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The Precipitation of Monodispersed α-Iron(III) Oxide Particles from Iron(III) Chloride-Glycine System in Aqueous and 2-Propanol/Water Media

Shuichi Hamada,* Shin Niizeki, and Yoshiyuki Kudo
Department of Applied Chemistry, Faculty of Science, and Institute of Colloid and Interface Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
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Monodispersed α-iron(III) oxide (hematite) particles were prepared by aging iron(III) chloride solutions in the presence of glycine at elevated temperatures, 98—100 °C. An aqueous solution of glycinatoiron (III) complex directly gave monodispersed double spheres of hematite, ≈4 μm in size, under the specified conditions, for example, 2.0×10^{-2} mol dm^{-3} $FeCl_3$, 0.60 mol dm^{-3} glycine, and 0.46 mol dm^{-3} HCl for 96 h. The hematite particles grew up through the polynuclear layers mechanism. By the forced hydrolysis in 2-propanol/water mixed solution of 30% by volume, monodispersed cuboidal hematite particles, 0.06—0.43 μm in size, were also obtained through the conversion of β-iron(III) hydroxide oxide previously deposited. The nucleation rate was markedly affected by acidity at the latter case. The formation processes of these monodispersed hematite particles are discussed.

The preparation of monodispersed (hydrous) metal oxide particles has been studied extensively.[1—10] Monodispersed α-iron(III) oxide (hematite) particles have also been produced by the forced hydrolysis of iron(III) salt solutions under a limited set of conditions.[2,4—6,8,9] In this process, iron(III) hydroxide oxide is usually produced first and then transforms into hematite. However, monodispersed double spheres of hematite have been directly prepared from an iron(III) chloride-glycine aqueous system[6] without precipitation of β-iron(III) hydroxide oxide, while glycinatoiron(III) complex acts as a reservoir of hydroxo complexes. In the present work, the preparation process of the monodispersed hematite particles was studied in both the aqueous and 2-propanol/water mixed solutions containing glycine.

Experimental

Materials. All of reagents used in this work were of a guaranteed grade and employed without further purification. A stock solution of iron(III) chloride was previously passed through a membrane filter, of 0.2 μm pore size, before use. The solution thus obtained (≈3 mol dm^{-3}) did not show any visual change over one month. An aliquot of the stock solution was diluted to the fixed concentration of 2.0×10^{-2} mol dm^{-3} together with desired amounts of glycine and hydrochloric acid with doubly distilled water or 2-propanol/water mixed solvent of 30% by volume.

Procedures. A freshly prepared mixed solution was tightly sealed in a screw-capped glass tube and then aged for 24—96 h at 100±1 °C in a thermostated air oven. After the reaction, the particles were centrifuged at 1700 g and then washed repeatedly with doubly distilled water. The morphology and size of the particles were observed with scanning and transmission electron microscopes.

To reveal the formation process of the monodispersed hematite particles, the iron(III) chloride-glycine aqueous solution was aged in a flask equipped with a condensor at 98±0.5 °C in an oil bath. The concentration of iron species remaining in a supernatant solution was followed colorimetrically using 1,10-phenanthroline at regular time intervals, after the solids had been centrifuged at 45000 g. The supernatant solution thus obtained did not show any Tyndall cone. The concentration of iron(II) species was determined in the presence of iron(III) species using absorbances at different wavelengths. The amount of iron(III) species was estimated from the difference between those of iron(II) and the total iron species: the latter value was determined after the iron(III) species had been completely reduced to the iron(II) state.

When the hematite particles were produced through the conversion of β-iron(III) hydroxide oxide in the 2-propanol/water system, changes in their amounts were also followed spectrophotometrically, after they had been separated by repeated centrifugation at 500, 1300, and 45000 g, followed by solution in hydrochloric acid.

The amounts of monomeric and polymeric iron(III) complexes were determined spectrophotometrically on the basis of reactivity to 8-quinolinol.[11] The total iron(III) concentration was determined after the polymeric species had been depolymerized in 0.1 mol dm^{-3} hydrochloric acid at 80 °C for 10 min. The 8-quinolinatoiron(II) complex was previously confirmed not to exhibit absorbance over the wavelength between 380 and 600 nm.

