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The Formation Process of Hydrous Gallium(III) Oxide Particles Obtained by Hydrolysis at Elevated Temperatures

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Hydrous gallium(III) oxide was produced as monodispersed spherical particles by forced hydrolysis in the presence of sulfate ions, though they partially dissolved and recrystallized. The rate of the reaction degree was empirically expressed under the given conditions as $d\alpha/dt=1.60\alpha^{2/3}(1-\alpha)^{0.874}$, where α is the reaction degree. Polymeric hydroxo complexes were confirmed to act as precursors of the monodispersed spherical particles, judging from the fractional changes of the monomeric and polymeric species during the hydrolysis. The role of sulfate ions in the formation of hydrous gallium(III) oxide particles was discussed.

Recently, the preparation of monodispersed (hydrous) metal oxide particles has been extensively studied.[1—7] One method, the hydrolysis of metal ions at elevated temperatures, gives excellent monodispersed particles under suitable conditions. The morphology, composition, and size-distribution of the particles depend strongly, however, on several parameters, such as the concentration of metal ions, the pH, the temperature, and the kind of anion present, in the method of forced hydrolysis. Especially, a great influence of anions has usually been shown on the morphology and the composition of the particles. It has also been reported that the presence of sulfate ions in a solution is essential to produce monodispersed spherical particles of hydrous aluminium(III)[8] and chromium(III)[9] oxides. In a previous paper,[7] a remarkable effect of sulfate ions was also shown in making monodispersed spherical hydrous gallium(III) oxide particles by forced hydrolysis.

In this work, the role of sulfate ions in the formation of monodispersed hydrous gallium(III) oxide particles was studied, as was their formation process.

Experimental

Materials. All of the reagents used in this work were of a guaranteed grade and were employed without further purification. Stock solutions of gallium(III) sulfate and nitrate were prepared by dissolving the salts in doubly distilled water at room temperature, together with a known amount of the corresponding acid. These stock solutions, when kept in a cold place, did not show any visual change over three months.

Procedures. The sulfate and the nitrate solutions were prepared as the initial gallium(III) ion and acid concentrations of $[Ga^{3+}]_i=9.8\times10^{-4}$ and $[H^+]_{add}=1.0\times10^{-3}$ mol dm^{-3} respectively. The initial concentration ratio of sulfate to gallium(III) ions, $[SO_4^{2-}]_i/[Ga^{3+}]_i$, was specified as 1.9 by the use of potassium sulfate for the gallium(III) sulfate system. This composition has been confirmed as one of the optimum conditions for making monodispersed spherical particles.[7] The solutions were filtered through a membrane filter, 0.2 μm in pore size, before aging.

An aliquot of the solution was placed in a screw-capped Pyrex glass tube or a flask equipped with a condenser, and heated initially at the heating rate of 0.4 °C min^{-1},[7] followed by aging at a specified temperature (70—98 °C) in an oil bath. After the solution had been heated, particles were separated by centrifugation at 1700 g and then washed repeatedly with doubly distilled water. The morphology and size of the particles were observed with a transmission electron microscope.

The concentrations of gallium(III) and sulfate ions remaining in a supernatant solution were followed at regular time intervals after the solids had been completely separated by centrifugation at 45000 g. The supernatant solution thus obtained did not show any Tyndall cone. The total amount of gallium(III) species in the solution was determined spectrophotometrically as follows: A small portion of sulfuric acid was first added to the solution ($[H^+]\approx2.4\times10^{-2}$ mol dm^{-3}) to convert the polymeric gallium(III) species into monomeric ones, since the polymeric species did not complete the reaction with 8-quinolinol, not even within 60 min. Then all of the gallium(III) species were extracted by shaking the solution for 10 s at pH 5.1 with 10 cm^3 of chloroform, just after adding a buffer solution and a 8-quinolinol solution.

The concentration of the monomeric species was determined in the same way as above, but without the conversion process. Consequently, the concentration of polymeric gallium(III) species was estimated from the difference between the two values.

