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Effects of citrate ions on the formation of ferric oxide hydroxide particles

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The effects of citrate ions on the formation of β- and α-FeOOH particles were investigated using various techniques. The formation and crystallization of both particles were inhibited by citrate ions, and their particle sizes decreased with increase in the concentration of these ions. Finally, aggregated amorphous particles were formed. The effects of citrate ions appeared to be more significant for β-FeOOH than for α-FeOOH. This difference could be explained by the pH dependence of the affinity of citrate ions to Fe^{3+} ions. The amorphous β-FeOOH particles prepared in the presence of > 10 mol% citrate ions selectively adsorbed water molecules.

1. Introduction

Ferric oxide hydroxides appear in the corrosion of iron and steel and they are also used as pigments, catalysts, coatings, etc. Recently, these particles have received considerable attention because of their application in the preparation of the raw material for γ-Fe_2O_3 used for magnetic tapes and discs. Despite numerous investigations on the preparation of ferric oxide hydroxides, little is known about the preparation method of the particles which are uniform in both shape and size [1–10]. Development of a simple and distinct preparation method of the monodispersed ferric oxide hydroxide particles is desirable.

Citrate ions are ligands for chelate or complex formation with metal ions and are used as a masking agent in analytical chemistry. Hence, it is expected that this anion will exhibit a high affinity to Fe^{3+} ions, will affect the hydrolysis reaction of particle formation and also will provide particles of characteristic shape, size and surface properties. Ozaki *et al.* [11] have found that small amounts of hypophosphite ions have a significant effect on the morphology of haematite particles produced by ageing ferric chloride solutions. Therefore, it seems useful to investigate systematically the changes introduced by the addition of anions in ferric oxide hydroxide particles. This is interesting not only in the industrial field but also in colloid chemistry in the preparation of monodispersed particles. The effects of citrate ions on the formation and properties of ferric oxide hydroxide particles were studied by various techniques, and the results are reported.

2. Experimental procedure

The preparation of β- and α-ferric oxide hydroxides, β- and α-FeOOH, respectively, was performed following the method reported previously [12]. The β-FeOOH particles were prepared by the forced hydrolysis reaction of 0.1 $mol\,l^{-1}$ ferric chloride solution containing various amounts of sodium citrate. The bottles were closed tightly and stored in an air oven at 100 °C for 5 h. The pH of the resulting suspensions was lower than unity at room temperature. The α-FeOOH particles were prepared by adding 1.0 $mol\,l^{-1}$ sodium hydroxide solution to 0.1 $mol\,l^{-1}$ ferric nitrate solution containing different amounts of sodium citrate up to pH 12, in a polypropylene screw-capped vessel at room temperature. The resulting precipitates were aged for 4 days in a thermostat at 30 °C. The amount of citrate to Fe ions was changed from 0–20 mol % for β- and α-FeOOH particles.

Both precipitates were thoroughly washed with water and dried in air at 70 °C for 16 h. Crystal structures and the crystallinity of the powders thus prepared were examined by X-ray diffraction (XRD). XRD patterns were taken using a Rigaku X-ray diffractometer with Ni-filtered CuK_α radiation, operated at 30 kV, 15 mA. The average crystallite sizes (L) of the particles prepared at different concentrations of citrate ions were determined by the X-ray diffraction line-broadening technique using a Scherrer equation

$$L = 0.94\lambda/b\cos\theta \qquad (1)$$

where λ is the wavelength of the X-ray used, and b is the half-width of diffraction peaks.

The infrared (IR) spectra in KBr were taken by a Digilab FTIR spectrometer. The concentration of the samples in KBr discs was 0.33 wt %.