Results

Concentration Changes of Soluble Iron(III) and (II) Species during Deposition of Monodispersed Hematite Particles in Aqueous Solution. The monodispersed doubly spherical hematite particles have been prepared under a limited set of conditions by the forced hydrolysis of the aqueous iron(III) chloride solution including glycine.[6] Figure 1 displays an example of monodispersed hematite particles prepared by aging a solution of 2.0×10^{-2} mol dm^{-3} $FeCl_3$, 0.60 mol dm^{-3} glycine, and 0.46 mol dm^{-3} HCl at 100 °C for 96 h. An average size of the particles was estimated as 4.1 μm with relative standard deviation of 0.08. The particles were attributable to aggregates of well-crystallized fine hematite particles, according to their X-ray powder diffraction pattern[12] and morphology.

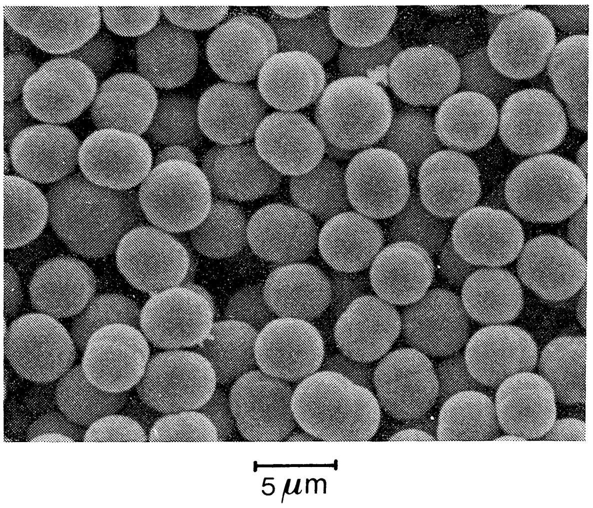

Fig. 1. Doubly spherical hematite particles obtained by hydrolysis at 100 °C for 96 h. Aging conditions: $[FeCl_3]=2.0\times10^{-2}$, $[HCl]=0.46$, and $[Gly]=0.60$ mol dm^{-3}.

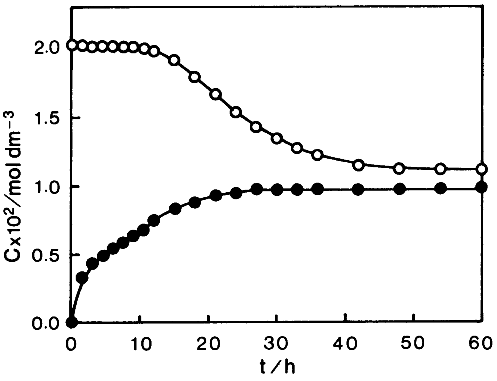

Fig. 2. Concentration changes in total and Fe(II) species in supernatnat solution during hydrolysis at 98 °C. Symbols: ○: total iron, ●: Fe(II).

The forced hydrolysis gave excellent monodispersed hematite particles only over a narrow composition range of the solution between 0.40 and 0.60 mol dm^{-3} for glycine and from 0.39 to 0.50 mol dm^{-3} for HCl under the fixed iron(III) chloride concentration of 2.0×10^{-2} mol dm^{-3}.[6] The pH of the solutions initially ranged between 1.5 and 1.8 and scarcely changed after the reaction because of the buffer action of the glycine.

Iron(III) nitrate and sulfate solutions containing glycine and the corresponding acid gave only irregularly shaped hematite or α-iron(III) hydroxide oxide particles.

In order to reveal the formation process of monodispersed hematite particles, the concentrations of iron species in the supernatant solution were followed at 98±0.5 °C up to 60 h. A starting solution was prepared similar to that shown in Fig. 1. The particles appeared after an induction period of around 10 h and then developed, while the iron(III) species were partially reduced into iron(II) state by glycine present, as shown in Fig. 2. Finally, the total iron concentration reached 1.1×10^{-2} mol dm^{-3} after 50 h. The concentration of iron(II) species became almost constant as 1.0×10^{-2} mol dm^{-3} after 30 h. Thus, effective concentrations of iron(III) for producing the hematite equal those between the upper and lower curves. The difference in the concentrations, C_s, between the total iron and iron(II) species at the final state corresponds to the solubility of hematite under the given conditions.

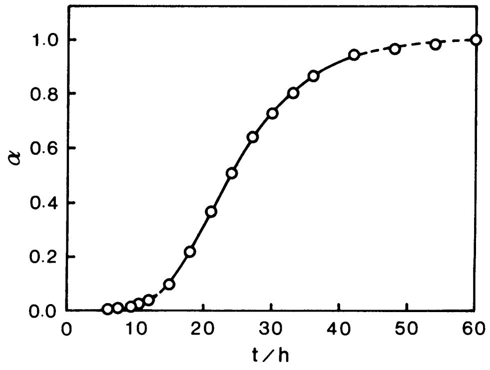

Fig. 3. Change in reaction degree during hydrolysis at 98 °C. ○: Observed, —: Calculated.