The concentration of sulfate ions in the supernatant solution was also determined colorimetrically with barium molybdate.[10]

Results

Morphology of Monodispersed Hydrous Gallium(III) Oxide Particles. Figure 1 shows the monodispersed spherical particles obtained by hydrolysis at 98 °C for 18 h. These particles were identified as amorphous-like hydrous gallium(III) oxide by means of X-ray powder diffractometry.[11]

Figures 2a—c show the change in the morphology of the particles during the reaction under the conditions shown in Fig. 1. The hydrous gallium(III) oxide was precipitated as monodispersed

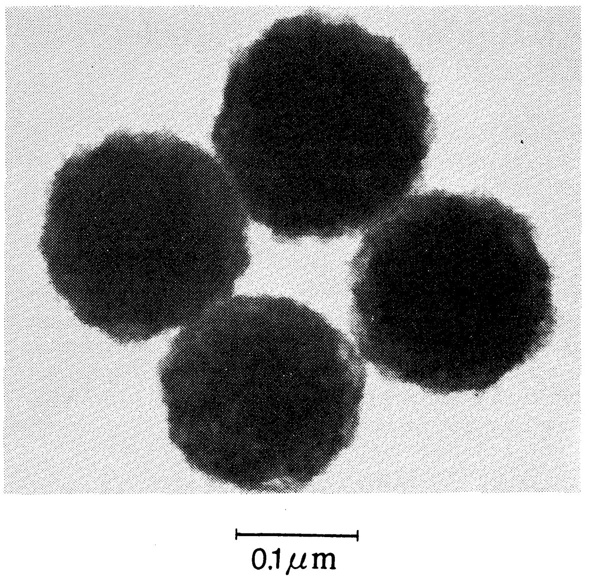

Fig. 1. Electron micrograph of monodispersed spherical hydrous gallium(III) oxide particles obtained at 98 °C. Aging conditions: $[Ga^{3+}]_i=9.8\times10^{-4}$ mol dm^{-3}, $2[H_2SO_4]+[HNO_3]=1.0\times10^{-3}$ mol dm^{-3}, and $[SO_4^{2-}]_i/[Ga^{3+}]_i=1.9$ respectively.

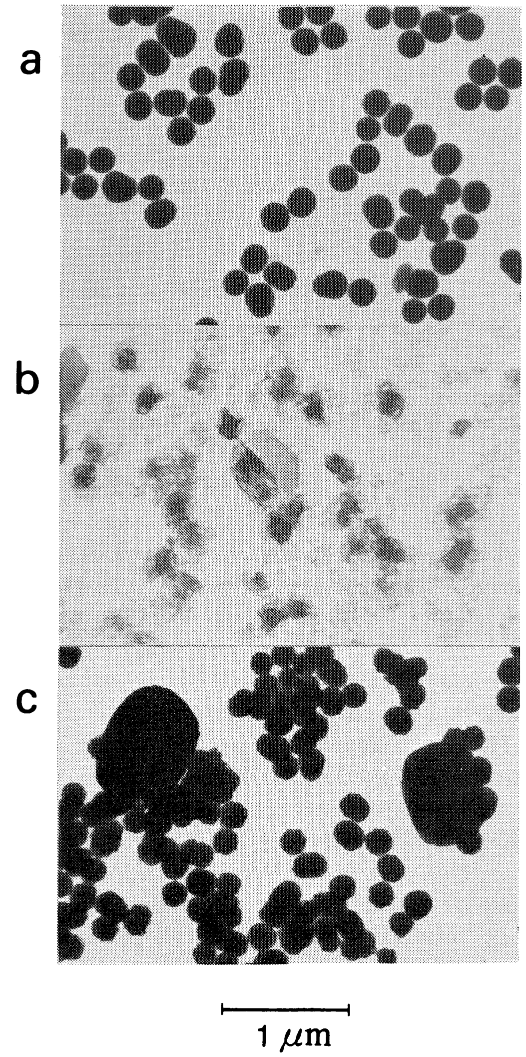

Fig. 2. Dissolution and recrystallization of hydrous gallium(III) oxide particles. Aging time: a; 3.5 h, b; 4.5 h, and c; 18 h.