The shape of the particles was inspected by TEM from a Jeol electron microscope. Simultaneous TG and DTA measurements were carried out by a Rigaku thermal analysis apparatus in air at a heating rate of 5 °C min^{-1}. The specific surface area of the powders was measured by nitrogen BET method by using an automatic volumetric apparatus. The adsorption isotherms of water were measured at 25 °C using an automatic gravimetric instrument [13, 14]. Prior to the adsorption measurements, the samples were treated under a vacuum of 10^{-2} Pa at 100 °C for 2 h. The total contents of iron and carbon were deter-

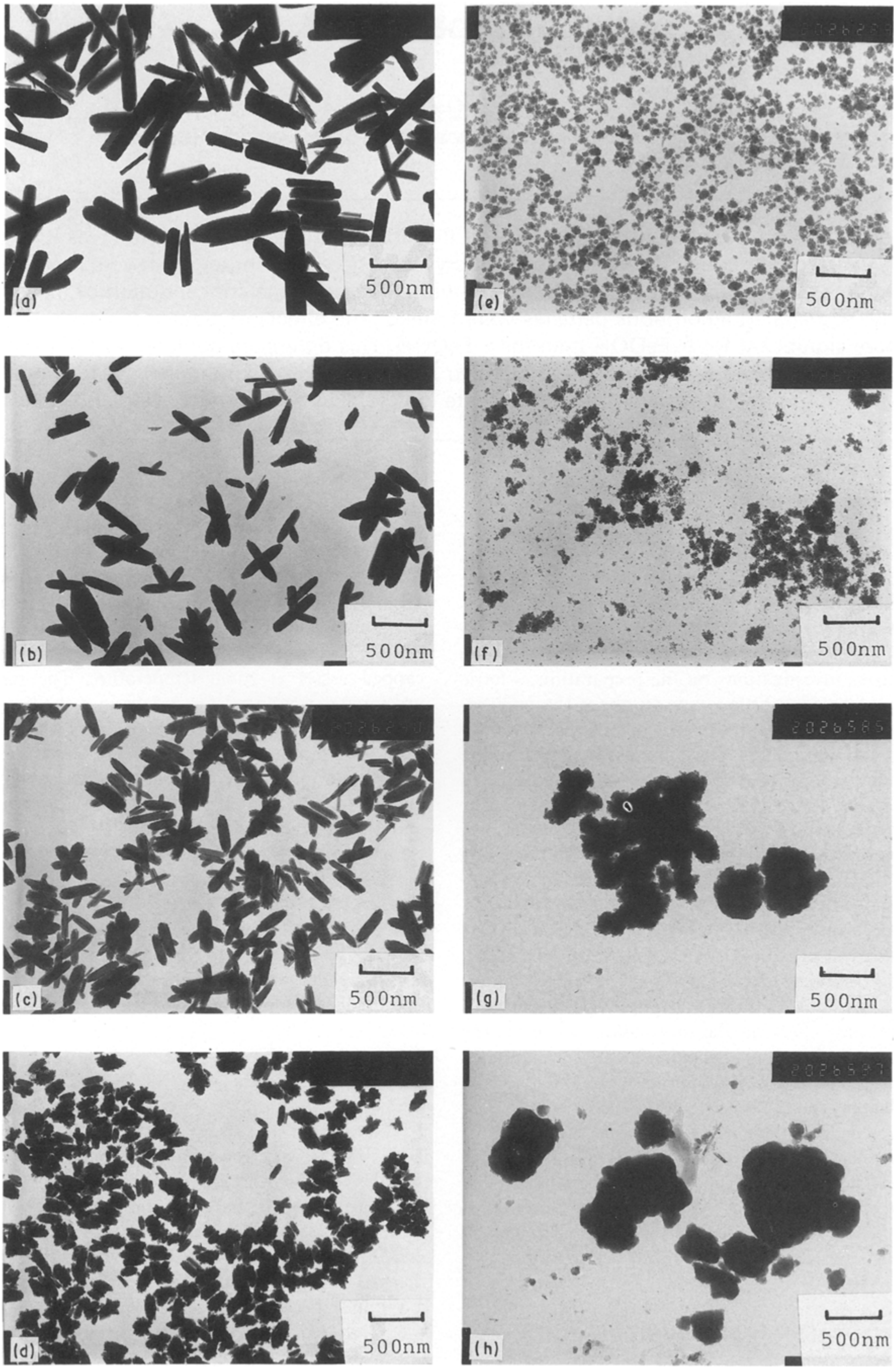

Figure 1 Electron micrographs of β-FeOOH particles prepared in the presence of citrate ions: (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 1, (f) 2, (g) 5, (h) 10 mol %.