Growth Process of Double Spheres of Hematite. The reaction degree, α, is defined as:

$$\alpha = (C_0-C)/(C_0-C_s-C_{Fe(II)}) \tag{1}$$

where C_0 is the initial concentration of iron(III), C the total concentration of iron species at reaction time t, and $C_{Fe(II)}$ that of iron(II), respectively. Based on the results in Fig. 2, the reaction degree, α, was estimated as shown in Fig. 3.

According to Nielsen,[13] the radial growth rate is expressed as Eq. 2 when the particles developed through a polynuclear layers mechanism.

$$dr/dt = 0.60\,dJ'^{1/3}R'^{2/3} \tag{2}$$

where J' and R' are the nucleation and growth rates of two-dimensional surface nuclei. Both terms are given as:

$$J' = k_m C_r^m \quad [C_r = C - C_s - C_{Fe(II)}] \tag{3}$$

$$R' = d^2 D C_r \tag{4}$$

where d is the height of the surface nuclei, k_m the apparent rate constant of surface nucleation, and D the diffusion coefficient, respectively. On the other hand, the radius of the monodispersed particles at t can be given as:

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

where r_f is the final radius of the particle. On the basis of differentiation of Eq. 5, the following equation is obtained as:

$$\mathrm{d}r/\mathrm{d}t = 0.33\, r_\mathrm{f}\alpha^{-2/3}\mathrm{d}\alpha/\mathrm{d}t \tag{6}$$

Finally, Eq. 7 can be derived by combining Eq. 6 with Eq. 1 as:

$$\mathrm{d}\alpha/\mathrm{d}t = KC_\mathrm{r}^{(\mathrm{m}+2)/3}\alpha^{2/3} \tag{7}$$

where

$$K = 1.8\, k_\mathrm{m}^{1/3}d^{7/3}D^{2/3}r_\mathrm{f}^{-1} \tag{8}$$

However, Eq. 7 was not integrable because the concentration of iron(II) changed continuously in this system; accordingly a numerical method was employed. At first, the parameters, m and K, were estimated as 1.22 and 22.6[14] by the least squares method using the logarithmic values of $\mathrm{d}\alpha/\mathrm{d}t$, C_r, and α. Equation 7 was integrated by the Runge-Kutta method using these values. The solid curve shown in Fig. 3 displays the reaction degree thus calculated, which agreed well with the experimental values over a wide range of the reaction degree from around 0.1 to 0.9. Similar studies were also made on the diffusional and mononuclear layer mechanisms,[13] but neither of them fitted the experimental values. These results indicated that the double spheres of hematite developed through the polynuclear layers mechanism including condensation and polymerization of hydroxoiron(III) complexes on the surface of particles, as suggested by Flynn.[15]

Hydroxoiron(III) Complexes in Iron(III) Chloride-Glycine Aqueous System. To reveal a role of the monomeric and polymeric hydroxoiron(III) complexes on the formation of hematite particles, the fractions of these species in the solution were examined spectrophotometrically during the forced hydrolysis. Murphy et al.[16] have mentioned that only unpolymerized iron(III) species were reactive to 8-quinolinol. Furthermore, Iwase et al.[11] have specified that monomeric and dimeric species, $\mathrm{Fe^{3+}}$, $[\mathrm{FeOH}]^{2+}$, and $[\mathrm{Fe_2(OH)_2}]^{4+}$, were extractable in chloroform as 8-quinolinate by shaking for 10 s, in addition to monomeric sulfatoiron(III) complex.

According to the above facts, the polymerization of iron(III) ions was examined first as follows: The pH values of 1.0×10^{-2} and 2.5×10^{-3} mol dm^{-3} iron(III) perchlorate solutions were adjusted in the range from 1.70 to 2.20 and from 1.98 to 2.43 respectively. After standing the solutions at 25±0.5° C for 24 h, 8-quinolinatoiron(III) complex was extracted in 10 cm^3 chloroform by vigorous shaking for 10 s. Figure 4 displays the fractions of extractable iron(III) species as a function of pH. These results clearly indicate that the hydroxoiron(III) complexes were drastically polymerized at pH 2.2 and 2.4, respectively, in spite of no precipitation, depending upon the total concentration of iron(III) species.

