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Preparation of monodispersed haematite particles by two-step hydrolysis of ferric chloride aqueous solutions

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Monodispersed haematite particles have been synthesized by two-step hydrolysis of dilute $FeCl_3$ aqueous solution. The first step is the hydrolysis of $FeCl_3$ solution at 70 ~ 90 °C, which provided β-FeO(OH) colloidal suspension, and the second step is the transformation from β-FeO(OH) to α-Fe_2O_3 at 100 ~ 120 °C via a dissolution and recrystallization process. Partial neutralization with NaOH solution promotes the hydrolysis of highly concentrated $FeCl_3$ solutions. Particle size of α-Fe_2O_3 can be controlled by neutralization degree, and it decreases with decreasing the electrolyte concentration.

1. Introduction

Particulate materials have been widely used in applications such as the pigments in paints [1], catalysts [2], gas sensors [3] and magnetic recording media [4]. Their characteristics depend significantly on particle size, particle morphology and size distribution. Among these control of size distribution is the most difficult problem. Therefore, there have been many studies on the preparation of monodispersed particles: precipitation methods [5, 6] sol–gel synthesis [7], spray-drying [8] and hydrothermal methods [9, 10].

Haematite (α-Fe_2O_3) is an antiferromagnetic semiconductor, the colour of which varies with particle size and aggregation form [11], and the electrical properties of which can be widely modified with some impurities [12]. Further, it is a starting material for the magnetic iron oxides used in magnetic recording tapes [13]. Therefore, α-Fe_2O_3 particles have high potential for some applications.

Some studies have been carried out on the preparation method of monodispersed α-Fe_2O_3 particles: the forced hydrolysis of dilute $Fe(NO_3)_3$–HNO_3, $FeCl_3$–HCl, and $Fe(ClO_4)_3$–$HClO_4$ aqueous solutions [14], that of dilute $FeCl_3$–glycine aqueous or 2-propanol/water solutions [15], and oxidation with NO_3- of a 2,2′-bipyridine ferrous complex [16]. However, in the above studies, the concentration of Fe^{3+} in the initial solution is not high enough and the complete precipitation requires a long period such as 24 ~ 72 h. These limitations are serious problems for the production process.

In this paper, we report on a two-step hydrolysis of $FeCl_3$ aqueous solutions. In dilute $FeCl_3$ aqueous solutions, the introduction of an intermediate fine β-FeO(OH) precipitate as the colloidal reservoir provided monodispersed α-Fe_2O_3 particles in a short ageing time. In highly concentrated $FeCl_3$ aqueous solutions, a ferric hydroxide gel, in addition to a fine β-FeO(OH) precipitate, was utilized as the colloidal reservoir, producing monodispersed α-Fe_2O_3 particles.

2. Experimental method

2.1. Sample preparation

$FeCl_3 \cdot 6H_2O$ (analytical grade) was dissolved in distilled water and adjusted to the concentration of $[Fe^{3+}]$ (< 1.0 mol dm^{-3}). First, the dilute solutions (500 ml) with $[Fe^{3+}] < 0.1$ mol dm^{-3} were aged at 70 ~ 90 °C under mechanical stirring for 1 h. It led to hydrolysis and produced yellow suspensions. The suspensions were put into 1000 ml screw-capped Pyrex bottles and placed in an oven maintained at 100 ~ 120 °C. After the forced hydrolysis for 6 h, they were cooled to room temperature.

The precipitates were separated by filtration, and dispersed again with 500 ml distilled water. The suspensions were in a highly dispersed state. Sedimentation velocity was very low and particle aggregation was very weak. Therefore, in order to promote particle aggregation, the pH value was adjusted to about 7 with a NaOH solution. The residual Fe^{3+} precipitated to ferric hydroxide, but the ferric hydroxide was transformed to a chelate, which was easily removed by washing, with the addition of an appropriate amount of sodium tartrate. After the above treatment with NaOH and sodium tartrate, the precipitates were filtrated, washed with distilled water, and dried in air at 120 °C.

For high concentration solutions of $[Fe^{3+}] >$ 0.1 mol dm^{-3}, solutions of 1000 ml were also aged at 70 ~ 90 °C under mechanical stirring for 1 h. They were partially neutralized with NaOH solution ($3[OH^-]/[Fe^{3+}] = 0.8 \sim 0.95$). The neutralization led to ferric hydroxide gel formation and fast sedimentation of the solid phases on the base of the vessel.