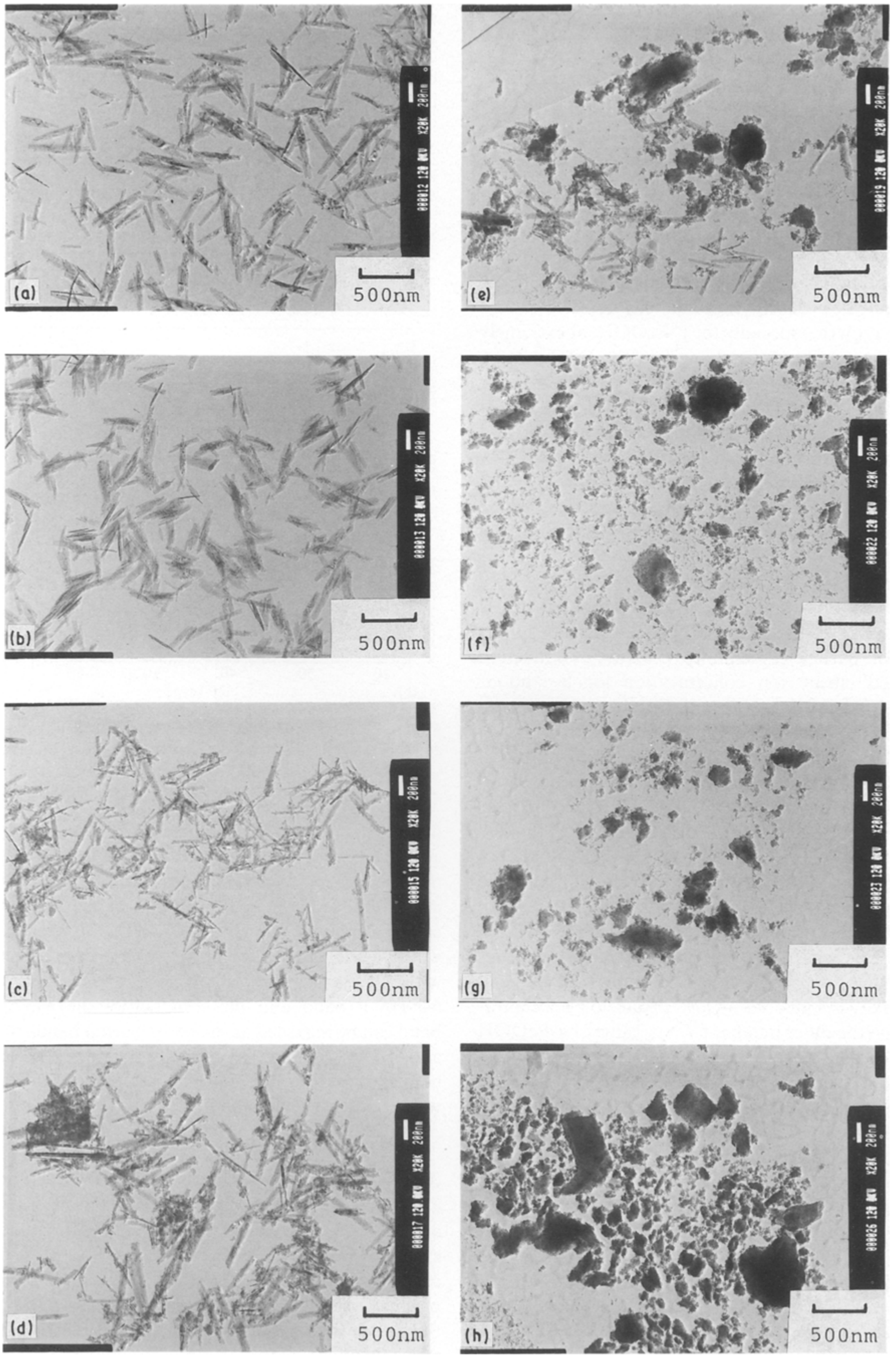

Figure 2 Electron micrographs of α-FeOOH particles prepared in the presence of citrate ions: (a) 0, (b) 0.2, (c) 0.5, (d) 1, (e) 2, (f) 5, (g) 10, (h) 20 mol %.

mined by inductively coupled plasma (ICP) spectrophotometry and C, H and N analysis, respectively.

3. Results and discussion

3.1. Effects of citrate ions on particle formation

The electron micrographs of β- and α-FeOOH particles prepared with various concentrations of added citrate ions are shown in Figs 1 and 2, respectively. As can be seen from these figures, the sizes of β- and α-FeOOH particles decreased with increasing concentration of citrate ions up to 0.5 or 2 mol %, respectively, and above these concentrations only large aggregates of very fine particles were formed. This indicates clearly that the citrate ions inhibit particle growth, especially for β-FeOOH, at extremely low concentrations. The changes in the XRD pattern with addition of citrate ions for β- and α-FeOOH are shown in Fig. 3a and b, respectively. The peaks characteristic for each FeOOH crystal diminished and broadened with addition of citrate ions. Finally, the amorphous particles were formed above 5 and 1 mol % for β- and α-FeOOH, respectively. These results correspond with the results of TEM shown in Figs 1 and 2.

The average crystallite sizes (L) of the particles were calculated from the results of XRD patterns because the L value is useful to discuss quantitatively the change in particle crystallinity. L values as a function of added citrate ion concentration for β- and α-FeOOH particles are shown in Fig. 4a and b, respectively. Here, L values of the (3 1 0) plane (L_{310}) of β-FeOOH and those of (0 2 1) and (1 1 0) planes of α-FeOOH were calculated. The L_{310} value of β-FeOOH corresponds to the particle width, because the crystalline β-FeOOH particles are rods elongated along the c-axis [15]. The L_{110} and L_{021} values of