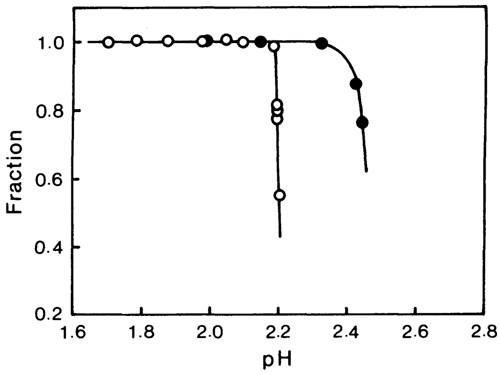

Fig. 4. Fractions of extractable Fe(III) species at 25 °C and I=0.5. Conditions: $[\mathrm{Fe(ClO_4)_3}]=1.0\times10^{-2}$ (○) and 2.5×10^{-3} (●) mol dm^{-3}.

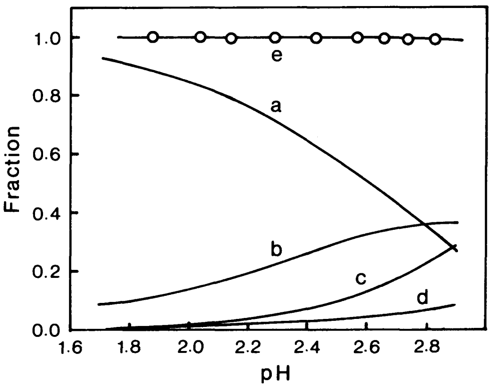

Fig. 5. Fractions of extractable Fe(III) species and respective species at 25 °C and I=0.5. Conditions: $[\mathrm{Fe(ClO_4)_3}]=5.0\times10^{-4}$ mol dm^{-3}, a: $\mathrm{Fe^{3+}}$, b: $[\mathrm{FeOH}]^{2+}$, c: $[\mathrm{Fe(OH)_2}]^{+}$, d: $[\mathrm{Fe_2(OH)_2}]^{4+}$, and e: total.

On the other hand, a much diluted solution (5.0×10^{-4} mol dm^{-3}) scarcely showed any polymerization in the pH range between 1.87 and 2.82, as shown in Fig. 5. The circles in Fig. 5 stand for the fractions of extractable iron(III) species. Furthermore, the solid curves a—d indicate the fractions of $\mathrm{Fe^{3+}}$, $[\mathrm{FeOH}]^{2+}$, $[\mathrm{Fe(OH)_2}]^{+}$, and $[\mathrm{Fe_2(OH)_2}]^{4+}$ which were calculated by the Newton-Raphson method using the formation constants for the respective hydroxo complexes at 25 °C and ionic strength of 0.5.[17—20] The curve e displays the sum of above fractions, which agrees well with the experimental values. The fraction of $[\mathrm{Fe_3(OH)_4}]^{5+}$ was confirmed to be negligible in this diluted solution. Thus, the results suggest that $[\mathrm{Fe(OH)_2}]^{+}$ is also extractable as the 8-quinolinatoiron(III) complex.

On the basis of above results, the behavior of the polymeric iron(III) species in the iron(III) chloride-glycine aqueous solution was examined in the following way. A solution with the same composition shown in Fig. 1 was aged for desired periods at 98±0.5 °C. After the reaction, the solids formed were

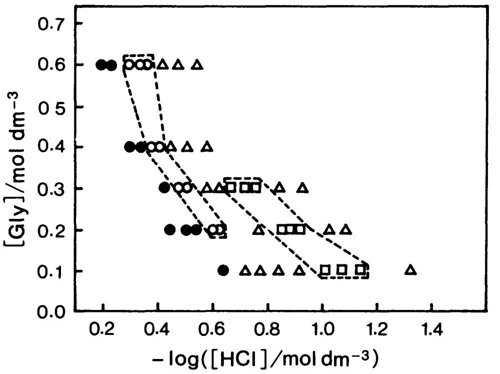

Fig. 6. Concentration domain of glycine and HCl for making hematite particles by hydrolysis at 100 °C for 48 h in 2-propanol/water mixture. Coditions: $[FeCl_3]=2.0\times10^{-2}$ mol dm^{-3}, 2-propanol; 30% by volume, Symbols: ○: double sphere, □: cube, △: irregular, and ●: no precipitation.

