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The Effect of the Addition of γ-FeOOH Nuclei at the Initial Stage of Oxidation on the Formation of γ-FeOOH

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The presence of green rusts has been considered to be indispensable for the formation of γ-FeOOH. Bernal *et al.* proposed, from a crystallochemical point of view, that γ-FeOOH was topotactically formed by the surface oxidation of the green rusts.[1] We recently reported that γ-FeOOH can be obtained not only from the green rusts in ferrous salt solutions, but also from acidic solutions containing ferrous ions, by selecting the oxidizing conditions.[2] It was found that, under the conditions where γ-FeOOH was formed together with α-FeOOH, the γ-FeOOH content in the oxidation product was affected by slight differences in the treatment before oxidation. The γ-FeOOH content may be determined by the ratio of the α-FeOOH nuclei to the γ-FeOOH nuclei formed at the initial stage of oxidation. In order to prove this assumption, an attempt has been made to change this ratio variously by adding very fine particles of α-FeOOH and γ-FeOOH to the solutions. The experimental results will be reported here.

Experimental and Results

The chemicals used in the present study were of a reagent grade. The fine particles of α-FeOOH used as nuclei were prepared by the hydrolysis of a ferric nitrate at 40°C for 50 hr, while those of γ-FeOOH were prepared *via* a green rust (I) by the oxidation of $Fe(OH)_2$ below 10°C in a ferrous chloride solution. The precipitates formed by hydrolysis and oxidation were filtered, washed with water, and then diluted with water to obtain turbid solutions containing 0.05 mol of the nuclei per liter. The particles of α-FeOOH were superfine (below 0.02 μ in size), while those of γ-FeOOH were flaky (about 0.3 μ in length).

Varying quantities of the turbid solutions were added to 3 l of a mixture of 0.21 M-$FeCl_2$ and 1.44 M-NaI solutions, and the resultant solutions were subjected to oxidation. The procedures of the oxidation and identification of the samples thus obtained were the same as have been described in a previous paper.[2] The contents of α-FeOOH, β-FeOOH, and γ-FeOOH were determined by comparing the relative intensities of the X-ray diffraction lines of α-FeOOH d(110) 4.18 Å, β-FeOOH d(110) 7.40 Å, and γ-FeOOH d(020) 6.3 Å.

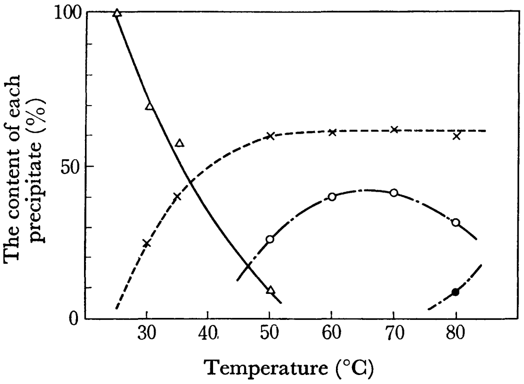

Fig. 1. The content of each precipitate in the oxidation products formed at various temperatures in a mixture of 0.21 M-$FeCl_2$ and 1.44 M-NaI solutions.
×: α-FeOOH, △: β-FeOOH, ○: γ-FeOOH, ●: α-Fe_2O_3

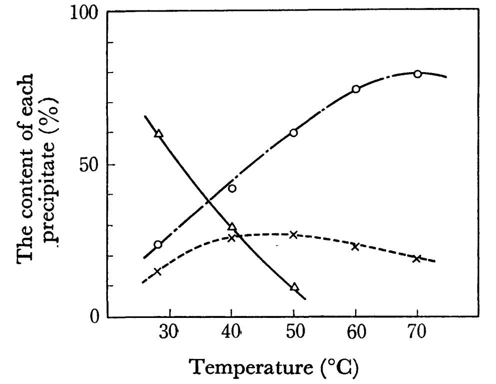

Fig. 2. The content of each precipitate in the oxidation products formed at various temperatures in the mixture containing 0.5 mmol of γ-FeOOH nuclei.
×: α-FeOOH, △: β-FeOOH, ○: γ-FeOOH