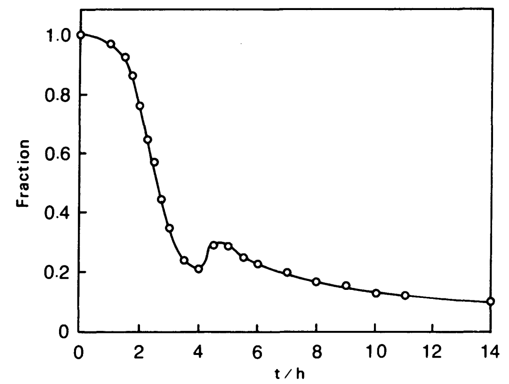

Fig. 3. Fractional change of gallium(III) species remained in supernatant solution during hydrolysis at 98 °C.

spherical particles during a reaction for 3.5 h (Fig. 2a). The particles, however, dissolved in part after 4.5 h (Fig. 2b). Figure 2c indicates a mixture of spherical and rod-like particles which has been aged for 18 h. Such a mixture gave weak X-ray powder diffraction peaks attributable to gallium(III) hydroxide oxide. Accordingly, it is obvious that the monodispersed spherical particles became unstable as the reaction proceeded and that they were then transformed partially into crystalline particles through recrystallization.

Variations in the Fraction of Gallium(III) Species in the Supernatant Solution and in the Content Ratio of Sulfate to Gallium(III) in Particles during Reaction. Figure 3 shows the fractional change of soluble gallium(III) species during hydrolysis at 98 °C under the same conditions as are shown in Fig. 1. The fraction of gallium(III) species in the supernatant solution decreased quickly up to around 4 h, but it abnormally reached a maximum at around 4.5 h. This time corresponded to that when the particles partially dissolved (Fig. 2b).

The molar ratio of the sulfate to the gallium(III) contents, $n(SO_4^{2-})/n(Ga^{3+})$, in the particles was estimated by subtracting the concentrations of both gallium(III) and sulfate ions in the solution from their initial values, so that the value involved the amount of sulfate ions adsorbed on the surfaces. The sulfate ions incorporated in the particles were quickly excluded as hydrolysis was enhanced, as is shown in Fig. 4. A similar phenomenon has been observed in the case of hydrous chromium(III) oxide, even though particular hydroxosulfato complexes acted as precursors of amorphous spherical particles.[9]

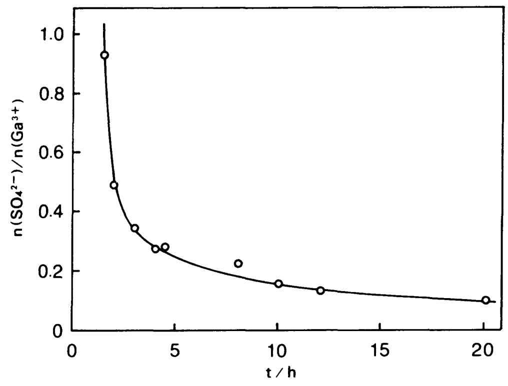

Fig. 4. Variation in composition of hydrous gallium (III) oxide particles during hydrolysis at 98 °C.

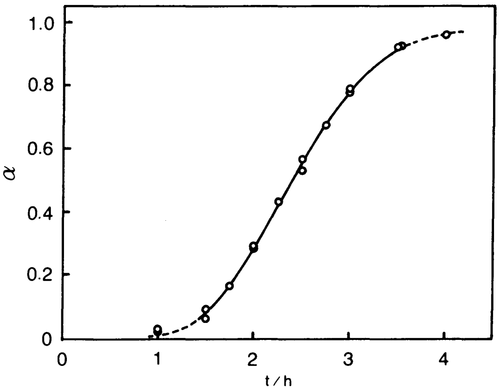

Fig. 5. Plots of reaction degree as a function of aging time at 98° C. ○; Observed, —; Calculated.