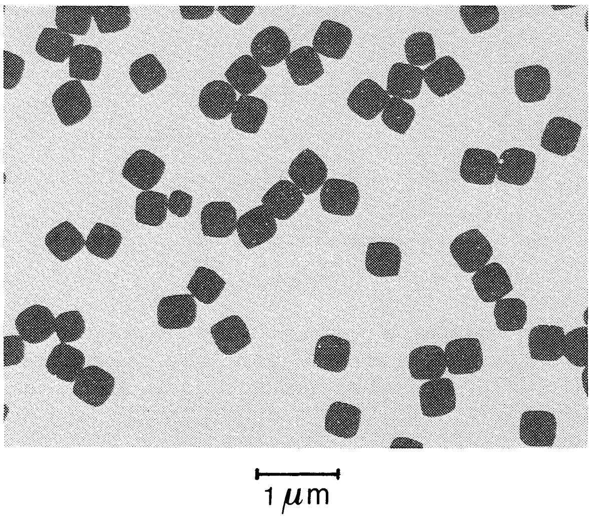

Fig. 7. Cuboidal hematite particles obtained by forced hydrolysis at 100 °C for 56 h in 2-propanol/water mixed solution. Conditions: $[FeCl_3]=2.0\times10^{-2}$, $[HCl]=0.16$, and $[Gly]=0.20$ mol dm^{-3}, 2-prpanol: 30% by volume.

completely removed by centrifugation at 45000 g. As mentioned above, iron(III) ions were partially reduced into the iron(II) state, so that the actual total iron(III) concentration was separately determined after depolymerizing the polymeric species. The presence of chloride ions and glycine in the solution did not have any influence on the determination with 8-quinolinol. However, the total fraction of the monomeric and dimeric iron(III) species remained constant as $1.00\pm0.00_6$ during the course of aging up to 48 h at intervals of 6 h. In addition, no polymeric iron(III) species was observed in the solution before aging.

Formation of Monodispersed Hematite Particles in 2-Propanol/Water System. Figure 6 shows the domain of hydrochloric acid and glycine concentrations for making hematite particles by the forced hydrolysis at 100 °C for 48 h under the fixed concentration of 2.0×10^{-2} mol dm^{-3} iron(III) chloride in 2-propanol/water mixed solutions of 30% by volume. The solutions with the composition indicated by the symbol ○ directly gave the monodispersed double spheres of hematite as in the aqueous solutions.

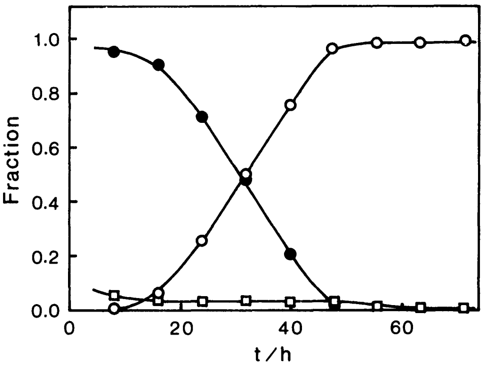

Fig. 8. Conversion of β-FeOOH during hydrolysis at 100 °C in 2-propanol/water mixed solution. Conditions: $[FeCl_3]=2.0\times10^{-2}$, $[HCl]=0.14$, and $[Gly]=0.20$ mol dm^{-3}, Symbols: ●: β-FeOOH, ○: hematite, □: Fe(III) species in supernatant solution.

In addition, monodispersed cuboidal hematite particles were obtained in the region shown by the symbol □, in contrast to the former case. In this process, β-iron(III) hydroxide oxide[21] appeared first and then transformed into cubes of hematite. Iron(III) ions are much more hydrolyzable in alcohol/water mixtures than in aqueous solutions.[22,23] Therefore, the β-iron(III) hydroxide oxide would result from much higher supersaturation of hydroxoiron(III) complexes at an initial stage of the forced hydrolysis in rather dilute acid. Thus, a mixture of hematite and fine hydroxide oxide particles was obtained by the forced hydrolysis. It was, however, easy to separate them by repeated slow and high speed centrifugation. Figure 7 shows the cuboidal particles thus separated. The symbols ● indicate the region in which no precipitation occurred even after 100 h.

