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Morphology of silica derived from various ammonium carboxylate templates

Fumiaki Miyaji*, Yasuhiro Watanabe, Yoko Suyama

Department of Materials Science, Faculty of Science and Engineering, Shimane University,
1060 Nishikawatsu, Matsue 690-8504, Japan

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Abstract

Synthesis of silica from tetraethyl orthosilicate (TEOS) in the presence of various ammonium carboxylate crystal templates was attempted and the effect of these templates on the shape and size of silica was investigated. The carboxylic acids examined immediately precipitated the crystals of their ammonium salts from ethanol and/or water by ammonia addition. The shape, size, and stability of thus formed crystal templates were varied depending on kinds of carboxylic acids and affected the morphology of TEOS-derived silica products. When the crystal templates formed were needle-like and less soluble, silica deposited not on the end faces but on the side faces of the crystals to form tubes with channels corresponding to the shape and size of the templates. On the other hand, when the crystal templates formed were particle-like with a few micron long and liable to re-dissolve into the solution, silica deposited on the whole surfaces of the templates. In this case, the morphology that silica particles with round edge were connected like twig was observed. It was also found that the size and its distribution of the silica tubes are variable to a certain extent by the reaction conditions such as acid and TEOS concentrations.

Keywords: A. Inorganic compounds; B. Chemical synthesis; C. Electron microscopy; D. Microstructure

1. Introduction

Since carbon nanotube was found [1], various inorganic hollow tubes have been exploited for boron nitride [2,3], silica [4–8] and titania [9,10] and so on, although their width and length are widely varied. Unique tubular structures of inorganic materials are potentially useful for applications such as catalyst carriers, sensors, electronic devices and storage and release systems [8].

In order to synthesize tubular materials, various organic and inorganic templates have been used so far. Hollow tubes of amorphous silica is one of the most extensively studied target materials. It has been

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* Corresponding author. Fax: +81-853-32-8893.
E-mail address: fmiyaji@riko.shimane-u.ac.jp (F. Miyaji).

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reported that the external surfaces of self-assembled phospholipid fibers [4], organic gel filaments [5], viroid cylinders [6], anodic alumina nano-array [7], and cylindrical assemblies of surfactant [8] are effective as templates of the silica tubes.

All the templates for the silica tubes described above are, however, specialized molecules or arrays. This has the potential drawback that the costs associated with scale-up are likely to be highly prohibitive. Thus, the process by Nakamura and Matsui on the formation of the silica tubes from $Si(OC_2H_5)_4$ (tetraethyl orthosilicate, TEOS)/H_2O/C_2H_5OH/NH_3 aqueous mixtures that contained a small amount of a simple organic acid, i.e. racemic D,L-tartaric acid is particularly interesting [11]. The size of the silica tubes obtained by this process was 0.1–1.0 μm in width and 200–300 μm in length. Although they speculated that the chains of hydrogen-bonded D,L-tartaric acid molecules act as a template of the silica tubes, the present authors clarified that needle-like ammonium D,L-tartrate crystal, which is formed almost simultaneously with polycondensed silica when aqueous NH_3 is added, play a role of template [12]. The key in this templating process is a dual role of aqueous NH_3. That is, it acts not only as a source of the crystal template but also as a basic catalyst for TEOS hydrolysis and polycondensation.

The present authors also synthesized the tubes of transition metal oxides such as TiO_2 and ZrO_2 by the modified process using the ammonium D,L-tartrate crystal template [13]. The usefulness of the ammonium D,L-tartrate crystal template suggests that the other ammonium carboxylate crystals could also be templates of the silica tubes. In fact, the present authors confirmed that ammonium oxalate is also useful as a template of the silica tubes [12]. In the case of the formation of worm-like silica particles in the presence of citric acid [14], ammonium salt of citric acid is assumed to work as a template of such silica particles, although the authors have not referred to the template. In the present study, synthesis of silica in the presence of various ammonium carboxylate crystal templates was attempted and the effect of these templates on the shape and size of silica was investigated. The effect of reaction conditions on the morphology of silica was also examined for the D,L-tartaric acid-containing system.