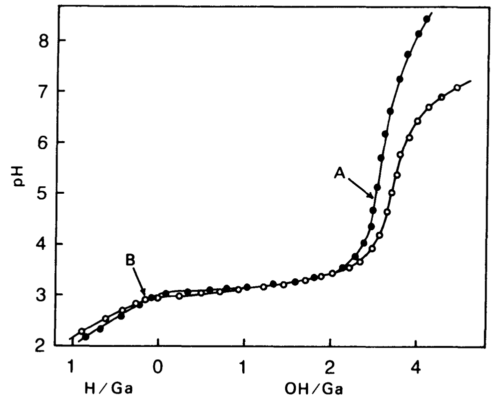

Fig. 6. Titration curves of gallium(III) nitrate (●) and sulfate (○) solutions. H/Ga and OH/Ga stand for $[H^+]_{add}/[Ga^{3+}]_i$ and $[OH^-]_{add}/[Ga^{3+}]_i$ respectively. Arrows A and B indicate points at which precipitates become visible for respective solution.

Change in Reaction Degree during Forced Hydrolysis. The rate of deposition of the solid phase during the growth of particles is approximately shown as:[12]

$$dP/dt = kS(C-C_s)^p \tag{1}$$

where P is the amount of solid formed; k, the apparent rate constant; S, the surface area of the particles; C, the concentration at the reaction time t; C_s, the final concentration, and p, the parameter of the concentration dependence. The P term can be expressed as mV, where m is the number of moles of gallium(III) species per unit volume and V, the volume of the particles. Thus,

$$dP/dt = mSdr/dt \tag{2}$$

where dr/dt is the radial growth rate. From Eqs. 1 and 2, the following equation can be obtained:

$$dr/dt = k'(C-C_s)^p \tag{3}$$

where k' is k/m.

On the other hand, the reaction degree, α, is defined as:

$$\alpha = (C_0-C)/(C_0-C_s) \tag{4}$$

where C_0 is the initial concentration. Accordingly, the modal diameter, r, of the monodispersed particles at t can be expressed as:

$$r = r_f\alpha^{1/3} \tag{5}$$

where r_f is the final modal diameter. Consequently, the following equation is obtained:

$$d\alpha/dt = K\alpha^{2/3}(1-\alpha)^p \tag{6}$$

where

$$K = 3k'(C_0-C_s)^p/r_f \tag{7}$$

Equation 6 was numerically integrated using the results obtained in Fig. 3. First, the parameters, p and K, were estimated as 0.874 and 1.60[13] respectively by a least-squares method using the logarithmic values of $d\alpha/dt$, α, and $1-\alpha$. Taking these values of the parameters, Eq. 6 was then integrated by the Runge-Kutta method. The solid curve in Fig. 5 displays the reaction degree thus calculated, which agreed very well with the experimental values over the wide range of reaction degrees from around 0.1 to 0.9. The rate of deposition, dP/dt or dV/dt, usually depends on the kinetic order between 1 and 2 with respect to the concentration during the growth process.[14,15] The value of the parameter p (0.874) obtained in this work was close to those presented above. Therefore, the hydrous gallium(III) oxide particles were confirmed to grow according to Eq. 1.

