of elongated-shaped colloidal particles desirable for film formation.

Most of the commercially available silica sols have spherical particles[1,2] of 4—150 nm in diameter or cocoon-like nonspherical particles.[3] Iler[4] prepared an amorphous silica sol by heating a wet silica gel in an autoclave.

However, he did not succeed in establishing the conditions to prepare sols with other shapes, such as an elongated shape which is desirable for filmformation.

In this note, we first report the preparation of elongated-shaped silica sols. The method is based on the addition of Ca^{2+} ions to an active silicic acid sol, and is represented by the following scheme:

Sodium silicate aq soln ⟶ (De-sodium)

$Ca(NO_3)_2$ aq soln ↓

⟶ Active silicic acid sol ⟶

↑ NaOH aq soln

(Heating in actoclave) ⟶ (Concentration)

⟶ Elongated-shaped silica sol

In this process, several factors such as (1) the amount of Ca^{2+} and Na^+ ions contained in silica sols, (2) the reaction temperature, and (3) silica concentration, significantly influenced on shape of the final silica sol particles.

The experimental findings are qualitatively summarized as follows:

1) The Ca^{2+} ion is strongly adsorbed to the surface of the active silicic acid sol. In the course of heating the sol in an autoclave, the Ca^{2+} ion plays a crucial role in the formation of elongated-shaped particles, namely, the ion controls the directionality of particle growth. Too high a Ca^{2+} ion content leads to rapid gelation of the sol, while too low a Ca^{2+} ion content makes the particle shape spherical.

2) A base such as NaOH is necessary for the particle growth of colloidal silica where the Na^+ ion is strongly adsorbed to the surface of the active silicic acid sol. When the Na^+ ion content is too high, the particleshape becomes spherical, while the sol is liable to gelate if it is too low.

3) When the silica content is too high, the sol readily gelates during the reaction.

4) A moderately high reaction temperature gives silica sols with a large specific surface area and the elongatedshape. Too high a temperature leads to rapid gelation of the silica sols, and too low a temperature gives spherical particles with a small specific surface area. To obtain the elongated-shaped silica sols it is essential to control these factors strictly. For instance, when a silica sol composed of SiO_2 3.2%, CaO 208 ppm, and Na_2O 550 ppm (SiO_2/Na_2O molar ratio=60) was allowed to react at 130 °C for 6 h and then concentrated up to 20% in silica content, the sol is elongated. A transmission electromicroscope (TEM) photograph of the elongated-shaped silica sol thus obtained is shown in Fig. 1. It is seen that the elongated-shaped sol growing in one direction has an almost uniform size of 10—15 nm in diameter. The average particleslength measured by the dynamic light scattering method (N4,

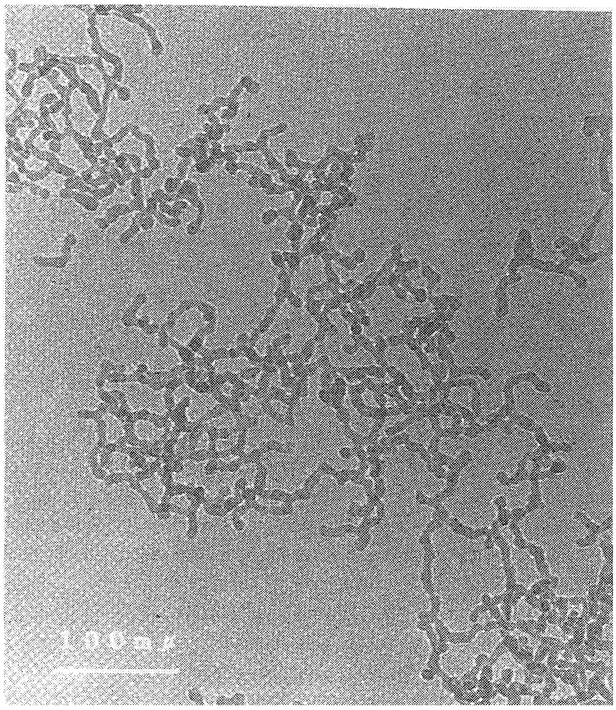

Fig. 1. TEM image of the elongated silica sol.

Table 1. Characteristics of the Elongated Silica Sol

Specific gravity (at 20 °C)	1.130
pH (at 25 °C)	9.65
Viscosity/cP[a] (at 25 °C)	46.3

a) 1 P=10^{-1} Pa s.

D1nm) was 65.8 nm, and the ratio of the particle size measured by this method and by the BET method (D2nm) was 5.4. The characteristics of the sol are given in Table 1.

Under the above-mentioned preparation conditions, the amounts of Ca^{2+} and Na^{+} ions correspond to 0.65 wt% and 1.7 wt% of SiO_2, respectively. Hence, on assumption that the silanol sites on the surface of the elongated-shaped silica particles are exchanged with these ions during the reaction, the fractions of these ions in the total surface silanol sites (i.e., the surface coverages of the ions) are 3.9% for Ca^{2+} and 18.7% for Na^{+}.

References

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