Influence of Sulfate Ions on Conversion of Fe(OH)$_3$ Gel to $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$

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Powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and chemical analyses were used for characterizing the effect of sulfate ions on the conversion rate of condensed Fe(OH)$_3$ gel, prepared from FeCl$_3$ and NaOH solution, to $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles by aging at 100 $^\circ$C. Fine particles and supernatant solution were sampled from the aged suspensions containing colloidal particles. XRD profiles and TEM observation showed that $\beta$-FeOOH was formed from the gel and subsequently converted into $\alpha$-Fe$_2$O$_3$. It was revealed that the addition of sulfate ions accelerated the $\beta$-FeOOH formation from the gel, but delayed the conversion from $\beta$-FeOOH to $\alpha$-Fe$_2$O$_3$. The concentration changes of sulfate and chloride ions in the supernatant solution phases were in agreement with the conversion from Fe(OH)$_3$ gel to $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles.

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1. Introduction

Sulfate ions are known to play a decisive role of control for the morphology of monodispersed hematite ($\alpha$-Fe$_2$O$_3$) fine particles, which are prepared in aqueous solution.\(^1\)\(^-\)\(^5\) The shapes can be controlled by the specific adsorption of the sulfate ions on the surface parallel to the $c$-axis of $\alpha$-Fe$_2$O$_3$ nucleus during conversion from akaganeite ($\beta$-FeOOH) to $\alpha$-Fe$_2$O$_3$ particles. The specific adsorption brings the delay of the crystal growth towards the $c$-axis, which lead to the anisotropic crystal growth. Thus, the anion adsorption is the determining factor for the shape controlling techniques of anisotropic crystal growth. Such information may be useful in discussing the stability of ferric oxyhydroxides and oxides.

On the other hand, among the ferric oxyhydroxides, $\beta$-FeOOH is considered to be the most detrimental to corrosion-resistance of steel, because of chloride ions in it.\(^6\)\(^,\)\(^9\) As related to the stability of $\beta$-FeOOH, the effects of metallic ions on the formation and structure of $\beta$-FeOOH particles have been reported.\(^10\)\(^,\)\(^11\) The results show that some alloying elements, especially titanium, strongly influences the formation of $\beta$-FeOOH. These results may give a hint on the control of the stability of ferric oxyhydroxides. The morphology of ferric oxyhydroxides is correlated with their local structure, which is fundamentally described by FeO$_6$ octahedral structural units. Such local structure is kept even in the amorphous state of Fe(OH)$_3$.\(^12\) and the local structure of the ferric oxyhydroxides is likely to be influenced by cations, being metallic ions. However, it is unclear yet whether anions influence the formation of ferric oxyhydroxides and oxides. Such information may be useful in discussing the stability of $\beta$-FeOOH, since Fe(OH)$_3$ is formed in corrosion process to be converted to ferric oxyhydroxides and oxides.\(^8\) These backgrounds prompt us to study the effect of sulfate ions on formation processes of $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$, i.e. the kinetics of the formation of these particles. In this work, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for characterizing the influence on sulfate ions for the solid particles obtained among the conversion processes of Fe(OH)$_3$. Furthermore, changes of pH of the supernatant solution and changes of chloride, sulfate, and ferric ion concentrations in the supernatant solution by aging were examined, and the results were used for discussion of the effect of sulfate ions on the formation of $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$.

2. Experimental

Reagent-grade ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), sodium hydroxide aqueous solution (10 mol L$^{-1}$), and anhydrous sodium sulfate (Na$_2$SO$_4$) were used as received. The method to prepare $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles was essentially identical to the previous one.\(^2\)\(^,\)\(^3\) The ferric chloride solution was filtered through 0.2 mm milli-pore filter to remove insoluble particulates. The concentration of sulfate ion was adjusted to be 0, 0.10, and 0.30 mol L$^{-1}$. Aqueous NaOH solution (5.4 mol L$^{-1}$) was added to the same volume of 2.0 mol L$^{-1}$ FeCl$_3$ containing Na$_2$SO$_4$ for more than 10 min at 0 $^\circ$C under agitation. The highly viscous Fe(OH)$_3$ gel, formed through these processes, was aged at 100 $^\circ$C for different periods between 4 h and 14 days, to form $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles. After a given aging time, the solution was cooled down to room temperature using running water. The solid particles separated by centrifugation of 18000 rpm for 30 min, was washed with doubly distilled water and freeze-dried.

The crystallographic structures of powder samples were identified by a Rigaku RAD-B XRD system using Ni-filtered Cu $K\alpha$ irradiation (40 kV, 40 mA). TEM observations were performed by using a JEOL JEM-1200EX II with an acceleration voltage of 120 kV. The supernatant solution separated from the suspension was analyzed with pH and concentrations of Cl$^-$ and SO$_4^{2-}$ using a Shimadzu HIC-VP ion chromatography. Inductively coupled plasma (ICP) measurements were carried out to measure ferric ion concentration using a Perkin-Elmer Optima 3300.