2. Experimental procedure

2.1. Template and silica formation

Table 1 shows the carboxylic acids used as templates of silica in this work. First, the solubility of each carboxylic acid for 100 ml of water or ethanol was examined at 25 °C. Next, 0.5% of the solubility of each acid for water or ethanol determined above was dissolved into 5 ml of water or ethanol, respectively, and then 2 ml of 28% aqueous NH_3 (Kanto Chemical Co., Inc.) was added to examine the formation of ammonium carboxylate crystal templates.

Silica synthesis was carried out with the carboxylic acids under the conditions that the acids precipitate ammonium carboxylate crystals to be templates. Typically, 0.73 g of TEOS (Kanto Chemical Co., Inc.) was added into 5 ml of C_2H_5OH (Kanto Chemical Co., Inc.) containing 0.02 g of D,L-tartaric acid (Tokyo Kasei Kogyo Co., Ltd.) and 0.06 g of distilled water, and the mixed solution was allowed to stand for 30 min. Subsequently, 2 ml of 28% aqueous NH_3 was added to the TEOS solution and the solution was allowed to stand for 30 min. The concentrations of D,L-tartaric acid, TEOS and NH_3, and H_2O/TEOS ratio are 17 mmol dm^{-3}, 0.45 and 3.7 mol dm^{-3}, and 1, respectively,

Table 1
Solubility of carboxylic acids and formation of ammonium carboxylate templates in water or ethanol by ammonia addition

Carboxylic acid	Solubility (g)[a]		Precipitated crystal[b]		Formed silica
	H_2O	C_2H_5OH	H_2O	C_2H_5OH	
D,L-Tartaric	20.6	5.0	–	Needle-like	Tube
L-Tartaric	139	42.5	–	Needle-like	Tube
meso-Tartaric	125	19.5	–	Particle[c]	Twig-like
Oxalic	11.8	54.6	Needle-like	Aggregate	Tube
Succinic	8.2	6.8	–	Needle-like	Tube
D,L-Malic	122	28.2	–	Particle[c]	Twig-like
Citric	194	80.0	–	Particle[c]	Twig-like

[a] Values as g/100 ml of each solvent at 25 °C.

[b] 0.5% of the solubility of each carboxylic acid was dissolved into 5 ml of H_2O or C_2H_5OH and then 2 ml of 28% aqueous NH_3 was added.

[c] Formed crystals were re-dissolved into the solution with time.

in this condition. The whole process described above was done at 25 °C. The products were washed with a large amount of water on a test sieve with 63 μm aperture or a 0.2 μm membrane filter, or unwashed. In the case of unwashed samples, the products were collected on a 0.2 μm membrane filter. As for the other carboxylic acids except oxalic acid, similar process was used for silica synthesis. With respect to oxalic acid, only water was used as a solvent because the crystal formed from the oxalic acid coagulates in ethanol. In this case, 0.6 g of oxalic acid was dissolved into 5 ml of H_2O and then 2 ml of 28% aqueous NH_3 was added without stirring to give a turbid suspension of the crystal templates. Next, 0.365 g of TEOS was added immediately after aqueous NH_3 addition and the mixture was stirred vigorously for 30 min. The products were washed with a large amount of water and collected on the test sieve with 63 μm aperture, or unwashed.

2.2. *Effect of reaction conditions on the formation and size of the tubes*

Effect of various reaction conditions on the formation and morphology of the silica tubes were examined for the D,L-tartaric acid-containing system. The concentrations of D,L-tartaric acid, TEOS and aqueous NH_3, H_2O/TEOS ratio, reaction temperature, and time allowed to stand after TEOS or aqueous NH_3 addition were varied. When one condition was changed, the other conditions were unified into the basic conditions described in Section 2.1.

2.3. *Characterization of silica products*

The products were subjected to SEM observation (HITACHI S-2500CX) and powder XRD measurement (Rigaku RINT-2000). The N_2 adsorption isotherms were measured for water-washed samples (Quantachrome AUTOSORB-1). The specific surface area, pore size distribution, and pore volume were calculated from the measured isotherm curves. In this work, the strict P/P_0 tolerance (−0.0001 to +0.0003) was used in the measurements at lower pressure region ($P/P_0 < 0.1$) in order to obtain accurate micropores data. The measurements were repeated at least three times for the same samples to confirm reproducibility.