α-FeOOH are a measure of the width and length of the long rectangular plates, respectively [16]. The L_{310} of β-FeOOH in Fig. 4a rapidly decreased on addition of citrate ions up to 0.5 mol %. This result indicates clearly that the particle growth of β-FeOOH along a- and b-axes is hindered at low citrate ion concentrations. On the other hand, the L_{110} value of α-FeOOH remained constant up to 0.5 mol % and abruptly decreased above this point, while the decrease in L_{021} began from low concentrations. This suggests that the particle growth of α-FeOOH along the long c-axis is hindered and that their lengths are shortened, while the size along short b-axis remains constant up to 0.5 mol %. This observation is supported by the morphology change in α-FeOOH particles seen in Fig. 2.

Fig. 5 shows the IR spectra of the materials formed in the presence of various amounts of citrate ions. The spectrum of pure β-FeOOH shows three bands at 845, 694 and 645 cm^{-1}. The former band possessed a shoulder in the low wave number side. The intensities of these bands decreased with increasing amount of citrate ions. Müller [17] assigned the 843 and 695 cm^{-1} bands to the deformation vibration of OH groups in the crystal. Therefore, the decrease in intensity of the 845 and 694 cm^{-1} bands is considered to be due to the reduction in particle size caused by the added citrate ions. Ishikawa and Inouye [18] found that the 645 cm^{-1} band diminished on removal of Cl$^-$ ions contained within the tunnels of the β-FeOOH crystal. The bulk OH groups of β-FeOOH exist in the walls of the tunnels, being perturbed by interacting with Cl$^-$ ions or water molecules [15]. Hence, the 645 cm^{-1} band and the shoulder of the 845 cm^{-1} band can be regarded as the perturbation bands of 695 and 845 cm^{-1} bands, respectively. These perturbation bands, as well as the 694 and 845 cm^{-1} bands, are weakened by the destruction of the tunnels.