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3. Results and Discussion

3.1 The formation of $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ by aging

Ferric hydroxide suspension with 0, 0.10, and 0.30 mol L$^{-1}$ Na$_2$SO$_4$ was aged at 100°C for 6 h, 12 h, and 14 days. XRD profiles of the solid particles separated from as prepared suspension are shown in Fig. 1(i), (ii), and (iii), respectively. Figure 2 shows TEM photos of solid particles obtained in the presence of 0, 0.10, and 0.30 mol L$^{-1}$ Na$_2$SO$_4$. Poorly crystallized $\beta$-FeOOH particles were formed from the Fe(OH)$_3$ gel by aging for 6 h (Figs. 1(i) and 2(i)). In the absence of sulfate, diffractions corresponding to $\beta$-FeOOH are weak and a broad halo due to amorphous Fe(OH)$_3$ is observed (Fig. 1(i)-(a)). In contrast, the amorphous halo is negligible for the solids prepared in the presence of sulfate ions (Fig. 1. (i)-(b) and (i)-(c)). The TEM photo (Fig. 2(i)) exhibits very fine $\beta$-FeOOH particles, which correspond to the line broadening in the XRD peaks in Fig. 1(i). Remarkable difference was found in the structure for 12 h-aged samples with different sulfate concentrations. All diffractions observed for Fig. 1(ii)-(a) are assigned to be $\alpha$-Fe$_2$O$_3$ structure. These peaks are corresponding to the formation of pseudocubic $\alpha$-Fe$_2$O$_3$ particles as shown in Fig. 2(a)-(ii). In contrast, in the presence of 0.10 and 0.30 mol L$^{-1}$ sulfate ions, $\beta$-FeOOH particles are still remain even after 12 h (Fig. 1(ii)-(b) and (ii)-(c) and Fig. 2(b)-(ii) and (c)-(iii)). Virtually, the conversion rate to $\alpha$-Fe$_2$O$_3$ particles is rather slow compared with sulfate-free system. With increasing sulfate ion concentration from 0.10 to 0.30 mol L$^{-1}$, the rate was reduced.

Figure 1(iii) exhibits the XRD profiles of solid particles obtained after aging for 14 days. All diffraction peaks are corresponding to the $\alpha$-Fe$_2$O$_3$ structure. Line broadening of the peaks by the addition of the sulfate is due to the decrease in the crystallite size, which must be brought by the crystal-growth inhibition effect of the sulfate ions. Pseudocubic $\alpha$-Fe$_2$O$_3$ particles of about 160 nm in diameter were formed by aging for 14 days with 0 mol L$^{-1}$ sulfate ions as shown in Fig. 2(a)-(iii). On the other hand, ellipsoidal $\alpha$-Fe$_2$O$_3$ particles of about 260 and 360 nm in particle long axis were formed after aging for 14 days with 0.10 and 0.30 mol L$^{-1}$, respectively (Fig. 2(b)-(iii) and Fig. 2(c)-(iii)). Thus, the shapes of solid particles were changed by the addition of sulfate ions. This morphological transformation was attributed to the specific adsorption of sulfate on the surface parallel to the c-axis of $\alpha$-Fe$_2$O$_3$ structure. $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ are transformed into the equilibrium state after aging for 96 h. However in the cases with 0.10 or 0.30 mol L$^{-1}$ sulfate ions, the increase of Fe$^{3+}$ concentrations starts after aging for 12-24 h.

3.2 Changes in the concentration of ion species by aging

In order to obtain information complementary to the formation of $\beta$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles in the condensed Fe(OH)$_3$ gel, pH and ion concentrations of the supernatant solutions separated from the aged sols were analyzed. In the present system, Fe(OH)$_3$ gel as an initial solid precipitate was converted into $\beta$-FeOOH and then to $\alpha$-Fe$_2$O$_3$ as a final form. This two-step phase transformation basically obeys Ostwald-step rule. In this case, initially formed solid is the most soluble but the most stable solid is finally formed. This is the reason why, in spite of the same solubility product of Fe(OH)$_3$, $\beta$-FeOOH, and $\alpha$-Fe$_2$O$_3$, the apparent solubility is basically different. Accordingly, it is expected that the most soluble Fe(OH)$_3$ gives highest pH but $\alpha$-Fe$_2$O$_3$ lowest pH.