3. Results and discussion

3.1. Template and silica formation

Table 1 summarizes the results of template formation by aqueous NH_3 addition for various carboxylic acids. The oxalic acid precipitated the needle-like crystals from water, whereas formed the aggregates in ethanol. The other carboxylic acids examined precipitated no crystal from water. The D,L-, L-tartaric, and succinic acids precipitated needle-like crystals from ethanol. The *meso*-tartaric, D,L-malic, and citric acids precipitated particle-like crystals, but the formed crystals gradually disappeared with time. This indicates that these crystal templates formed are very soluble in water and therefore re-dissolved into water from aqueous NH_3. It was found from the preliminary experiments that malonic, glutaric and L-malic acids form crystal templates from neither water nor ethanol.

Fig. 1 shows the SEM photographs of silicas formed in the presence of various ammonium carboxylate crystal templates. In the case of the D,L- and L-tartaric acids (Fig. 1a–c), silica tubes with rectangular-shaped channels were formed. The sizes of the tubes were 50–300 μm in length and 0.1–1.0 μm in width. Regarding the oxalic acid (Fig. 1d), shorter (50–100 μm in length) and thicker (1.0–15 μm in width) tubes were formed, compared to the D,L- and L-tartaric acids-derived tubes. As for the succinic acid (Fig. 1e), short (ca. 10–30 μm in length) macaroni-like tubes in which the edges were oblique were aligned to the length direction. The width of the tubes was about 2 μm.

On the other hand, with respect to D,L-malic, *meso*-tartaric and citric acids (Fig. 1f–h), the morphology that silica particles with round edge direction were connected like twig was observed. The sizes of each silica particle were 4–8 μm in length and about 0.5–1.0 μm in width. Although the length of the silica particles is not so different among the three kinds of acids, the width tended to increase in the order citric, *meso*-tartaric and D,L-malic acids. It was reported that worm-like silica with 0.6–1.2 μm in width and 8–12 μm in length was formed in the presence of citric acid [14]. Although the length of the worm-like silica particle is a little longer than that of the present twig-like silica particle formed in the presence of citric acid, both silicas are essentially same in shape. In summary, the silica formed in the presence of ammonium carboxylate templates are classified into two groups, i.e. end-opened "tubular" silica and end-closed "twig-like" one. This structural difference is explained in terms of the rates of the template growth along needle direction and the stability of the templates in solution, as discussed in Section 3.2.

Table 2 shows the results of specific surface area and pore volume of silicas derived from some ammonium carboxylate templates. As a representative, pore size distribution curve of silica tubes

Table 2
Specific surface area and pore volume of silicas derived from some carboxylic acids

Template	Specific surface area ($m^2 g^{-1}$)	Pore volume ($ml g^{-1}$)
Ammonium D,L-tartrate	410	0.31
Ammonium L-tartrate	508	0.32
Ammonium oxalate	1628	0.83
Ammonium citrate	790	0.48

The samples were heated at 100 °C in vacuo for 3 h prior to measurements.