Conversion of β-Iron(III) Hydroxide Oxide to Hematite in 2-Propanol/Water System. In order to examine the conversion process, the respective amounts of β-iron(III) hydroxide oxide and hematite were followed at regular time intervals during the forced hydrolysis, in addition to that of the soluble iron species in the supernatant solution. A solution was prepared as $[FeCl_3]=2.0\times10^{-2}$, $[HCl]=0.14$, and $[Gly]=0.20$ mol dm^{-3} in the 2-propanol/water mixture of 30% by volume. The solution was aged at 100±0.5 °C in an oil bath. After the reaction, the precipitates were first separated by centrifugation at 45000 g and then the extremely fine β-iron(III)

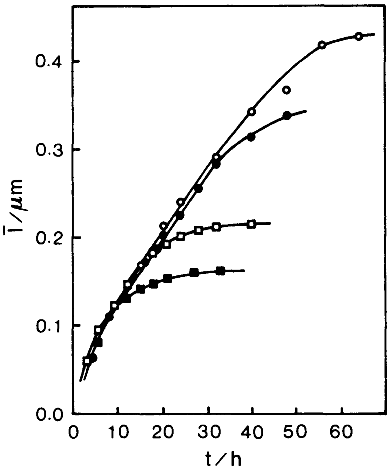

Fig. 9. Growth of cuboidal hematite particles at 100 °C in 2-propanol/water mixed solution. Conditions: $[FeCl_3]=2.0\times10^{-2}$, $[Gly]=0.20$, $[HCl]=0.12$ (■), 0.13(□), 0.15 (●), and 0.16(○) mol dm^{-3}, 2-propanol: 30% by volume.

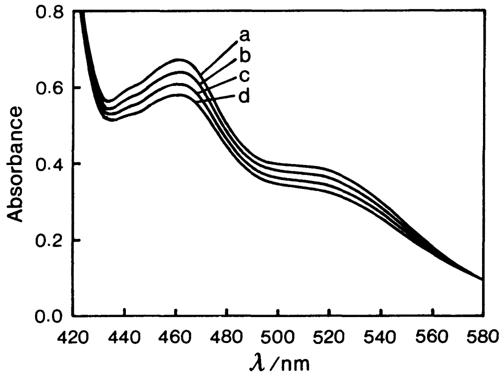

Fig. 10. Spectra of $Fe(ClO_4)_3$–glycine aqueous solution at $I=0.5$. Conditions: $[Fe(ClO_4)_3]=1.9\times10^{-2}$, $[HClO_4]=0.45$, and $[Gly]=0.80$ mol dm^{-3}, temperature: a: 15, b: 20, c: 25, and d: 30 °C, cell length: 1 cm.

hydroxide oxide particles were isolated from the solid phase by repeated slow and fast centrifugation. The amounts of iron(III) in the each phase were determined spectrophotometrically using 1,10-phenanthroline.

Figure 8 displays the fractions of the β-iron(III) hydroxide oxide, hematite, and soluble iron(III) species as a function of the reaction time. The rate of appearance of the hematite was the same as that of the disappearance of the β-iron(III) hydroxide oxide and the conversion continued until all the β-iron(III) hydroxide oxide had disappeared. This fact clearly indicated that the cuboidal hematite particles developed through the conversion of β-iron(III) hydroxide oxide. The total concentration of hydroxo, chloro, and glycinato complexes of iron(III) in the supernatant solution remained constant (6.0×10^{-4} mol dm^{-3}) throughout the conversion. The soluble iron (III) species were scarcely reduced to the iron(II) state by glycine in this process, in contrast to the aqueous system.

The results in Fig. 8 indicate that the soluble iron(III) species were continuously supplied by the dissolution of β-iron(III) hydroxide oxide and the supersaturation of hydroxoiron(III) complexes was appropriately maintained during the growth of the monodispersed hematite particles.

Growth of Cuboidal Hematite Particles. Figure 9 shows the growth of the cubes at 100±0.5 °C as a function of aging time. A starting solution was prepared similar to that shown in Fig. 8 except for the acid concentration. The relative standard deviation of the particle size remained almost constant in the range 0.11—0.13 in 0.15 mol dm^{-3} hydrochloric acid during the growth from 12 to 40 h. The size of the cuboidal particles reached a plateau at which the β-iron(III) hydroxide oxide was completely consumed.

Though the growth rate of the particles was almost identical ($\approx6.7\times10^{-3}$ µm h^{-1} in the linear part), the final particle size significantly increased with the acid concentration even in a narrow range from 0.12 to 0.16 mol dm^{-3} (pH 2.0—1.6). According to the final size and the consumption time of the β-iron(III) hydroxide oxide, the nucleation rate of the hematite was greatly enhanced with increasing pH even at the same concentrations of iron(III) and glycine.

Excellent monodispersed cuboidal hematite particles have also been obtained through a similar conversion process in alcohol/water mixed solutions without glycine.[4,5] In this case, the particles developed to around 4 µm through slow nucleation even at the same concentration of iron(III) chloride.

