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Preparation of γ-FeOOH by Aerial Oxidation of Iron(II) Chloride Solution

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Synopsis. Detailed conditions for preparing γ-FeOOH by aerial oxidation of iron(II) chloride solution were studied. The upper limit of temperature for obtaining only the γ-FeOOH decreased with increases in the pH value and the initial concentration of Fe(II) ions. The shapes of the prepared γ-FeOOH particles were examined in connection with the oxidizing conditions.

The kind of aerial oxidation products of iron(II) salt solutions has been well known to be dependent on the preparative conditions. No detailed conditions for preparing the γ-FeOOH, one of the iron(III) hydroxide oxides, have been studied, though its formation has been reported.[1-5] In this work, such preparative conditions for γ-FeOOH as the concentration of Fe(II) ions, the reaction temperature, and the acidity were studied. Furthermore, the shapes of the prepared γ-FeOOH particles were examined in connection with the oxidizing conditions.

Experimental

The iron(II) chloride solution was used as the starting material. The dissolved oxygen was removed by passing nitrogen into the iron(II) chloride solution before the oxidation. The Fe(II) ions were oxidized at the specified temperatures and acidities by bubbling air, free from carbon dioxide, through a glass filter at a constant flow rate with vigorous stirring.

As the acidity of the solution increased with the progress of oxidation, the pH value of the reaction mixture was kept within ±0.15 of the specified acidity by using a pH-stat model HS-2A, from Toa Electronics Ltd., and aqueous ammonia, except for solutions at higher basicities. The air was bubbled for 3 h after the reaction ended under the same conditions in order to age the precipitates. The oxidation product was washed with water until chloride ions were no longer detectable, followed by air-drying for 3 weeks.

The X-ray powder diffraction patterns of the products were taken using Fe$K\alpha$ radiation with a Rigaku Denki Geigerflex, model D-3F, X-ray diffractometer. The identification of the products and the estimation of their relative amounts were carried out by using the diffraction peaks at (020) and (031) of the γ-FeOOH, that at (110) of the α-FeOOH, and those at (311) and (440) of the Fe_3O_4.

The shapes of the prepared γ-FeOOH particles were observed with the magnifications of from 10000 to 30000 times by using an electron microscope, model HU-200F, from Hitachi Seisakusho.

Results and Discussion

The final oxidation products of the iron(II) chloride solution were identified as the γ-FeOOH, the α-FeOOH, and the Fe_3O_4: the β-FeOOH was not detectable in this work, though Kiyama *et al.*[6] have reported the formation of β-FeOOH together with γ-FeOOH. In order to estimate the conditions for preparing the pure γ-FeOOH, the kind of products and their relative amounts were examined over a wide range of oxidizing conditions.

The influence of the flow rate of air on the kind of products was determined to be as follows:

$$\text{Flow rate (l/min)}\quad 0.1 \underset{\alpha\text{-},\,\gamma\text{-FeOOH}}{\rule{2cm}{0.4pt}} 1.0 \underset{\gamma\text{-FeOOH}}{\rule{2cm}{0.4pt}} 2.4 \underset{\alpha\text{-},\,\gamma\text{-FeOOH}}{\rule{2cm}{0.4pt}} 2.8$$

(pH 6.5, 25°C, and 0.064 mol/l)

Though the flow rate range for preparing only the γ-FeOOH was not found at higher concentrations of Fe(II) ions under the same conditions of the pH and the temperature, the relative amount of the γ-FeOOH was large enough in the flow rate from 1.0 to 2.4 l/min even at higher concentrations. Therefore, subsequent oxidations were carried out at the constant flow rate of 2.0 l/min.

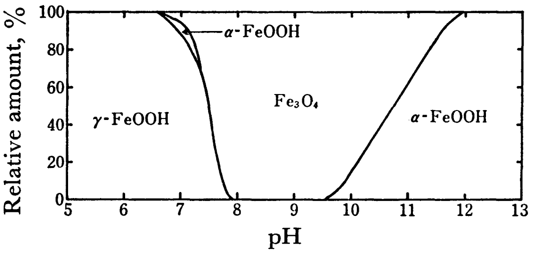

Fig. 1. Relationship between relative amounts of products and acidity.
Temp; 25 °C, init. concn; 0.064 mol/l, flow rate; 2 l/min.

Figure 1 shows the relationship between the relative amounts of the products and the acidity. Only the γ-FeOOH was obtained up to pH 6.5 by the aeration at 25 °C in the 0.064 mol/l solution, though only the Fe_3O_4 was obtained in the pH range from about 8.0 to 9.5. Misawa *et al.*[7,8] also reported the formation of Fe_3O_4 by the solid state oxidation of $Fe(OH)_2$ formed in a slightly alkaline solution of iron(II) chloride. Even if the aeration was allowed to continue, the Fe_3O_4 was no longer completely oxidizable into the γ-FeOOH. This solid state oxidation is considered to be difficult

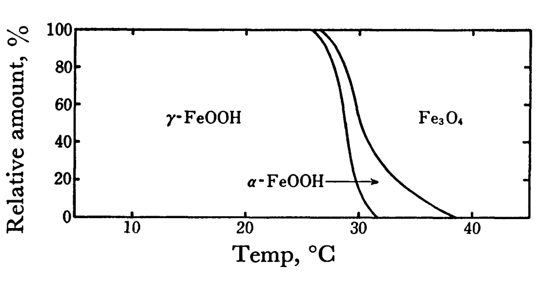

Fig. 2. Relationship between relative amounts of products and reaction temperature.
pH; 6.5, init. concn; 0.064 mol/l, flow rate; 2 l/min.

because the OH groups must be introduced into the Fe_3O_4 lattice which has a cubic close-packed structure of oxygen.[9]

Figure 2 shows the relationship between the relative amounts of the products and the reaction temperature. Only the γ-FeOOH was obtained below 25 °C, while the formations of the α-FeOOH and the Fe_3O_4 were observed at the temperatures higher than 25 °C.