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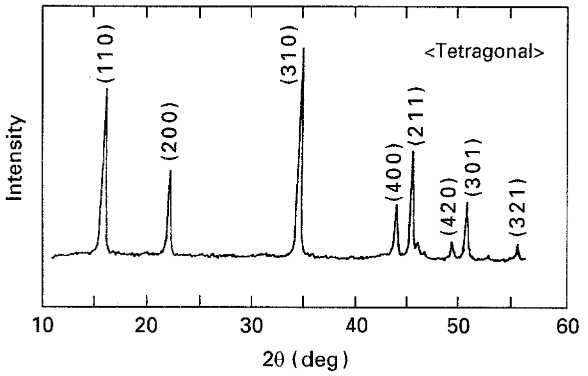

Figure 1 Powder X-ray diffraction pattern of the precipitates obtained by the hydrolysis of $FeCl_3$ aqueous solution ($[Fe^{3+}] = 0.2\ mol\ dm^{-3}$) at 80 °C for 1 h (β-FeO(OH)).

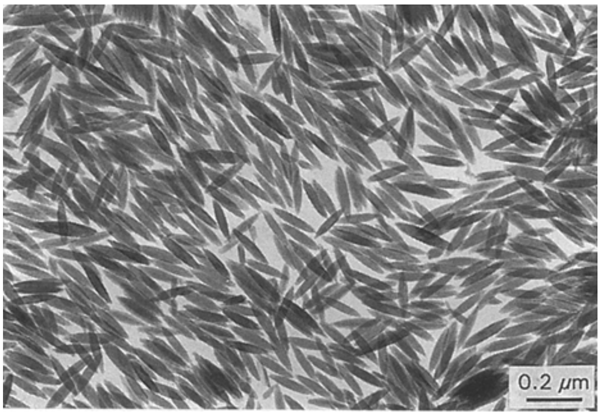

Figure 2 TEM photograph of β-FeO(OH) particles obtained by the hydrolysis of $FeCl_3$ aqueous solution ($[Fe^{3+}] = 0.2\ mol\ dm^{-3}$) at 80 °C for 1 h.

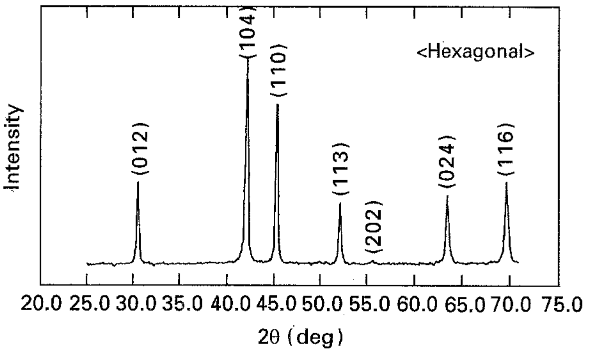

Figure 3 Powder X-ray diffraction pattern of the precipitates synthesized by the hydrothermal ageing of fine β-FeO(OH) colloidal suspension ($[Fe^{3+}] = 0.05\ mol\ dm^{-3}$) at 120 °C for 6 h ($\alpha$-$Fe_2O_3$).