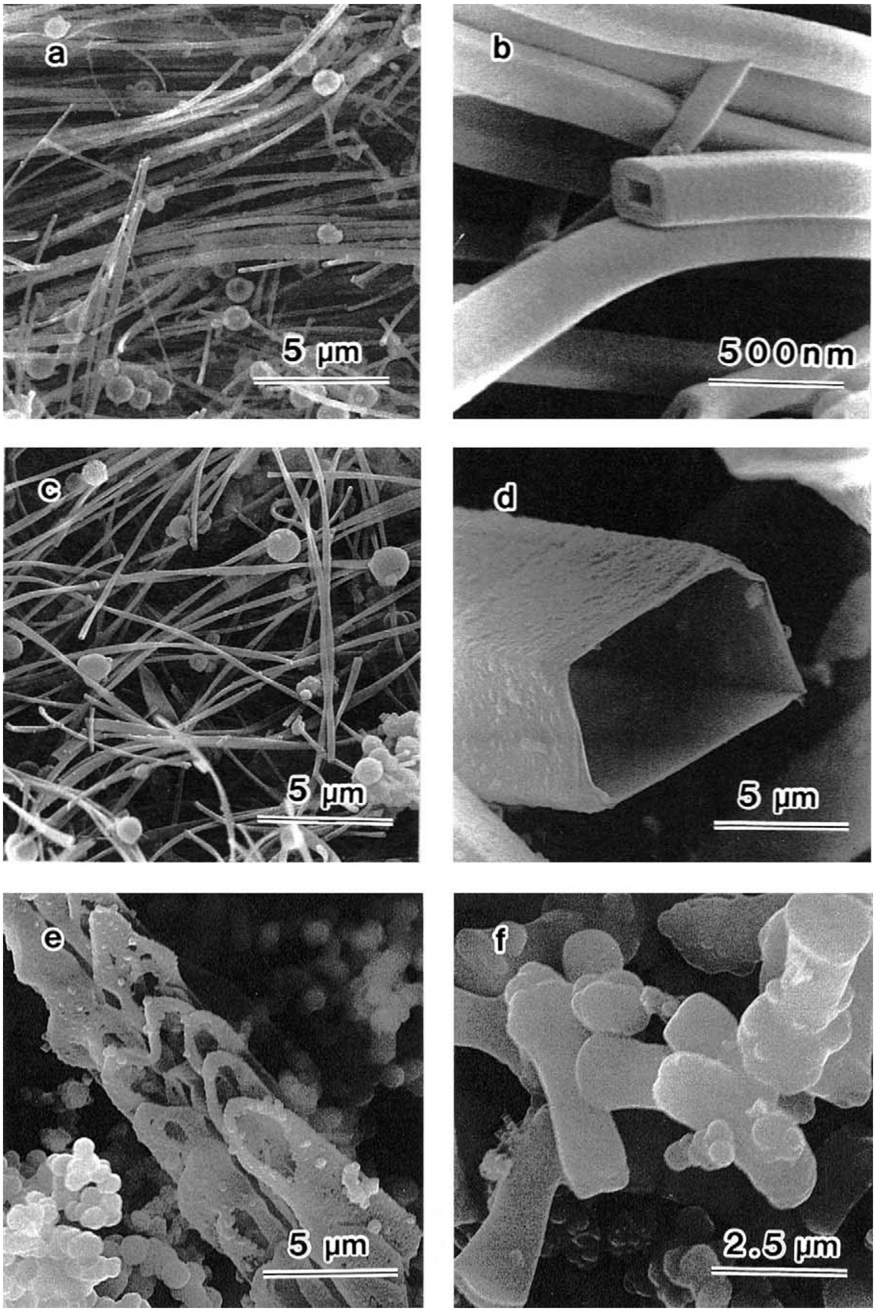


Fig. 1. SEM photographs of silicas derived from various ammonium carboxylate crystal templates: (a and b) ammonium D,L-tartrate; (c) ammonium L-tartrate; (d) ammonium oxalate; (e) ammonium succinate; (f) ammonium D,L-malate; (g) ammonium *meso*-tartrate; (h) ammonium citrate.

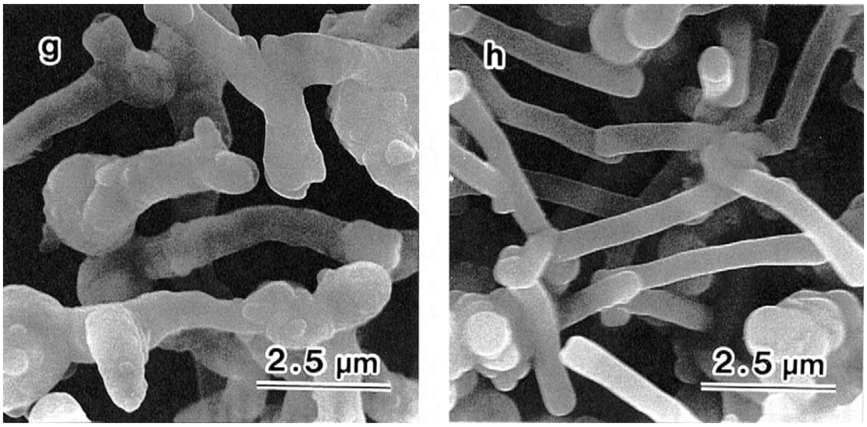


Fig. 1. (*Continued*).