Figure 3 shows pH as well as the ion concentrations in the supernatant solution as a function of aging time at 100°C. By aging, pH decreases with increasing aging time. In the initial stage from 0 to 4 h, pH in the sulfate addition is rapidly decreased in contrast to that in the absence of sulfate. In this stage, the conversion from Fe(OH)$_3$ gel to $\beta$-FeOOH particles are promoted by the sulfate addition, which is confirmed by the XRD (Fig. 1(i)). Then, the subsequent stage is observed for about 8-12 h and 12-24 h for the systems with 0 and 0.30 mol L$^{-1}$ sulfate ions, respectively. In this stage, very fine $\beta$-FeOOH particles are converted into the $\alpha$-Fe$_2$O$_3$ particles. The reduction of conversion rate by sulfate ions is confirmed with the XRD, as shown in Fig. 1. Broken lines in Fig. 3 exhibit the changes of Fe$^{3+}$ concentrations. In the initial stage, the Fe$^{3+}$ concentrations are kept nearly equal to 0. The maximum change of the Fe$^{3+}$ ion concentration is observed after aging between 8-12 h for the sulfate-free system. It is in agreement with the formation of $\alpha$-Fe$_2$O$_3$ particles. Further aging at 100°C decreases the Fe$^{3+}$ concentration and the resulting concentration is reached to the equilibrium state after aging for 96 h. However in the cases with 0.10 or 0.30 mol L$^{-1}$ sulfate ions, the increase of Fe$^{3+}$ concentrations starts after aging for 12-24 h.

Figure 3 also shows changes in the concentration of
chloride and sulfate ions in the solution phase as a function of aging time at 100°C. The initial chloride ion concentrations in the supernatant solution become higher by the addition of sulfate ions. On the other hand, the initial sulfate ion concentrations of the supernatants become 0.05 and 0.16 mol L⁻¹ by the addition of 0.10 and 0.30 mol L⁻¹ of sulfate ions, respectively. IR measurements revealed that the sulfate ions were adsorbed on the initial solid precipitates, and the adsorption amount was increased by the further addition of the sulfate ions. Thus, the increase of the initial chloride ion concentrations may be due to the competitive adsorption of the sulfate ions against the chloride ions. The chloride and sulfate ions concentrations in the supernatant solution were changed by aging. The initial decrease of the chloride ion from 6 to 8 h and from 4 to 6 h for respective 0 and 0.30 mol L⁻¹ sulfate addition systems is ascribed to the incorporation of the chloride ion into β-FeOOH structure. By the further aging between 8 h and 24 h, the increases of chloride ion concentrations are observed. In this process, conversion from β-FeOOH to α-Fe₂O₃ was completed, which was speculated from the XRD measurements. Thus, the increase of chloride ion concentrations is corresponding to the release of the chloride ion by the conversion from β-FeOOH to α-Fe₂O₃. The final concentration of the chloride ion is 2.45 mol L⁻¹ for the sulfate-free system, which is lower than the systems with sulfate ions. This result suggests that the appreciable amounts of chloride ions are adsorbed on the α-Fe₂O₃ particles, but the presence of sulfate ion prevents the chloride ion adsorption.

On the other hand, the sulfate ion concentration for the system with 0.30 mol L⁻¹ of sulfate ions is increased by the aging process from 8 h to 24 h. This result indicates that the adsorption amount of sulfate ion on β-FeOOH is higher than that of α-Fe₂O₃. In the case of α-Fe₂O₃, the adsorption-desorption experiments of sulfate ions reveal that the sulfate ions are only adsorbed on the surface of the solid particles. One might consider that the sulfate ions were adsorbed only on the β-FeOOH surface or incorporated in the crystal cells in place of chloride ions. XRD results provide a possibility of the incorporation of the sulfate ions in the crystal cells because the diffraction peaks due to (211) lattice shifted to small angles from 35.7 to 35.1 degree by the addition of

Fig. 2 TEM images of solid particles prepared in the presence of (a) 0, (b) 0.10, and (c) 0.30 mol L⁻¹ Na₂SO₄ by aging for (i) 6 h; (ii) 12 h; (iii) 14 days at 100°C.
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4. Conclusions

Powder XRD, TEM, and chemical analyses have been used for characterizing the effect of sulfate ions on the conversion of Fe(OH)₃ gel into solid particles of β-FeOOH and α-Fe₂O₃. Main concluding remarks obtained this work are as follows:

1. β-FeOOH particles were formed from Fe(OH)₃ gel, and subsequently converted α-Fe₂O₃ particles. The addition of sulfate ions was shown to accelerate the formation of very fine β-FeOOH particles from the gel, but delay the conversion from β-FeOOH into α-Fe₂O₃ particles.

2. The pH of the supernatant decreased with increasing aging time. These results were consistent with the structural data obtained by XRD.

3. The concentrations of sulfate and chloride ions in the supernatant solution phases were changed during aging in characteristic manner.

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REFERENCES