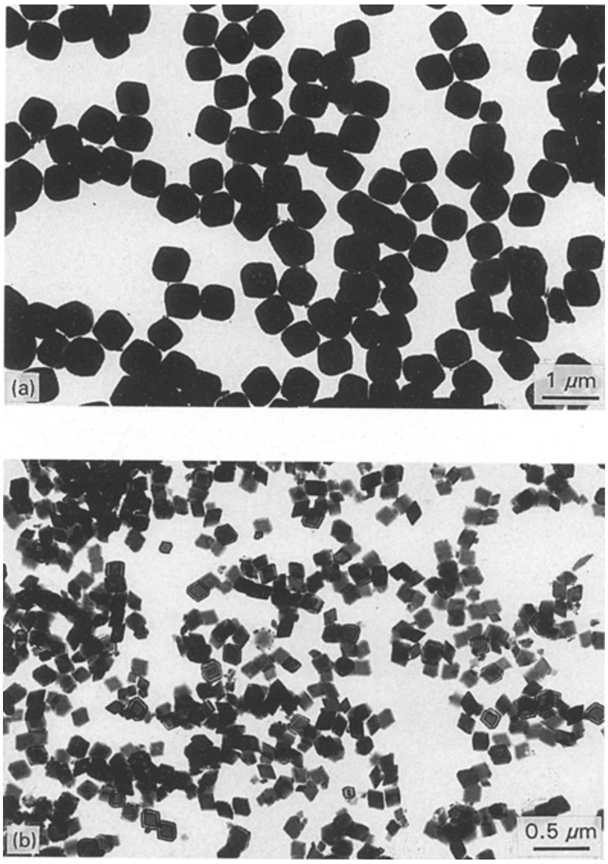

Figure 4 TEM photographs of α-Fe_2O_3 particles precipitated by the hydrothermal ageing of fine β-FeO(OH) colloidal suspension at 120 °C for 6 h: initial concentration of $[Fe^{3+}] = 0.05\ mol\ dm^{-3}$ (a) and ($[Fe^{3+}] = 0.01\ mol\ dm^{-3}$ (b).

Figure 5 TEM photograph of rodlike β-FeO(OH) particles obtained by the hydrothermal ageing of fine β-FeO(OH) colloidal suspension ($[Fe^{3+}] = 0.3\ mol\ dm^{-3}$) at 120 °C for 6 h.

The solution was separated into two parts. For one part, 250 ml of the supernatant was removed and 250 ml distilled water was added, reducing the electrolyte concentration by one half. No treatment was carried out on the other part. The two parts were put into screw-capped Pyrex bottles and hydrolysed at 100 ~ 120 °C for 6 h. After the hydrolysis, they were cooled to room temperature. The suspensions were neutralized with NaOH solution, and mixed with an appropriate amount of sodium tartrate. The precipitates were filtrated, washed with distilled water, and dried in air at 120 °C.

2.2. Characterization

For all hydrolysed products, powder X-ray diffraction measurement (Rigaku, Mn-filtered FeK_α, 40 kV and 20 mA) was carried out to identify the precipitated phases. The re-dispersed aqueous suspension of the hydrolysed product was poured onto a carbon mesh on a copper grid, and the particle size and shape were observed with transmission electron microscopy (TEM) (Jeol, JEM-100S, acceleration voltage of 100 kV).