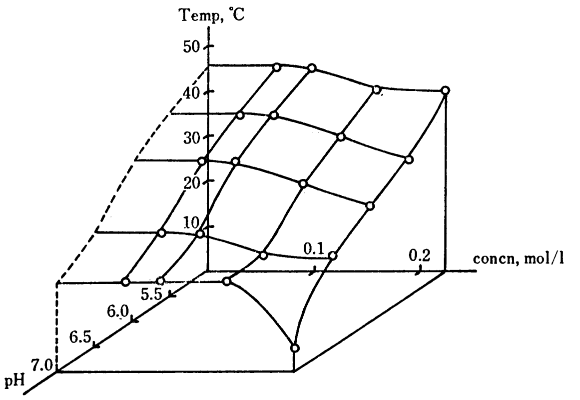

Fig. 3. Upper limit of temperature for preparing only γ-FeOOH as functions of initial concentration and acidity.
Flow rate; 2 l/min.

The critical conditions for preparing only the γ-FeOOH around neutrality varied according to changes in the temperature, the concentration of Fe(II) ions, and the acidity. A curved surface in Fig. 3 shows the upper limit of temperature for obtaining only the γ-FeOOH as the functions of the concentration and the acidity in the ranges from 0.064 to 0.224 mol/l and from pH 5.0 to 7.0 respectively. At the temperatures above this curved surface, the α-FeOOH and/or the Fe_3O_4 were precipitated with the γ-FeOOH. The upper limit of temperature for forming only the γ-FeOOH was found to decrease as both the pH value and the concentration increased, as is shown in Fig. 3. The reaction mixture showed a gradual change in color as follows:

pH 6.0 (higher temp)—7.0

light green → dark greenish blue → yellowish brown

pH 5.0—6.0 (lower temp)

faint green → reddish brown

The γ-FeOOH was formed *via* the green rust I,[1,10] its oxidation intermediate, under the former conditions, but it was formed directly from the solution without passing through the green rust I in the latter cases.[11] Bernal *et al.*[1] stated that the green rust I formed only in neutral and slightly alkaline solutions of iron(II) chloride. Misawa *et al.*[8] proposed a mechanism for direct formation of γ-FeOOH: after the $FeOH^+$ ions have been oxidized, the $Fe(OH)_2^+$ ions dimerized into $[(OH)_2Fe\text{–}O\text{–}FeOH]^+$ and then polymerized into $[n\text{FeOOH}\cdot\text{Fe(OH)}_2]^+$ by forming oxo-bridges, Fe–O–Fe, followed by precipitation of γ-FeOOH.

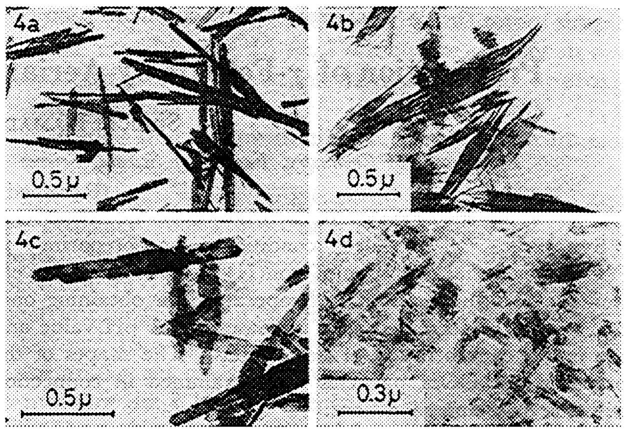

Fig. 4. Shapes and sizes of γ-FeOOH particles prepared as several conditions.
a; pH 6.0, 30 °C, 0.096 mol/l, b; pH 6.5, 15 °C, 0.224 mol/l, c; pH 6.0, 25 °C, 0.096 mol/l, d; pH 6.0, 10 °C, 0.064 mol/l.

The shape and the size of γ-FeOOH particles were extremely dependent on the preparative conditions. Needle-like particles were obtained in the oxidation just below the upper limit of temperature for preparing only the γ-FeOOH at pH 6.0—7.0, while irregularly shaped plate particles were precipitated at lower temperatures for pH 6.5—7.0, as is shown in Figs. 4a and 4b. On the contrary, elongated hexagonal plate particles were obtained at lower temperatures at pH 6.0, as is shown in Fig. 4c. When the γ-FeOOH was formed without formation of the green rust I as the intermediate, the particles lost their uniformity in shape; in particular, fine particles showing broad X-ray powder diffraction peaks were obtained at much lower temperatures, as is shown in Fig. 4d.

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