Discussion

The hematite particles have been recognized to form through the transformation of β-iron(III) hydroxide oxide in acidified iron(III) chloride solutions at elevated temperatures.[4,5,21,24] Highly-polymerized cationic hydroxoiron(III) complexes have been confirmed to form at an initial stage of hydrolysis of iron(III) chloride solution, followed by their precipitation as β-iron(III) hydroxide oxide.[25,26] However, Atkinson et al.[24] have observed that rather low-molecular-weight hydroxoiron(III) complexes would act as the precursor of hematite. Actually, the aqueous solutions of iron(III) chloride–glycine system did not show the presence of any polymeric iron(III) species before and after aging, from which the monodispersed hematite particles directly originated.

Figure 10 displays the spectra of an iron(III) perchlorate-glycine aqueous solution at different temperatures. The absorption bands ranged between around 435 and 580 nm were charasteristic of the glycinatoiron(III) complex.[27] A decrease in the absorbance was clearly shown as the temperature increased, which indicated that the glycinatoiron(III) complex was dissociated at higher temperatures in spite of the negative enthalpy change of protonation of glycine anions (−45.0±0.2 kJ mol^{-1}).[28,29] Thus, the enthalpy change of the formation of glycinato-iron(III) complex would be negative: this consideration can be reasonable because the formation of glycinatometal complexes is mostly exothermic except for indium and lanthanoids.[30]

By the use of the formation constants for hydroxo,[17–20] chloro,[31,32] and glycinato[27] complexes of iron(III) and the dissociation constants of glycine,[33] the sum of the fractions of chloro and glycinato complexes was numerically estimated as 0.84 at 25 °C under the conditions given in Fig. 1. According to the enthalpy changes of the formation of the respective species (36 kJ mol^{-1} for $Fe^{3+}+H_2O=[FeOH]^{2+}+H^+$,[17] −33 kJ mol^{-1} for $2[FeOH]^{2+}=[Fe_2(OH)_2]^{4+}$,[19] 72 kJ mol^{-1} for $Fe^{3+}+2H_2O=[Fe(OH)_2]^{+}+2H^+$,[17] 21 kJ mol^{-1} for $Fe^{3+}+Cl^-=[FeCl]^{2+}$,[31] and 5.0 kJ mol^{-1} for $[FeCl]^{2+}+Cl^-=[FeCl_2]^+$,[34] the amounts of $[FeOH]^{2+}$ and $[Fe(OH)_2]^+$ would increase much more than those of chloro complexes at higher temperatures by the degradation of glycinato complex. Although it is uncertain which hydroxoiron(III) complex is the actual precursor of hematite paricles, the glycinato-iron(III) complex was obviously indicated to participate as the soluble reservoir of hydroxo complex for originating the monodispersed hematite particles.

The monodispersed double spheres of hematite obtained in the 2-propanol/water mixed solution would be produced through a process similar to that in the aqueous solution.

When β-iron(III) hydroxide oxide, which was separately prepared and washed, was treated at 100 °C in the same solution given in Fig. 8 but without iron(III) chloride, the dissolution of hydroxide oxide quickly reached an equilibrium state in around 15 min. On the basis of the mass balance during the dissolution of hydroxide oxide and the deposition of hematite, it was concluded that the total concentration of the iron(III) species was not controlled by the dissolution rate of the β-iron(III) hydroxide oxide but by the solubility of the hydroxide oxide. Thus, the suspension of β-iron(III) hydroxide oxide would give an appropriate supersaturation of hydroxoiron(III) complexes to form the monodispersed hematite particles under the conditions suitably adjusted.

In addition, the formation mechanism of monodispersed cuboidal hematite particles in the presence of glycine would be basically the same as that in the alcohol/water mixtures without glycine.[5] However, the final size of the particles was greatly reduced by the presence of glycine even under the same concentrations of total iron(III) chloride, depending on the acid concentration. As the size distribution was kept almost constant (the relative standard deviation of 0.11—0.13 for 40 h) throughout the forced hydrolysis, the nucleation of the hematite particles would be completed at an early stage of the conversion. The dependence of acid concentration on the final size of hematite particles was also examined by a different way as follows: A solution contained 0.13 mol dm^{-3} hydrochloric acid and the same concentrations of iron(III) chloride and glycine as shown in Fig. 8 was aged at 100±0.5 °C for specified periods, t_1, from 3 to 60 min. The solution was then quenched to room temperature and its acidity was immediately changed to 0.15 mol dm^{-3} by adding hydrochloric acid, followed by repeated heating for 48—60 h.