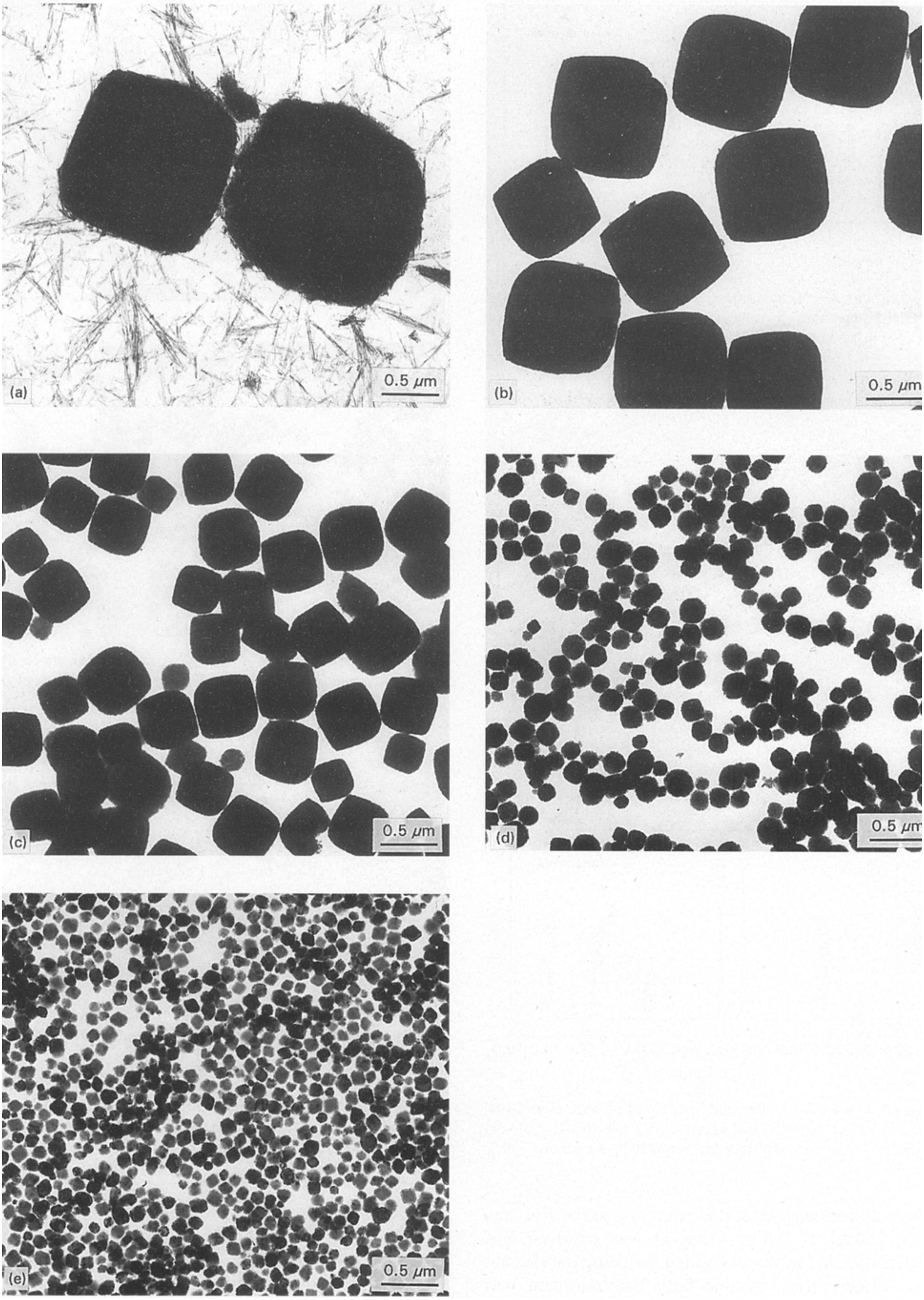

Figure 6 TEM photographs of the products precipitated by the hydrothermal ageing of the partially neutralized β-FeO(OH)–$FeCl_3$ suspensions (initial concentration of ($[Fe^{3+}] = 0.4\ mol\,dm^{-3}$) at 110 °C for 6 h: neutralization degree of $3[OH^-]/[Fe^{3+}] = 0.80$ (a), $3[OH^-]/[Fe^{3+}] = 0.85$ (b), $3[OH^-]/[Fe^{3+}] = 0.90$ (c), $3[OH^-]/[Fe^{3+}] = 0.92$ (d), and $3[OH^-]/[Fe^{3+}] = 0.95$ (e).

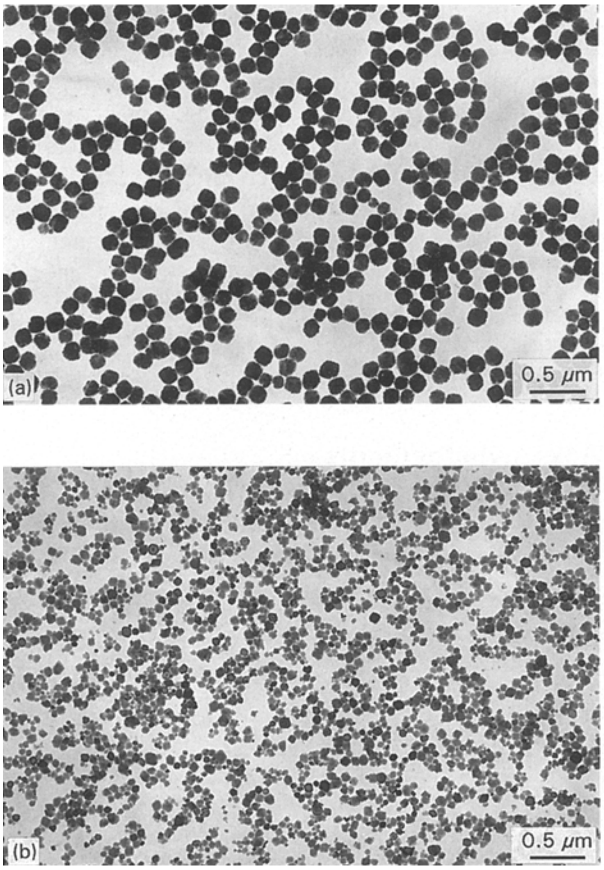

Figure 7 TEM photographs of α-Fe_2O_3 particles obtained by the hydrothermal ageing of the partially neutralized β-FeO(OH)–$FeCl_3$ suspensions (initial concentration of $[Fe^{3+}] = 0.4\ \text{mol dm}^{-3}$) at 110 °C for 6 h after the removal of 50% electrolyte: neutralization degree of $3[OH^-]/[Fe^{3+}] = 0.90$ (a) and $3[OH^-]/[Fe^{3+}] = 0.95$ (b).