Fractional Changes of Monomeric and Polymeric Species in Partially Neutralized Gallium(III) Salt Solutions. The gallium(III) nitrate and sulfate solutions of 9.2×10^{-3} mol dm^{-3} containing a known amount of the corresponding acid were titrated very slowly with a potassium hydroxide solution of the same concentration at room temperature. The arrows in Fig. 6 display points at which visual precipitation occurred. The two titration curves were almost identical, except at the later stages. Such a discrepancy in pH values at the later stages can be considered to arise from the replacement of sulfate ions incorporated in the precipitates by hydroxyl ions as neutralization proceeds. In the gallium(III) sulfate solution, however, precipitates appeared at an earlier stage (pH 2.9) ($[H^+]_{add}/[Ga^{3+}]_i=0.13$), while precipitation was retarded up to pH 4.8 ($[OH^-]_{add}/[Ga^{3+}]_i=2.5$) in the nitrate solution.

Such a clear difference in the precipitation process indicated that sulfate ions exerted a remarkable effect on the formation of hydrous gallium(III) oxide. Hek et al.[13] observed similar facts in aluminium(III) salt solutions.

The amounts of monomeric and polymeric aluminium(III) species have also been determined.[14-17] Turner[14] defined the respective amount on the basis of reactivity to 8-quinolinol. The definition for the monomeric and polymeric gallium(III) species was taken to be the same as that for aluminium(III). Furthermore, Iwase et al.[21] confirmed that a dimer, $[M_2(OH)_2]^{4+}$, was also easily extractable with 8-quinolinol, so that the term "monomer" will include this dimer hereafter.

The gallium(III) nitrate and sulfate solutions (9.2×10^{-3} mol dm^{-3}) were carefully neutralized with vigorous stirring to minimize the heterogeneity of the pH in the solutions; then, both the species were estimated in order to reveal their behavior, depending on neutralization. Figure 7 displays the fractions of the monomeric and polymeric species in the gallium(III) nitrate solution as a function of the degree of neutralization. The monomeric species was gradually polymerized as neutralization proceeded, while a solid phase did not appear in this $[OH^-]_{add}/[Ga^{3+}]_i$ range, even when a great amount of polymeric species existed.

On the contrary, the gallium(III) sulfate solution showed different features in the fractional change of the species, as is shown in Fig. 8. Precipitates appeared at a fraction of about 0.4 of the polymeric species. These results indicated that the precipitation of the polymeric gallium(III) species was enhanced in the presence of sulfate ions, combined with those produced on titration. This effect also takes place at forced hydrolysis, not only in the partially neutralized solutions.

Fractions of Monomeric and Polymeric Gallium(III) Species in Solutions during Forced Hydrolysis. Figures 9 and 10 show the changes in the fractions of the soluble gallium(III) species and the precipitates during the forced hydrolysis of the nitrate and the sulfate solutions at 98 °C. Though nearly identical fractions of the polymeric species were initially indicated in both salt solutions, the fraction of the monomeric species gradually decreased as it was converted into the polymeric species at an earlier stage of hydrolysis in the nitrate solution. The concentration ratio of the monomeric to the polymeric species, [monomer]/[polymer], decreased continuously as the hydrolysis was enhanced.

On the other hand, in the sulfate solution the precipitates appeared at an earlier stage of hydrolysis, even at a low fraction of the polymeric species. The [monomer]/[polymer] ratio gradually increased except around 4.5 h, while the fraction of the monomeric species changed similarly to that in the nitrate solution. These results clearly indicate that sulfate ions promote the deposition of hydrous gallium(III) oxide as spherical particles.

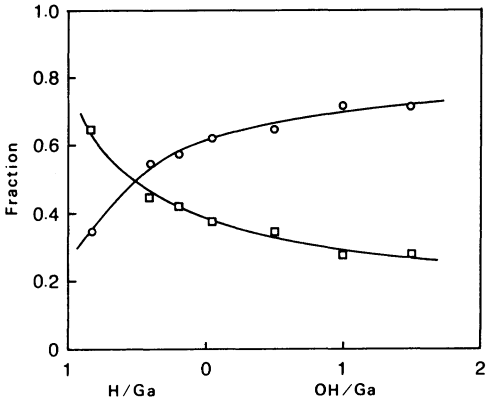

Fig. 7. Fractional changes of mono- and polynuclear hydroxo complexes in gallium(III) nitrate system at 25 °C. Symbols: □; Monomer, ○; polymer.