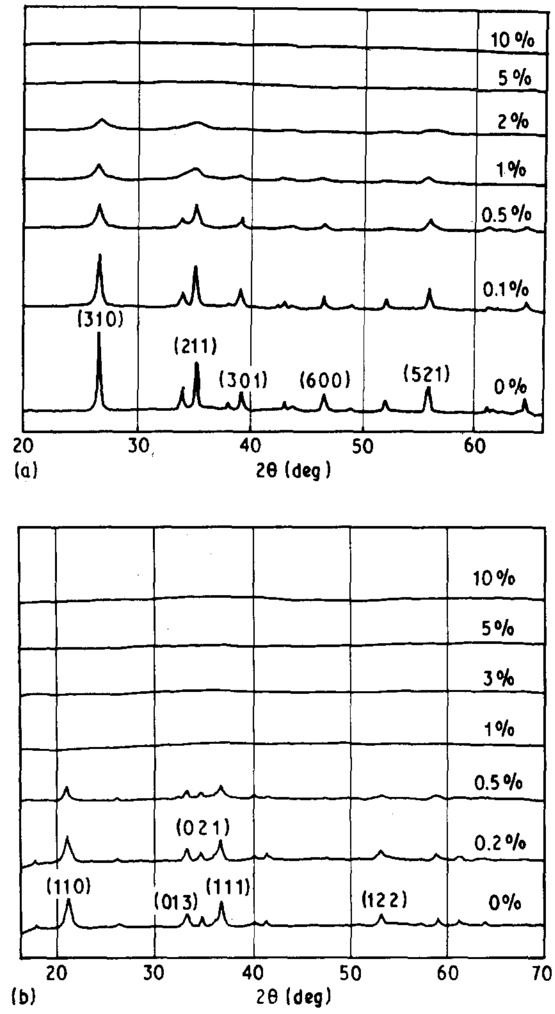

Figure 3 The XRD patterns obtained with different amounts of added citrate ions for (a) β-FeOOH and (b) α-FeOOH particles.

3.2. Properties of β- and α-FeOOH particles

The N$_2$ BET specific surface area (A_s) of both the β- and α-FeOOH particles is shown as a function of added citrate ion concentration in Fig. 6. It is a characteristic of Fig. 6, that the A_s values of both particles rise sharply at low concentrations, but that the A_s value of β-FeOOH drops dramatically above this maximum point of 2 mol %, while that of α-FeOOH saturates around 330 m^2 g^{-1} above 1 mol %. To clarify this difference, the TG-DTA, ICP measurements and C, H and N analysis were done. The TG–DTA curves of β-FeOOH are shown in Fig. 7. The characteristic exothermic peaks could be recognized at