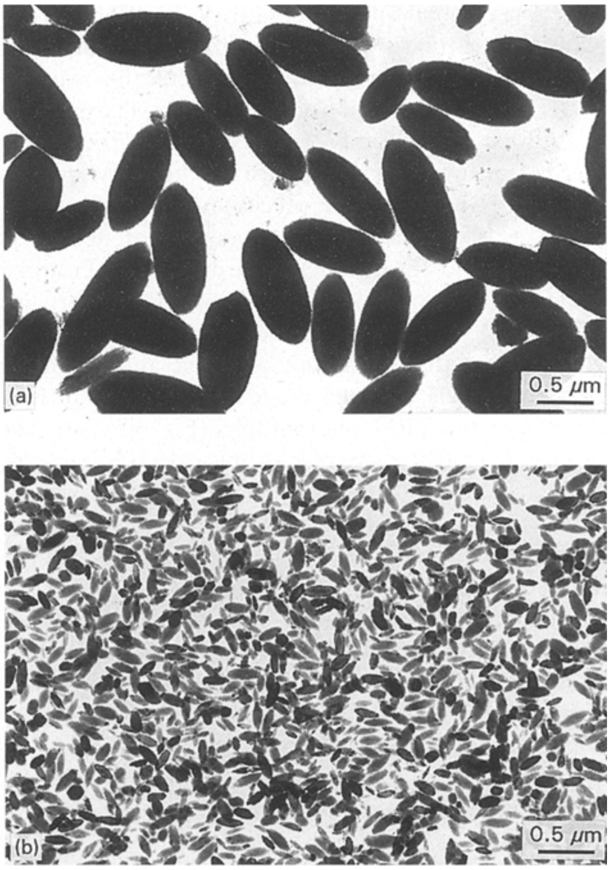

Figure 8 TEM photographs of ellipsoidal α-Fe_2O_3 particles obtained by the hydrothermal ageing of partially neutralized β-FeO(OH)–$FeCl_3$ suspensions (initial concentration of $[Fe^{3+}] = 0.4\ \text{mol dm}^{-3}$) at 110 °C for 6 h with the presence of phosphate ion $[PO_4^{3+}] = 0.002\ \text{mol dm}^{-3}$; neutralization of degree of $3[OH^-]/[Fe^{3+}] = 0.85$ (a), and $3[OH^-]/[Fe^{3+}] = 0.95$ (b).

3. Results and discussion

On heating the $FeCl_3$ aqueous solution at 80 °C the initial brown clear solution turned cloudy in a few minutes. The precipitates were centrifuged to remove the supernatant and re-dispersed with distilled water. Following several repetitions of the washing process, the precipitated particles were identified with powder X-ray diffraction. The X-ray pattern is shown in Fig. 1 and can be identified as β-FeO(OH). Fig. 2 presents the TEM photograph of the precipitated β-FeO(OH). The particles are fine (average particle length of 0.15 μm), ellipsoidal in shape, and have narrow size distribution (monodispersed).

The β-FeO(OH) suspensions, prepared by hydrolysis of dilute $FeCl_3$ solution ($[Fe^{3+}] < 0.1\ \text{mol dm}^{-3}$) at 80 °C, were hydrothermal-treated at 120 °C for 6 h. The fine β-FeO(OH) precipitates were transformed into reddish-brown precipitates. They were identified as α-Fe_2O_3 from the powder X-ray diffraction pattern (Fig. 3). The TEM photographs are shown in Fig. 4. The particles of α-Fe_2O_3 have narrow size distribution, i.e. they are monodispersed. The average particle size decreases with decreasing initial Fe^{3+} concentration, and the particle shape also varies with initial Fe^{3+} concentration. For the concentration $[Fe^{3+}] = 0.05\ \text{mol dm}^{-3}$ (Fig. 4(a)), the particles have isotropic shape and an average particle size of about 0.6 μm. For the concentration $[Fe^{3+}] = 0.01\ \text{mol dm}^{-3}$ (Fig. 4(b)) they have rhombohedral shape and an average particle size of 0.15 μm. It is likely that these α-Fe_2O_3 are formed via the dissolution of β-FeO(OH) particles and recrystallization, and that the fine β-FeO(OH) serves as a colloidal reservoir in the hydrolysis process. The monodispersed β-FeO(OH) colloidal reservoir produces the narrow size distribution of the final α-Fe_2O_3 product.