Air was bubbled into the mixtures with and without 10 ml of the turbid solution of γ-FeOOH (containing 0.5 mmol of γ-FeOOH) at the rate of 300 l/hr for 20 hr at various temperatures for oxidation. The contents of three forms of FeOOH in the oxidation product thus obtained are plotted against the oxidizing temperature in Figs. 1 and 2. The γ-FeOOH content increases with the temperature and attains, at temperatures between 60 and 70°C, the maximum value, which is 40% when no turbid solution of γ-FeOOH has been added and 80% when it has been added.

Varying quantities of the turbid solutions were added to 3 l portions of the mixture, and the resultant solutions were oxidized at 60°C for 20 hr. About 7 g (87 mmol) of an oxidation product was obtained from each solution, and the product consisted of only α-FeOOH, only γ-FeOOH, or their mixture. The γ-FeOOH content of the products is plotted against the amount of α-FeOOH or γ-FeOOH added in Fig. 3. When 2.5 mmol or more of γ-FeOOH was added to the mixture, only γ-FeOOH was formed, whereas when

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[1] J. D. Bernal, E. R. Dusgputa, and A. L. Mackay, *Clay Min. Bull.*, **4** (21), 15 (1959).

[2] M. Kiyama and T. Takada, This Bulletin, **45**, 1923 (1972).

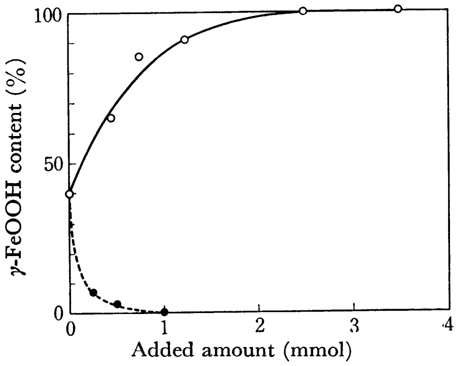

Fig. 3. The γ-FeOOH content of the oxidation products formed at 60°C in the mixtures containing different amounts of α-FeOOH and of γ-FeOOH nuclei.
●: α-FeOOH nuclei, ○: γ-FeOOH nuclei

1 mmol or more of α-FeOOH was added to it, only α-FeOOH was formed as the oxidation product. The effect of the addition of the nuclei on their formation may depend upon the particle size of the nuclei.

On oxidation, γ-FeOOH was not obtained from the $FeSO_4$ and $FeCl_2$ solutions, but other precipitates, such as α-FeOOH and β-FeOOH, were obtained. A turbid solution (100 ml) containing 5 mmol of γ-FeOOH was added to 3 l portions of these solutions containing 0.21M-ferrous ions, and the resultant mixtures were oxidized at 60°C for 20 hr. The oxidation products thus obtained consisted of α-FeOOH only (when these solutions containing no γ-FeOOH nuclei were oxidized under the same conditions as above, too, only α-FeOOH was formed).

By oxidation, a hydroxo ferric complex which has H_2O and OH^- ligands may be formed together with other ferric complexes which have halogen ligands besides H_2O and OH^- ligands. The concentration of the hydroxo ferric complex depends on the conditions, such as the concentration of the halogen ions and the temperature. The precipitation of β-FeOOH may be due to the hydrolysis of the halo ferric complexes, while that of α-FeOOH and γ-FeOOH may be due to the hydrolysis of the hydroxo ferric complex. Which is formed, α-FeOOH or γ-FeOOH, presumably depends upon whether or not an epitaxial reaction occurs between the γ-FeOOH nucleus and the hydroxo ferric complex. The hydroxo ferric complexes may be epitaxially deposited on the γ-FeOOH nucleus to give a precipitate of γ-FeOOH. The formation of the γ-FeOOH nuclei and their growth on the nuclei may be influenced by the rate of formation of the hydroxo ferric complex.