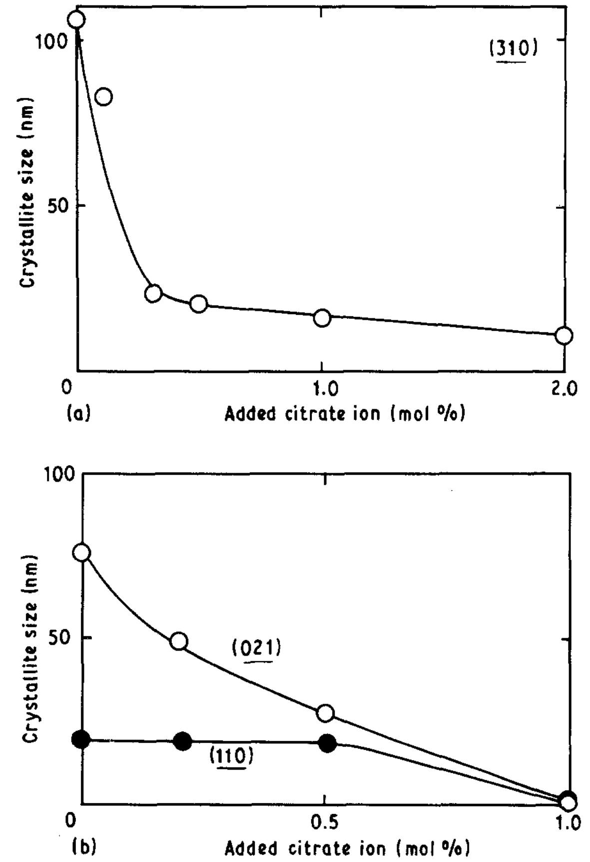

Figure 4 The change of crystallite size as a function of added citrate ion concentration for (a) β-FeOOH and (b) α-FeOOH particles.

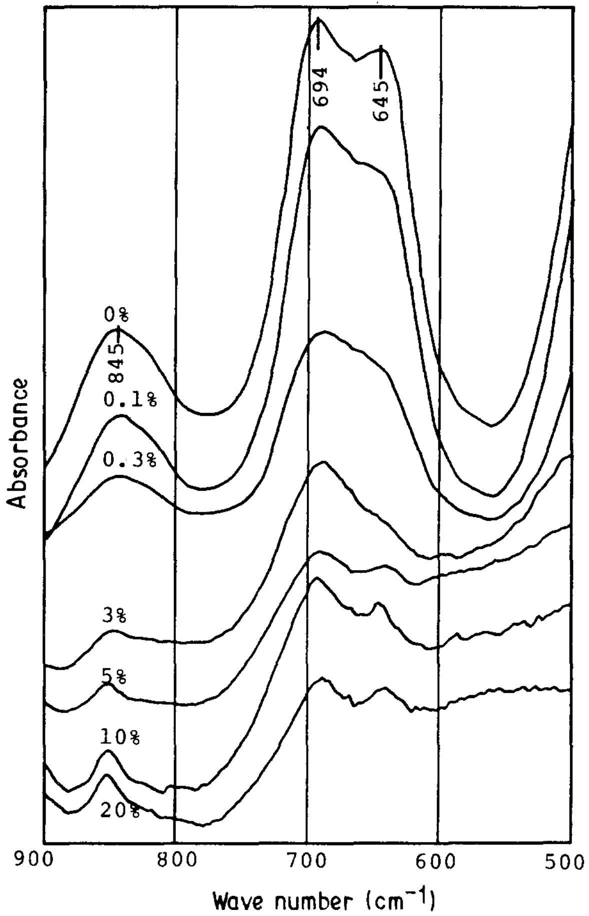

Figure 5 The IR spectra of β-FeOOH formed in the presence of different amounts of citrate ions.

~ 200, 260 and 400 °C in the DTA curves and their intensities increased with increasing amount of citrate ions added. The first two peaks seem to be caused by the decomposition and/or oxidation of the citrate ion contained in the particles, because a large weight loss occurred around the temperatures of these two peaks, as shown in the TG curves. The 400 °C peak would be derived by the crystallization from the amorphous phase to α-Fe_2O_3. On the other hand, in DTA curves of α-FeOOH, the intensive peaks at 200 and 260 °C could not be clearly detected, even though 20 mol % citrate ions were added, and the TG curves did not show a large weight loss, such as that for β-FeOOH. However, the endothermic peak at 60–70 °C, due to

