Transformation of γ-FeO(OH) to Fe_3O_4 by Adsorption of Iron(II) Ion on γ-FeO(OH)

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When the pH of a reaction mixture of γ-FeO(OH) and the iron(II) ion is raised from 5 to 9, the γ-FeO(OH) is transformed to stoicheiometric Fe_3O_4 at 25 °C. The transformation reaction is triggered by the adsorption of the iron(II) ion on γ-FeO(OH) at a pH above 7.3, and the adsorbed Fe^{II}–γ-FeO(OH) is subsequently transformed to Fe_3O_4. In each step, one proton is released, a total of two protons being released in the reaction. The reaction of the transformation step is written as follows: $[\gamma\text{-FeO(OH)}]_2FeOH^+ \longrightarrow Fe_3O_4 + H_2O + H^+$ and includes a dissolution–precipitation process. The adsorption of iron(II) ion on Fe_3O_4 seems to take place along with the formation of the intermediate by the adsorption of iron(II) ion on γ-FeO(OH).

The formation of Fe_3O_4 (magnetite) and metal-ion-bearing ferrites in solution by air oxidation of $Fe(OH)_2$ suspensions with and without other metal ions at temperatures above 60 °C have been studied.[1–9] We and other workers have investigated the reaction mechanisms of the formation of Fe_3O_4 and ferrites in solution.[1,7,8] Kaneko and Katsura [1] reported the importance of the hydrolysis of metal ions for the incorporation of metal ions into the lattice points of the ferrites which are formed during air oxidation. Kiyama [7] suggested that Fe_3O_4 is formed by condensation of $[Fe(OH)]^+$ with an iron(III) hydroxo-complex which is formed by the oxidation of $[Fe(OH)]^+$. Recently, Tamaura *et al.*[8] reported that the formation of Fe_3O_4 by air oxidation of $Fe(OH)_2$ suspensions proceeds in three stages: (i) formation of iron(III) oxides and slower formation of Fe_3O_4; (ii) rapid formation of Fe_3O_4; and (iii) linear formation of Fe_3O_4. They also suggested that iron(II) ion is oxidized on the surface of the solid phases [iron(III) oxides and Fe_3O_4] during the course of air oxidation, and that in the first stage, the slower formation of the Fe_3O_4 is caused by the transformation of the amorphous γ-FeO(OH).

In the present paper, we have studied the transformation reaction of γ-FeO(OH) to Fe_3O_4. The transformation reaction takes place at room temperature, therefore experiments were carried out at 25 °C. The mechanism for the transformation reaction is also discussed.

Experimental

Chemicals.—All chemicals were of analytical grade, and distilled water was used for the preparation of the solutions. Sodium hydroxide solutions were prepared by dissolving NaOH in distilled water through which nitrogen gas had been passed to remove the dissolved oxygen. The compound γ-FeO(OH) was prepared according to the method by Hamada and Kuma;[10] an $FeCl_2$ solution (0.03 mol dm^{-3}) was oxidized at pH 6.5 and 20 °C (0.23 mol dm^{-3} NaCl).

Apparatus.—The reaction vessel used in previous work was adopted.[2–5]

Procedure.—After passing nitrogen gas through a γ-FeO(OH) suspension [0.75 dm^3, 0.03 mol dm^{-3} of iron(III) ion, pH 5.0] for 2 h to remove dissolved oxygen and carbon dioxide, a $FeCl_2$ solution (0.02 dm^3, 0.56 mol dm^{-3}, pH 5.0) was added. The pH of the reaction suspension was raised to a given pH by adding NaOH solution, and the pH was kept constant at 25 °C by adding the alkaline solution and passing nitrogen gas through the reaction suspension. The pH of the reaction suspension was kept constant here and it is referred to as 'the reaction pH'. After 60 h, the reaction suspension was centrifuged at 4 000 r.p.m. The precipitate obtained was washed with an acetate buffer solution (pH 4.1, 0.05 mol dm^{-3}) to remove unreacted iron(II) ion. The precipitate was washed further with distilled water and repeatedly with acetone to remove water as completely as possible. To prevent oxidation of the Fe_3O_4 formed, the acetate buffer solution, distilled water, and acetone had been deaerated with nitrogen gas. Finally, the precipitate was dried under a nitrogen atmosphere at room temperature. The precipitate thus obtained was examined by *X*-ray diffractometry and Mössbauer spectroscopy, and its chemical composition determined.