synthesized in the presence of oxalic acid is shown in Fig. 2. A large micropore peak was observed around 0.6 nm. There was no remarkable difference in pore volume and micropore size distribution among the silicas derived from different carboxylic acids. The exceptionally large specific surface area of silica derived from oxalic acid is ascribed to the different synthetic process. In this case, TEOS is hydrolyzed and polycondensed at the interface between upper TEOS phase and lower water phase under stirring. Since the size of thus formed silica particles is very small and such fine silica particles gradually attach onto the ammonium oxalate templates to form the silica tubes, the specific surface area becomes higher in the oxalic acid-derived silica tubes than in the other silica tubes.

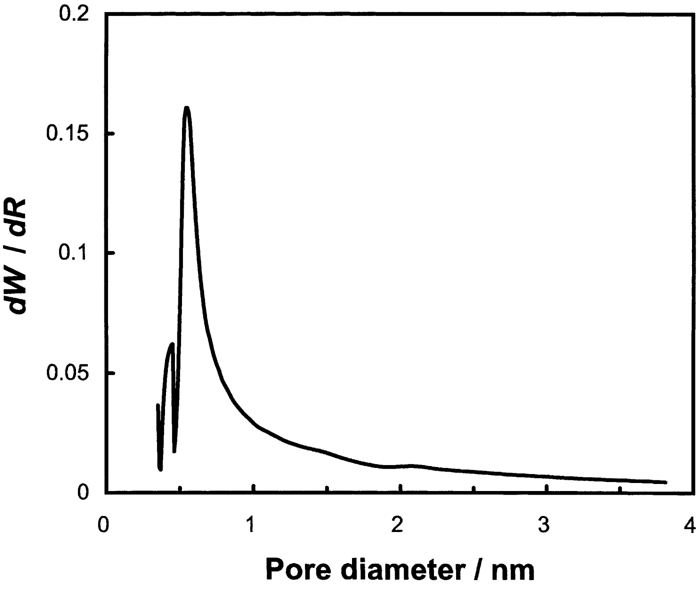


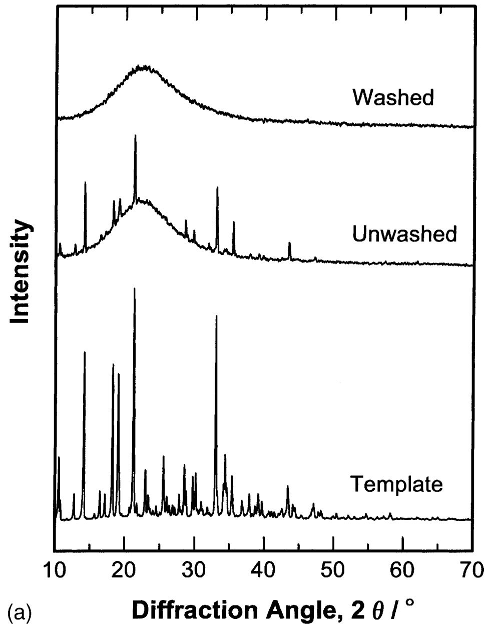
Fig. 2. Pore size distribution of silica tubes derived from ammonium oxalate template.

3.2. Formation process of tubular and twig-like silica

In the process of tubular silica formation, the formation of ammonium carboxylate templates and the deposition of silica onto the side faces of the templates proceeds almost simultaneously when the aqueous NH_3 is added to the solution [12], although the oxalic acid system is excluded owing to the different processing that the crystal templates were formed prior to silica deposition, as mentioned in Section 3.1. Since the crystal templates could not grow further when silica starts to deposit on them, the width of the tube would increase with increasing the ratio of the crystal growth rate along the width direction to the TEOS deposition rate. As in the succeeding discussion, the width of the tube changed with some reaction conditions, e.g. the acid and TEOS concentrations. This phenomenon is also explained in terms of the change in the rates of the template growth and/or silica deposition.