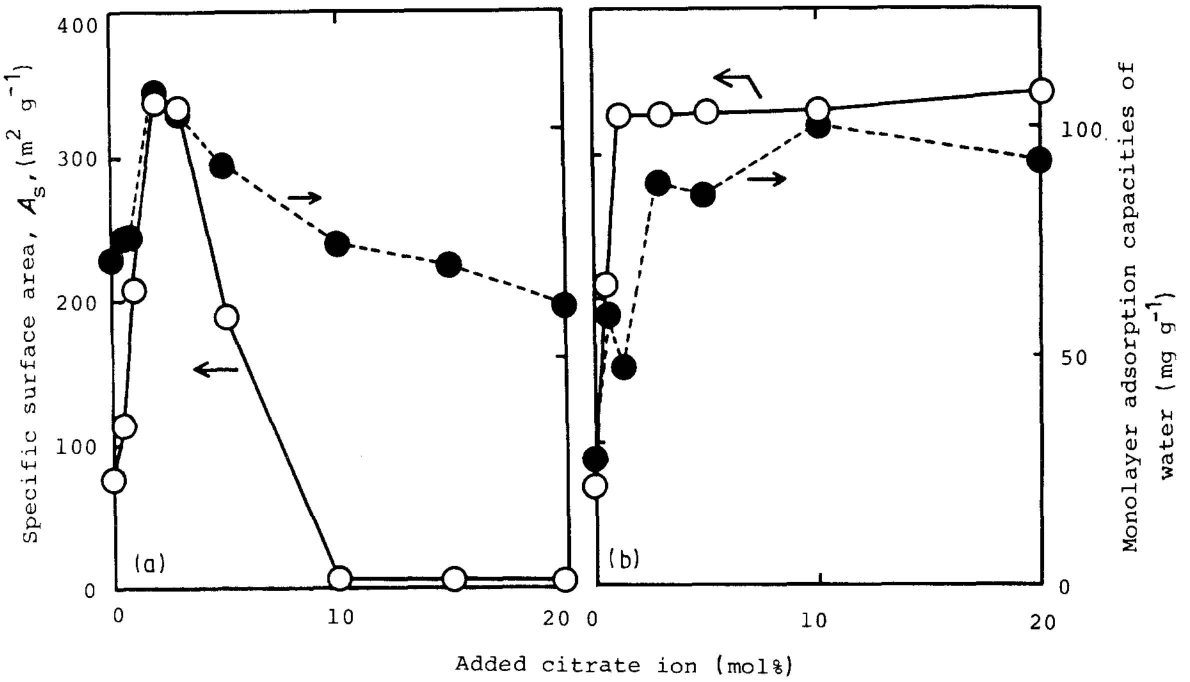

Figure 6 The change of specific surface area and amounts of adsorbed water with addition of citrate ion for (a) β-FeOOH and (b) α-FeOOH particles.

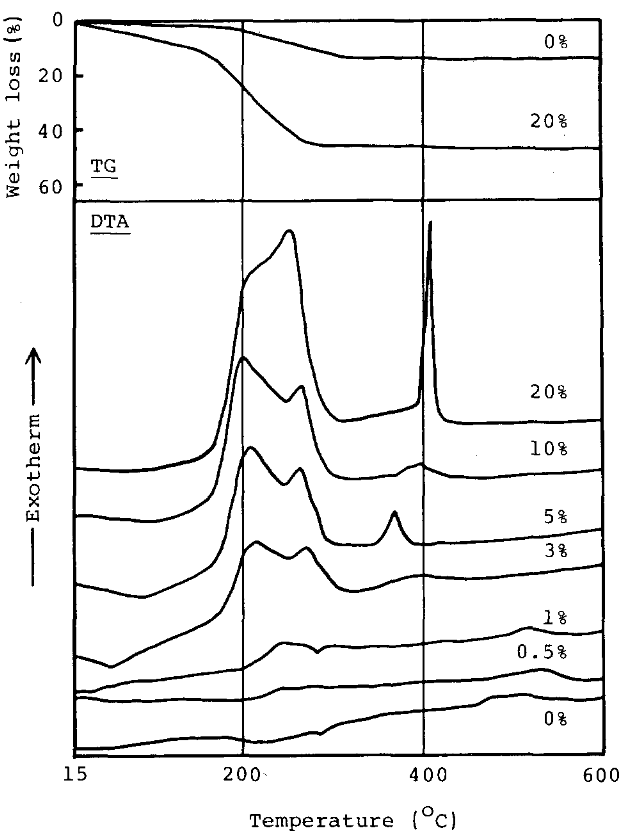

Figure 7 TG–DTA curves of β-FeOOH particles prepared with different amounts of citrate ions.

the elimination of adsorbed or bound water, and the exothermic peak at 420–470 °C, of phase transition from the amorphous phase to α-Fe_2O_3, became progressively greater when more than 3 mol% citrate ions were added. This clearly suggests that α-FeOOH particles became smaller and less crystalline with increasing amount of added citrate ions, as seen by TEM and XRD.