Kinetic Experiments.—In a kinetic experiment to investigate the adsorption step of iron(II) ion on γ-FeO(OH) and the transformation step to form Fe_3O_4, the concentration of iron(II) ion was lowered to 8×10^{-4} mol dm^{-3} to avoid precipitation of the iron(II) ion. After passing nitrogen gas through distilled water (0.7 dm^3) for 2 h, an $FeCl_2$ solution (0.01 dm^3, 0.061 mol dm^{-3}) was added, and the pH adjusted to the the desired pH ('the reaction pH') with a 0.05 mol dm^{-3} NaOH solution. When the pH became constant, 0.05 dm^3 of the γ-FeO(OH) suspension [0.024 mol dm^{-3} of iron(III)] whose pH had been adjusted to 'the reaction pH' was added; the reaction was initiated and the pH began to decrease fairly rapidly, therefore to keep the reaction pH constant, a 0.02 mol dm^{-3} NaOH solution was added. 'The reaction pH' was kept constant during the reaction to ±0.01 pH unit. Here, the time from the addition of the γ-FeO(OH) suspension is referred to as 'the reaction time'. In the course of the reaction, 0.03 dm^3 samples of the reaction suspension were taken at constant time intervals using a syringe. Under a nitrogen atmosphere, 0.015 dm^3 of the sample was transferred to an acetate buffer solution (0.01 dm^3, 0.01 mol dm^{-3}, pH 4.1), and 0.015 dm^3 of the mixture rapidly filtered using a syringe on the tip of which a Milliporefilter (0.22 µm pore size) was fitted with the sample of the filtrate. The acetate buffer sample was centrifuged at 4 000 r.p.m. under a nitrogen atmosphere to give supernatant– and precipitate–acetate buffer samples. The iron(II) ion concentrations in the filtrate sample, supernatant–acetate buffer sample, and precipitate–acetate buffer sample were determined.

Chemical Analysis.—The iron(II) and total iron concentrations were determined by using 2,2′-bipyridyl.[11] The total iron concentration was determined after reducing the iron(III) ion to iron(II) with hydroxylamine.

Results and Discussion

Transformation of γ-FeO(OH) *to* Fe_3O_4 *in the Presence of Iron*(II) *Ion*.—An *X*-ray diffraction pattern of γ-FeO(OH) showed only peaks corresponding to γ-FeO(OH). An electron micrograph showed irregularly shaped particles, and plate and rod shaped particles. In the i.r. spectrum, only bands due to γ-FeO(OH) appeared (3 120, 1 025, 881, 738, and 456 cm^{-1}).[12,13] However, in the *X*-ray diffraction pattern of the product formed by raising the pH of the reaction suspension of the mixture [γ-FeO(OH) and iron(II) ion] from 5 to 9, only peaks for the spinel type compounds appeared. The lattice constant of the spinel type compound was 8.396 ± 0.0005 Å, which corresponds to that of stoicheiometric Fe_3O_4. In the Mössbauer spectrum of the product, only lines due to the hyperfine structure of the spinel type compound appeared, and the internal field and isomer shift estimated [A site, 481 ± 5 kOe (Oe = $cm^{-\frac{1}{2}}$ $g^{\frac{1}{2}}$ s^{-1}), 0.39 mm s^{-1}; B site, 454 ± 5 kOe, 0.72 mm s^{-1}] were the same as those for stoicheiometric Fe_3O_4. The molar ratio of the iron(II) to Fe_{total} of the product was 0.32, which is very close to that of stoicheiometric Fe_3O_4. Thus, at pH 9.0 (25 °C), γ-FeO(OH) was transformed to stoicheiometric Fe_3O_4 in the presence of iron(II) ion. [Under the same conditions, α-FeO(OH) was not transformed to Fe_3O_4.] The electron micrograph showed cubic particles of Fe_3O_4; this suggests that transformation of γ-FeO(OH) to Fe_3O_4 takes place *via* a dissolution–precipitation process.

The effect of pH on the transformation of γ-FeO(OH) to Fe_3O_4 was studied. *X*-Ray diffraction patterns of products obtained above pH 7.3 showed strong peaks of Fe_3O_4. However, in *X*-ray diffraction patterns below pH 6.5, only peaks for γ-FeO(OH) were seen. Thus, the transformation reaction of γ-FeO(OH) to Fe_3O_4 takes place at a pH above 7.3.

Adsorption of Iron(II) *Ion on* γ-FeO(OH) *and* Fe_3O_4.—The transformation reaction appears to be triggered by the adsorption of the iron(II) ion on γ-FeO(OH). Benjamin and Leckie[14] suggested that the adsorption of metal ions on iron oxides takes place when the pH is increased. The fact that the transformation reaction of γ-FeO(OH) to Fe_3O_4 takes place at a pH above 7.3 suggests that the adsorption of the iron(II) ion on γ-FeO(OH) takes place at a pH above 7.3. Here, we studied kinetically the adsorption step of the iron(II) ion on γ-FeO(OH) in the transformation reaction. Experiments were carried out at a low iron(II) concentration (8×10^{-4} mol dm^{-3}) to avoid precipitation of the iron(II) ion in the pH range 8.0—8.6. The molar ratio of the iron(II) ion to iron(III) ion of γ-FeO(OH) was fixed at 1 : 2. At such a low iron(II) ion concentration at a pH above 8.0, γ-FeO(OH) was transformed to Fe_3O_4.