On the other hand, no silica is deposited on the end faces of the crystal templates, and this is a reason of formation of the hollow silica tubes in the presence of some carboxylic acids such as D,L- and L-tartaric acids. The growth rate of the crystal templates along the needle direction is very rapid on aqueous NH_3 addition. Since the growth along the needle direction is much faster than that of silica deposition onto the end faces, the edges are remained uncoated with silica. One question is why the edges of the crystal templates were remained uncoated for the ammonium oxalate template, although the template was formed prior to the TEOS addition. One possible explanation is concerned with preferential re-dissolution of the template along the needle direction. Although ammonium oxalate crystal rapidly grows with along the needle direction similarly to ammonium D,L-tartrate, it re-dissolves in part into water from aqueous NH_3. If the rate of re-dissolution of the crystal along the needle direction is higher than that of silica deposition, the end faces of the crystal would be remained uncoated with silica. In fact, the end faces of the ammonium D,L-tartrate templates also remained uncoated with transition metal oxides in spite of prior formation of the templates [13].

The morphology of the twig-like connection of the end-closed silica particles with a few micron in length, which were formed in the presence of D,L-malic, *meso*-tartaric, and citric acids, is clearly distinguished from that of the silica tubes described above. The crystal templates of ammonium D,L-malate, *meso*-tartrate and citrate grow slower along the needle direction than the crystal templates such as ammonium D,L- and L-tartrates. In this case, silica is deposited on the end faces as well as on the side faces of the crystal templates, which is responsible for the formation of end-closed morphology. It should also be noted that the edges of thus formed silica particles are not angular but round. The formation of such a characteristic morphology is interpreted as follows. Since the crystal templates of ammonium D,L-malate, *meso*-tartrate and citrate are highly soluble in water, they rapidly re-dissolve into the water from aqueous NH_3 and then silica is deposited on the whole surfaces of the templates before complete dissolution of them. This is consistent with the results of powder XRD patterns of the citric acid-containing system (Fig. 3b) that the unwashed silica product already contains no crystal template, i.e. ammonium citrate. No presence of the templates was also confirmed for the unwashed products derived from D,L-malic and *meso*-tartaric acids. On the contrary, the unwashed product involving the silica tubes contained the crystal templates, as shown in Fig. 3a as a representative. These results indicate that the inside of each twig-like silica particle is hollow before rinse with water The twig-like connection of the silica particles might be appeared in the midway of silica growth. When one silica particle is contacted to the other, silica is assumed to deposit so as to close the gap between the particles in order to lower the interfacial energy.



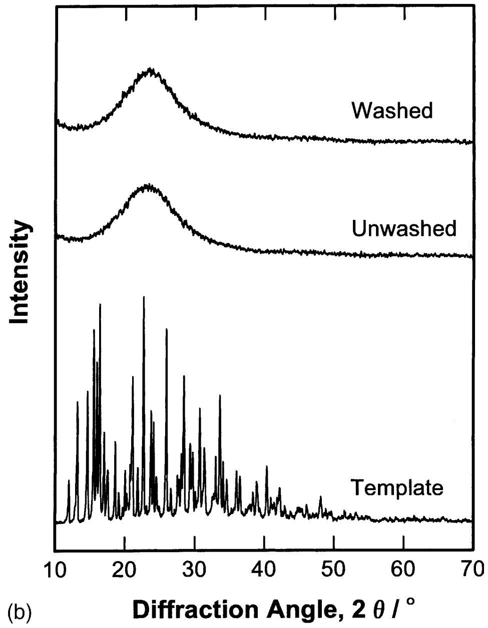


Fig. 3. Powder XRD patterns of ammonium carboxylate crystal templates, unwashed and washed silica products: (a) ammonium D,L-tartrate; (b) ammonium citrate.