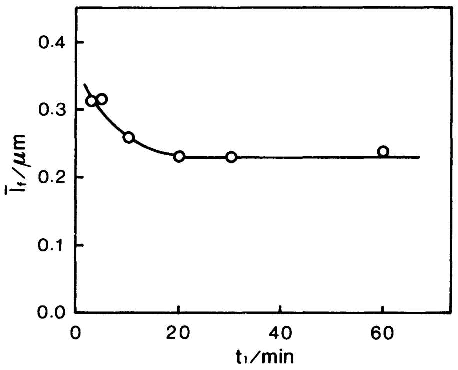

Fig. 11. Influence of acid concentration changed at t_1 on final size of cuboidal hematite particles at 100 °C. Conditions: $[HCl]_1=0.13$ and $[HCl]_f=0.15$ mol dm^{-3}.

Figure 11 displays the final size of the hematite particles as a function of t_1. The particles grew larger when the acidity was increased only at very early stages of aging. As shown in Fig. 9, the solution gave the final sizes of 0.22 and 0.35 μm at 0.13 and 0.15 mol dm^{-3} of hydrochloric acid respectively. Thus, these facts indicated that the final size was scarcely affected by the acidity applied after completion of the nucleation.

On the other hand, the cuboidal hematite particles can be also obtained when β-iron(III) hydroxide oxide particles were separately prepared and then aged in a solution without iron(III) ions under suitable conditions. In order to examine the dependence of the nature of β-iron(III) hydroxide oxide on the final size of hematite particles, three kinds of the hydroxide oxide were prepared under the conditions shown in Table 1. These were centrifuged and washed ten times with distilled water. These particles, as the iron(III) concentration of 2.0×10^{-2} mol dm^{-3}, were aged under the conditions shown in Table 2. The final sizes of the hematite particles thus prepared are also given in Table 2. The samples B and C gave hematite particles with final sizes of 0.22—0.37 μm which depended merely on the initial pH for preparing β-iron(III) hydroxide oxide, regardless of the original size of the

Table 1. Preparing Conditions for β-FeOOH at 100 °C[a)]

Sample	$[FeCl_3]\times 10$ / mol dm^{-3}	[Gly] / mol dm^{-3}	$[HCl]\times 10^2$ / mol dm^{-3}	pH[b)]	$\bar{l}\times 10^{2}$ [c)] / μm
A	2.0		0.25	1.58	7.2
B	0.20	0.20	13	2.14	6.0
C	0.20	0.20	16	1.93	24

a) 2-Propanol: 30% by volume. b) Observed at 25 °C before aging. c) Average size of acicular β-FeOOH particles.

Table 2. Aging Conditions and Final Size of Cuboidal Hematite Particles Obtained from β-FeOOH Suspension at 100 °C[a)]

Sample	[Gly] / mol dm^{-3}	$[HCl]\times 10^2$ / mol dm^{-3}	pH[b)]	$\bar{l}_f$ / μm
A	0.20	17	2.12	0.85[c)]
B	0.20	17	2.11	0.22
B		4.5	1.52	0.23
C	0.20	20	2.10	0.34
C	0.20	17	1.80	0.37

a) $[Fe(III)]=2.0\times 10^{-2}$ mol dm^{-3} as β-FeOOH, 2-propanol: 30% by volume. b) Observed at 25 °C before aging. c) The reaction did not complete even for 120 h.

hydroxide oxide, the presence of glycine, and the pH at aging. Contrary to the above results, the sample A, obtained from the solution without glycine, yielded much larger hematite particles in spite of the almost identical size of the original β-iron(III) hydroxide oxide and the aging conditions.

These facts imply that the nature of the hematite nuclei would depend definitively on the initial conditions in producing β-iron(III) hydroxide oxide. The nuclei would originate on the surfaces of the hydroxide oxide, probably by epitaxial nucleation, at the beginning of the reaction and tightly bind to the original hydroxide oxide. In the pH range applied in this work, the fraction of glycine anions is of the order of 10^{-9}, so that the adsorption of the anions would be negligible. If glycine anions adsorbed on the surfaces and reduced an interfacial energy of hematite particles, the growth rate should be also strongly affected by the acidity even in the narrow range of pH similar to the nucleation rate. Actually, little adsorption was observed even at pH 4.

However, glycine anions would combine strongly with embryos of hematite prior to the formation of stable nuclei even at low pH, because of a large excess surface energy of the embryos. In such a situation, the interfacial energy of the embryos would be significantly reduced, depending on the amount of adsorbed glycine anions, i.e., the acidity, which enhances the nucleation rate. Actually, the aging of the solutions without glycine gave much slower nucleation rates.[4,5)]

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