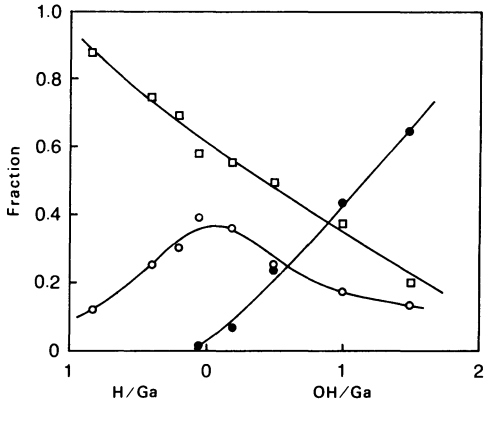

Fig. 8. Fractional changes of mono- and polynuclear hydroxo complexes in gallium(III) sulfate system at 25 °C. Symbols: □; Monomer, ○; polymer, ●; precipitate.

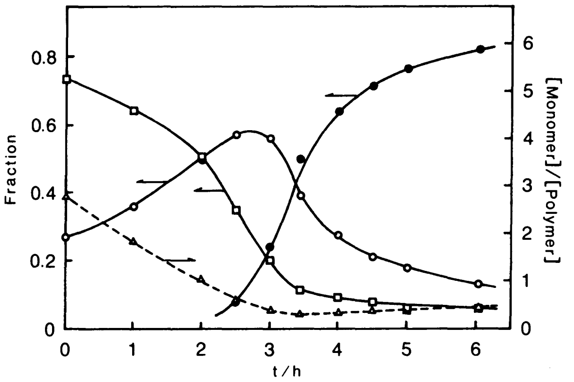

Fig. 9. Fractions of mono- and polynuclear hydroxogallium(III) complexes and precipitate during hydrolysis of nitrate solution at 98 °C. Symbols: □; Monomer, ○; polymer, ●; precipitate, △; [monomer]/[polymer] ratio. Aging conditions: $[Ga^{3+}]_i = 9.8 \times 10^{-4}$ mol dm^{-3}, $[HNO_3] = 1.0 \times 10^{-3}$ mol dm^{-3}.

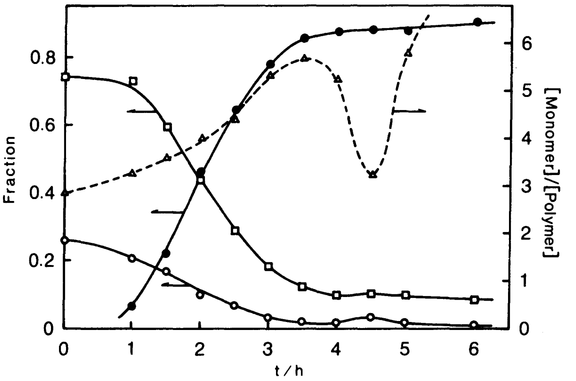

Fig. 10. Fractions of mono- and polynuclear hydroxogallium(III) complexes and precipitate during hydrolysis of sulfate solution at 98 °C. Symbols: □; Monomer, ○; polymer, ●; precipitate, △; [monomer]/[polymer] ratio. Aging conditions: $[Ga^{3+}]_i = 9.8 \times 10^{-4}$ mol dm^{-3}, $2[H_2SO_4] + [HNO_3] = 1.0 \times 10^{-3}$mol dm^{-3}, and $[SO^{2-}]_i/[Ga^{3+}]_i = 1.9$ respectively.

Discussion

On the formation of monodispersed spherical particles of amorphous hydrous aluminium(III) and chromium(III) oxides, it has been confirmed that polynuclear hydroxo and/or hydroxosulfato complexes act as precursors of such particles in the presence of limited amounts of sulfate ions.[8,9,22,23] The monodispersed spheres of hydrous gallium(III) oxide have also been clearly indicated to consist of polymeric species of hydroxo complexes.