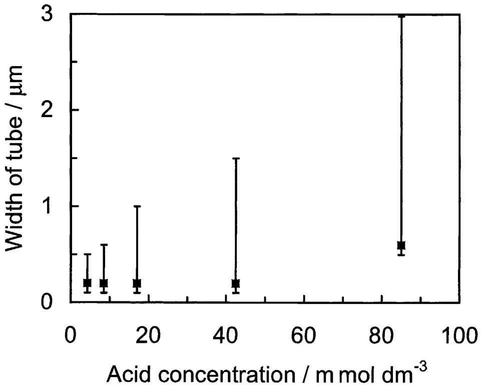


Fig. 4. Width of ammonium D,L-tartrate-derived silica tubes as a function of D,L-tartaric acid concentration. Closed square and vertical bars indicate the average width and the observed range, respectively.

3.3. *Effects of synthetic conditions on the silica tube formation*

3.3.1. *Effect of acid concentration*

First of all, the yield of the silica tube was about 20% at most under every synthetic condition. The silica other than tubular form was the colloidal particles which are same as ones formed in the presence of basic ammonia catalyst. The yield of the tubes increased with increasing the concentration of D,L-tartaric acid up to 17 mmol dm^{-3}. Over 17 mmol dm^{-3}, the yield of the formed tube gradually decreased, and in contrast the amount of the aggregates of silica increased. In this case, the aggregation of the crystal templates would also give rise to the aggregation of silica. In addition, the amount of the colloidal silica particles attached on the outer surfaces of the tubes increased with increasing the acid concentration. The increase in the width of the tubes due to increase in the acid concentration, as discussed below, might be favorable for the attachment of the colloidal particles to the tube surfaces.

Fig. 4 shows the width of the silica tube as a function of D,L-tartaric acid concentration. There was a tendency that the average and distribution of the width increased with increasing the acid concentration. This is explained as follows. The growth rate of the crystal templates increases with increasing the acid concentration. This causes the increase in the width of the crystal templates at which silica starts to deposit on them, resulting in the formation of thicker tube. While the curved tubes were mainly observed when their widths were below 1 µm, the straight tubes were majority when the widths were over 1 µm. The formation of the curved tubes is attributed to the stress by the deposited silica to the crystal template during its growth. When the crystal growth is quite rapid and the resultant template is thicker (>1 µm), the crystal template is strong enough not to be curved by the stress due to the deposited silica. In this case, the thick straight tubes are formed.

3.3.2. *Effect of TEOS concentration*

Fig. 5 shows the width of the silica tube as a function of TEOS concentration. No tube was formed at the smallest concentration (0.08 mol dm^{-3}). In this case, TEOS concentration is too low to deposit silica on the surface of the templates. On the other hand, at the largest concentration (0.8 mol dm^{-3}) a large amount of colloidal particles was attached on the surfaces of the tubes, although the total amount

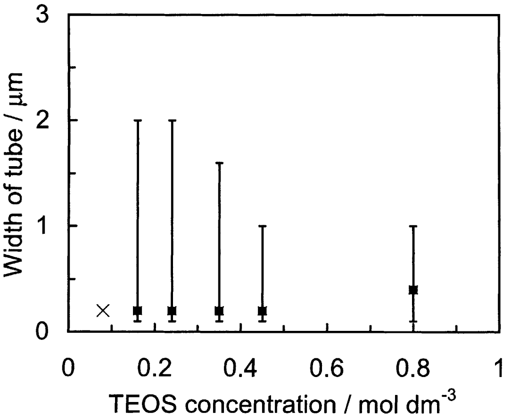


Fig. 5. Width of ammonium D,L-tartrate-derived silica tubes as a function of TEOS concentration. Closed square and vertical bars indicate the average width and the observed range, respectively. The cross means no formation of tube.

of the tubes was larger than that for lower concentration (0.45 mol dm^{-3}). This indicates that the fraction of silica precipitated not on the templates but in the solution increased with increasing TEOS concentration. The distribution of the width of the tubes was wider in 0.16–0.35 mol dm^{-3} than in 0.45 mol dm^{-3}. Since the decrease in TEOS concentration retarded the silica deposition on the templates, the period of the crystal templates growth was prolonged. As a result, the distribution of the widths of the templates and the resultant tubes became wider.