Table I summarizes the results of ICP measurements and C, H and N analysis together with the weight loss values from TG measurements. It is noticeable in Table I that the citrate ion contents of β-FeOOH are a few times higher than those of the corresponding starting solutions, whereas in the case of α-FeOOH the former is only slightly lower than the latter. Also, the weight loss of β-FeOOH increases with increasing citrate ion content, while that of α-FeOOH remains almost constant, at slightly more than the weight loss of 10% by the dehydration reaction

$$2FeOOH \rightarrow \alpha\text{-}Fe_2O_3 + H_2O \qquad (2)$$

This result would be due to the difference between the preparation pH of β- and α-FeOOH: the pH of β- and α-FeOOH were less than unity and 12, respectively. It can be reasonably considered that the Fe^{3+}–citrate complex is much more stable in acidic solutions, and hinders the hydrolysis reaction in the formation of β-FeOOH. The exchange of citrate ions coordinating with Fe^{3+} ions for OH^- ions occurs readily at pH 12, so that the hydrolysis reaction for α-FeOOH proceeds more easily than that for β-FeOOH. Therefore, it can be concluded that this difference in the hydrolysis reaction strongly affects the properties of the resulting β- and α-FeOOH particles.

The monolayer adsorption capacities of water on β- and α-FeOOH, which were calculated using the BET equation, are plotted against the amount of citrate ion added in Fig. 6. An unexpectedly large amount of water was adsorbed on the β-FeOOH particles above

TABLE I The results of C, H and N analysis and ICP and TG measurements for the citrate ion added system

Initial concentration (mol %)	Products			
	Citrate ion[a] (mmol g^{-1})	Fe[b] (mmol g^{-1})	[Citrate]/[Fe] (mol %)	Weight loss[c] (%)
β-FeOOH				
0	0	8.53	0	12
0.5	0.13	8.52	1.6	9
1	0.24	8.25	3.0	13
2	0.31	7.74	4.0	16
3	0.87	7.35	11.8	20
5	1.30	6.68	19.4	22
7	1.42	6.50	21.8	26
10	1.71	6.27	27.3	27
20	2.21	5.92	37.3	32
α-FeOOH				
0	0	–	0	10
0.2	7.36×10^{-3}	10.46	7.04×10^{-4}	9
0.5	13.6×10^{-3}	11.12	12.2×10^{-4}	13
1	15.9×10^{-3}	10.62	15.0×10^{-4}	12
3	24.0×10^{-3}	9.72	24.7×10^{-4}	12
5	25.6×10^{-3}	9.72	26.3×10^{-4}	14
10	32.5×10^{-3}	9.83	33.1×10^{-4}	12
20	44.6×10^{-3}	9.51	46.9×10^{-4}	12

[a] From C, H and N analysis.
[b] From ICP measurement.
[c] From TG measurement.

10 mol %, as compared with nitrogen. There are two possible reasons to explain this result: the first is the existence of ultramicropores which are accessible to water molecules but not to nitrogen molecules, and the second is the penetration of water molecules into the cavities which were formed in the particles in the vicinity of the Fe^{3+} ion through the removal of water ligands by the pretreatment of adsorption [19, 20]. However, β-FeOOH particles prepared at the citrate concentrations of > 5 mol % were amorphous and included large amounts of citrate ions, as mentioned above. Therefore, it is difficult to consider that these particles possess ultramicropores of uniform size. Consequently, from the present data, the molecular sieve character of β-FeOOH seems to be due to the penetration of water into the particles. A more detailed study of this molecular sieve character will be published elsewhere [21].

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