According to the mass balance during the deposition of the solid phase, the following equation can be obtained:

$$\mathrm{d}f_{\mathrm{ppt}}/\mathrm{d}t = -\mathrm{d}t_{\mathrm{mono}}/\mathrm{d}t - \mathrm{d}f_{\mathrm{poly}}/\mathrm{d}t \qquad (8)$$

Table 1. Rates of Change in Precipitate, Monomer, and Polymer Fractions in a Sulfate System

Reaction time h	$\mathrm{d}f_{\mathrm{ppt}}/\mathrm{d}t$ h^{-1}	$-\mathrm{d}f_{\mathrm{mono}}/\mathrm{d}t$ h^{-1}	$-\mathrm{d}f_{\mathrm{poly}}/\mathrm{d}t$ h^{-1}
1.0	0.263	0.166	0.082
1.5	0.402	0.298	0.107
2.0	0.415	0.316	0.104
2.5	0.342	0.259	0.082
3.0	0.222	0.166	0.050
3.5	0.092	0.077	0.014

where f_{ppt}, f_{mono}, and f_{poly} are the fractions of the precipitate, the monomer, and the polymer respectively. Table 1 shows the values of the above three terms at different times in the sulfate system; these values were obtained from the respective fraction curves calculated by the least-squares method (Fig. 10). The results in Table 1 indicate that the values of $-\mathrm{d}f_{\mathrm{mono}}/\mathrm{d}t$ are 2.0—5.4 times those of $-\mathrm{d}f_{\mathrm{poly}}/\mathrm{d}t$. This fact implies that the reaction change in the monomer rather controlled the overall growth rate of the particles. However, a direct deposition of the monomer is unlikely, for the [monomer]/[polymer] ratio should decrease if the particles grow through this process. The [monomer]/[polymer] ratio may increase through a rapid degradation of the polymer, followed by a slow deposition of the monomer. This process is also unlikely, however, because the rate of the degradation of the polymer is usually not so fast.

Thus, the following reaction path, through slow polymerization and fast deposition steps, seems reasonable in the sulfate system:

$$\text{Monomer} \xrightarrow{\text{slow}} \text{Polymer} \xrightarrow{\text{fast}} \text{Amorphous particles.} \qquad (9)$$

The first step can be accompanied by a build-up of the polymer as:

$$\text{Polymer}_{(a-b)} + \text{b Monomer} \longrightarrow \text{Polymer}_{(a)} \qquad (10)$$

where Polymer$_{(a-b)}$ and Polymer$_{(a)}$ refer to species of a lower and higher degree of polymerization respectively.

On the other hand, a direct deposition of the polymer is hardly acceptable in the nitrate system, because the solid phase does not appear, even in the cases of large fractions of the polymer-for instance, around 0.5 at 2 h, as is indicated in Fig. 9. Additionally, the [monomer]/[polymer] ratio may decrease if the monomer species are polymerized faster than the deposition of the polymer, but this process is also improbable judging from the difference in $\mathrm{d}f_{\mathrm{poly}}/\mathrm{d}t$ and $\mathrm{d}f_{\mathrm{ppt}}/\mathrm{d}t$ at the early stages of the polymerization (up to 2 h) and of the deposition.

As is shown in Fig. 9, the rates of deposition

($\mathrm{d}f_{\mathrm{ppt}}/\mathrm{d}t$) are comparable to those of the decrease in the polymer fraction ($-\mathrm{d}f_{\mathrm{poly}}/\mathrm{d}t$) after around 3 h. It has been reported in a previous paper[7] that only rod-like crystalline particles of gallium(III) hydroxide oxide were produced through the forced hydrolysis of the nitrate solution under the same conditions except for the kind of anion. Taking these facts into account, the rate of the particle growth would seem to be governed by that of the degradation of the polymer, and the monomer and/or low molecular-weight hydroxo complexes would seem to act as actual precursors of the crystalline particles. This process is supported by the fact that the [monomer]/[polymer] ratio increased again after 3.5 h and then returned to 2.8 at the final stage of forced hydrolysis (24 h).