3.3.3. Effect of ammonia concentration

Fig. 6 shows the width of the silica tube as a function of ammonia concentration. The average and maximum width of the tube and the amount of particles attached onto the tube increased with decreasing concentration of ammonia. This is explained as follows. The hydrolysis and polycondensation of TEOS is drastically retarded by the decrease in concentration of ammonia, whereas the rate of the crystal templates formation is not changed so much. This causes the increase in

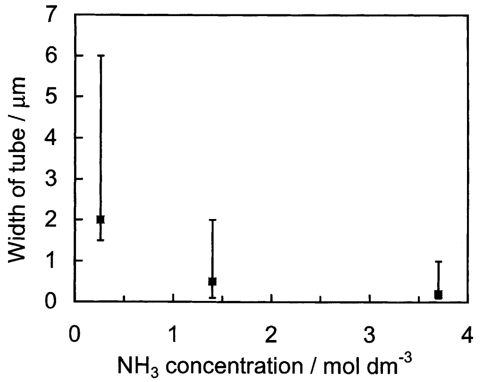


Fig. 6. Width of ammonium D,L-tartrate-derived silica tubes as a function of ammonia concentration. Closed square and vertical bars indicate the average width and the observed range, respectively.

the width of the template at which silica starts to deposit onto them. Consequently, thicker tubes are formed as in the case of increase in acid concentration.

3.3.4. Effect of H_2O/TEOS ratio

The effect of H_2O/TEOS ratio on the formation and morphology of the silica tube was examined for the $H_2O/TEOS = 0$, 1, and 4. When the H_2O/TEOS ratios were 0 and 1, silica tubes with a relatively small amount of colloidal particles were formed. When the H_2O/TEOS ratio was 4, colloidal silica particles were preferentially formed, and the yield of the silica tube was much lower than that for the $H_2O/TEOS = 1$. The H_2O/TEOS ratio did not affect the shape and size of the silica tubes.

It is known that acid-catalyzed TEOS solution with low H_2O/TEOS ratio is comprised of linear polymer, whereas solution with high H_2O/TEOS ratio causes the formation of non-linear or network polymers in hydrolysis–polycondensation [15]. It is therefore assumed that silica linear polymer is mainly present in the solutions for the lower H_2O/TEOS ratios (0 and 1) before ammonia addition. Since flexible silica linear polymer may quickly deposit on the templates on ammonia addition, the yield of the silica tube increases. On the contrary, in the case of higher H_2O/TEOS ratio (4), non-linear or network polymers of silica would preferentially form colloidal silica particles. In other words, less-hydrolyzed silica linear polymer would be favorable for deposition on the surfaces of the crystal templates.

3.3.5. Effect of reaction temperature

The average width of the tube increased and the distribution of the width widened when the temperature was raised over 40 °C. This reflects the increase in the rate of growth of the crystal templates. The width of the tube was not changed in the range 5–25 °C. This indicates that both rates of the crystal growth and silica deposition did not change so much relatively in this temperature range.

3.3.6. Effect of time allowed to stand after TEOS addition

The width and its distribution were not changed with variation of time allowed to stand after TEOS addition. The colloidal silica particles attached onto the tubes, however, increased when the time was longer than 30 min. Moreover, too long standing time, 24 h, gave not silica tubes but gelatin-like silica gel aggregates. The extremely prolonged time develops a cross-linked network of silica sol and it immediately aggregates on ammonia addition.

3.3.7. Effect of time allowed to stand after ammonia addition

Almost no tube was formed when the time allowed to stand after ammonia addition was below 1 min. If the time is too short, the polycondensation of TEOS is insufficient and silica cannot deposit onto the surfaces of the crystal templates. In the case of the tube formation, the width of the tubes and its distribution were hardly changed depending on the time.

4. Conclusions

Silica was synthesized from TEOS in the presence of various ammonium carboxylate crystal templates. The morphology of silica formed was classified into two groups. When the crystal templates formed were needle-like and less soluble, silica tubes with channels corresponding to the shape and size of the template were formed. When the crystal templates formed were particle-like with a few micron long and liable to re-dissolve into the solution, silica particles with round edge were connected like twig. The size and its distribution of the silica tubes varied to a certain extent depending on the reaction conditions such as acid and TEOS concentrations.

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