On the other hand, the hydrothermal treatment of β-FeO(OH) suspensions, prepared by hydrolysis of highly concentrated $FeCl_3$ aqueous solution ($[Fe^{3+}] > 0.1\ \text{mol dm}^{-3}$) at 80 °C, provided yellow precipitates, the TEM photograph of which is shown in Fig. 5. The precipitated products were identified as β-FeO(OH), the particles of which are rodlike in shape with an average particle length of about 0.3 μm. In highly concentrated $FeCl_3$ aqueous solution, a part of e^{3+} is not hydrolysed and not transformed to β-FeO(OH). Therefore, a fine β-FeO(OH) colloidal reservoir alone is not enough to hydrolyse to α-Fe_2O_3. The other reservoir must be introduced into the system to hydrolyse the suspension completely to α-Fe_2O_3.

The addition of an alkaline solution into the Fe^{3+} aqueous solution leads to the formation of a ferric hydroxide gel, and the hydroxide gel is a good candidate for the colloidal reservoir. A NaOH aqueous solution was mixed with the incompletely hydrolysed $FeCl_3$–β-FeO(OH) suspensions, where the ratio of $3[OH^-]/[Fe^{3+}]$ varied from 0.80 to 0.95. The partially neutralized suspensions were subjected to hydrothermal ageing at 110 °C for 6 h. The TEM photographs of the obtained precipitates are shown in Fig. 6. For the neutralization degree of $3[OH^-]/[Fe^{3+}] < 0.80$, the products were a mixture of rodlike β-FeO(OH) and isotropic α-Fe_2O_3 particles (Fig. 6(a)). From suspensions with a neutralization degree of more than 0.85, only isotropic and monodispersed α-Fe_2O_3 particles could be precipitated. It is clear from the TEM photographs (Fig. 6(b)–(e)) that the average particle size of isotropic α-Fe_2O_3 particles is remarkably reduced when the neutralization degree is raised. It is considered that the presence of alkali promotes both the hydrolysis of Fe^{3+} species and the nucleation rate of α-Fe_2O_3 particles.

Furthermore, the average particle size of the isotropic α-Fe_2O_3 particles decreases when the electrolyte concentration in the suspension is decreased. Fig. 7(a) and (b) are the TEM photographs of the obtained precipitates from the suspensions containing one half of the NaCl electrolyte. The presence of the electrolyte may serve as inhibitor of the α-Fe_2O_3 particle nucleation.

The effects of some anions coexisting in the mixed suspension of β-FeO(OH) and ferric hydroxide on the control of the hydrothermally precipitated particle morphology were investigated. In particular, the TEM photographs of the precipitated particles in the presence of a small amount of phosphate ion are shown in Fig. 8. The addition of phosphate ion provided the formation of ellipsoidal shaped α-Fe_2O_3 particles instead of the isotropic shaped α-Fe_2O_3 particles. The average axial ratio is about 4. Such particles are considered good candidates for the starting materials of magnetic recording materials. Studies on the magnetic properties of magnetic iron oxides such as Fe_3O_4 and γ-Fe_2O_3, prepared by reduction under H_2 atmosphere and following oxidation in air, are being carried out.

4. Conclusions

Monodispersed β-FeO(OH) fine particles have been prepared by forced hydrolysis of a $FeCl_3$ aqueous solution. The hydrothermal treatment of the β-FeO(OH) colloidal suspensions led to the precipitation of monodispersed α-Fe_2O_3 particles with isotropic shape, the particle size of which decreases with decreasing the initial concentration of $FeCl_3$. In the hydrolysis of a highly concentrated $FeCl_3$ aqueous solution, it is effective for the hydrolysis that ferric hydroxide gel coupled with fine β-FeO(OH) colloid is utilized as the intermediate colloidal reservoir. The average diameter of the precipitated isotropic shaped α-Fe_2O_3 particles decreases with increasing neutralization degree and with decreasing co-existing electrolyte concentration. The particle morphology of the precipitated α-Fe_2O_3 can be changed to ellipsoidal with the addition of a small amount of phosphate ion.

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