Ruff and Tyree[24] expressed the cationic polymers of hydroxogallium(III) complexes as having a linear structure of $[\mathrm{Ga}_{n+1}(\mathrm{OH})_{2n}]^{(n+3)+}$. They estimated, on the basis of pH measurements of a perchlorate solution, that the degree of polymerization, n, varied up to around 21 at the $[\mathrm{OH}^-]_{\mathrm{add}}/[\mathrm{Ga}^{3+}]_{\mathrm{i}}$ ratio of 1.75. Contrary to this, however, a much higher degree of polymerization (64) was observed by the light-scattering technique under the same conditions.[24] Patterson and Tyree,[25] by an isopiestic method, also estimated the degree of polymerization as 84 at the $[\mathrm{OH}^-]_{\mathrm{add}}/[\mathrm{Ga}^{3+}]_{\mathrm{i}}$ ratio of 2.0. It can be expected to have a feature similar to the hydrolysis of gallium(III) ions at elevated temperatures, though specified degrees of polymerization could not be obtained in this work.

Highly-polymerized hydroxogallium(III) complexes tend to reduce their large positive charges by converting the OH^--bridges in the polymers into O^{2-}-bridges. Cyclic structures composed of a hexamer unit are also possible, as are those of polymeric hydroxo complexes,[26] which have less positive charges than those of the linear structure for the same degree of polymerization. These highly-charged cationic polymers can more easily associate with sulfate ions compared with univalent anions, such as nitrate and perchlorate, while gallium(III) ions form sulfato complexes[27] in part. Hester and Plane,[28] by means of a Raman spectroscopic techique, have suggested that the sulfatogallium(III) complexes exist as outer-sphere complexes rather than as inner-sphere complexes. The sulfate ions thus paired with the polymers would effectively reduce the positive charge of the polynuclear hydroxo complexes and promote further polymerization.

After the nuclei were generated, their positively-charged surfaces would strongly adsorb sulfate ions in an acidic solution.[8] Then fine colloidal particles of hydrous gallium(III) oxide would easily associate according to the Schulze-Hardy rule, in addition to the surface nucleation of the polymeric species. Hek et al.[16] have confirmed, on the basis of the replacement behavior of labeled sulfate ions, that sulfate ions were incorporated in amorphous precipitates of hydrous aluminium(III) oxide as an adsorbed, but tightly-bound, state. The rapid exclusion of sulfate ions, as is shown in Fig. 4, would support this consideration. Such a spontaneous exclusion of sulfate ions may originate from the substitution by hydroxyl groups as the hydrolysis is enhanced. Hydrous aluminium(III) oxide particles also easily excluded the incorporated sulfate ions upon dialysis or repeated washings, and were transformed into crystalline α-AlOOH at elevated temperatures.[8,29]

In addition, there should be important conditions to obtain the monodispersed particles of hydrous gallium(III) oxide. As one of them, an appropriate formation rate of polynuclear hydroxo complexes is essential to gain a suitable supersaturation, leading to proper nucleation rates, whereas in general hydrolysis reactions take place faster than condensation.[30] These conditions have been shown in connection with the heating rate and the starting composition of the solutions.[7] The interfacial energy of embryos would be reduced according to the amount of sulfate ions adsorbed on the surfaces and would control the nucleation rate, in addition to the secondary surface-nucleation rate, though the detailed mechanisms are still not clear. This effect was distinctly reflected in the morphology of the particles during the forced hydrolysis of gallium(III) ions.[7] If many sulfate ions existed in the solutions ($[\mathrm{SO}_4^{2-}]_{\mathrm{i}}/[\mathrm{Ga}^{3+}]_{\mathrm{i}}>2.0$), only polydispersed particles were produced because of the fast deposition rates.

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