Figure 1 shows the changes in the iron(II) ion concentration of the supernatant of the reaction suspension (curve A) and of the Fe_3O_4 (curve C), changes in the amount of iron(II) ion adsorbed on the precipitates (curve B), and changes in the amount of iron(III) ion of γ-FeO(OH) (curve D) with reaction time at pH 8.4. Curves A and C were determined from the iron(II) ion concentrations in the filtrate sample and precipitate-acetate buffer sample respectively. With acetate buffer solution (pH 4.1), only the iron(II) ions adsorbed on the iron oxides dissolved (iron oxides including Fe_3O_4 are not dissolved in the acetate buffer solution),[8,15] then the supernatant-acetate buffer sample contains the iron(II) ion of the supernatant of the reaction suspension [iron(II) ion in the filtrate sample] and that adsorbed on the precipitates of the iron oxides [γ-FeO(OH) and Fe_3O_4]. The amount of iron(II) ion adsorbed on the precipitates (curve B) was determined from the difference between the iron(II) ion concentrations of filtrate sample and supernatant–acetate buffer sample. The amount of iron(III) as γ-FeO(OH) was evaluated from the difference between the amount of iron(III) initially present as γ-FeO(OH) in the reaction suspension and that of the Fe_3O_4 formed, assuming that the chemical composition of the Fe_3O_4 formed is stoicheiometric.

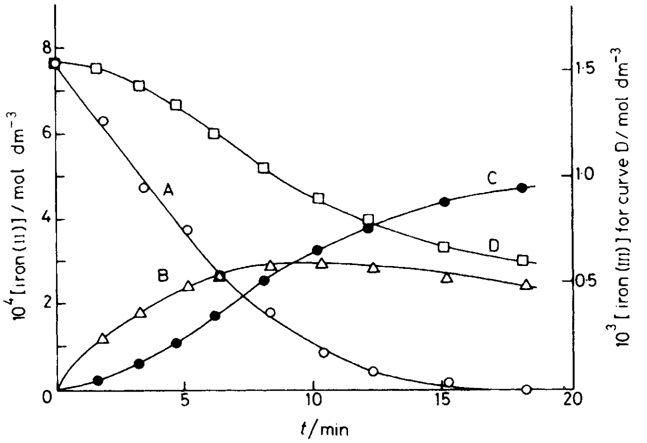

Figure 1. Changes in iron(II) ion concentration of the supernatant of the reaction suspension (curve A) and of Fe_3O_4 (C), those in the amount of iron(II) ion adsorbed on the precipitates (B), and those in the amount of iron(III) ion of γ-FeO(OH) (D) with the reaction time at pH 8.4

As seen in Figure 1, when the reaction is initiated, the iron(II) ion in the supernatant decreases fairly rapidly with reaction time (curve A), and the iron(II) ion adsorbed on the precipitates increased abruptly (curve B). However, the iron(II) of Fe_3O_4 increased slowly (curve C). This shows that the iron(II) ion is adsorbed on γ-FeO(OH) and subsequently transformed into Fe_3O_4.

The adsorption step of iron(II) ion on γ-FeO(OH) is given by equation (1) where $Fe_{sup}{}^{2+}$ represents the iron(II) ion

$$Fe_{sup}{}^{2+} + -\mathrm{s}\{\gamma\text{-FeO(OH)}\} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{2+}-\mathrm{s}\{\gamma\text{-FeO(OH)}\} \tag{1}$$

in the supernatant of the reaction suspension, k_1 and k_{-1} represent the rate constants for adsorption and desorption of iron(II) ion on γ-FeO(OH), respectively, and $-\mathrm{s}\{\gamma\text{-FeO(OH)}\}$ is the surface of γ-FeO(OH) before the transformation reaction. The surface means the preferential adsorption sites for the iron(II) ion. The surface concentration, $[-\mathrm{s}\{\gamma\text{-FeO(OH)}\}]$, will be designated by its site numbers (mol) per dm^3. The adsorption rate may be expressed as in equation (2). When

$$d[Fe_{sup}{}^{2+}]/dt = -k_1[Fe_{sup}{}^{2+}][-\mathrm{s}\{\gamma\text{-FeO(OH)}\}] + k_{-1}[Fe^{2+}-\mathrm{s}\{\gamma\text{-FeO(OH)}\}] \tag{2}$$

the adsorption site number is considered to be kept constant during the course of the reaction, equation (2) can be reduced to equation (3); $-k_1' = -k_1[-\mathrm{s}\{\gamma\text{-FeO(OH)}\}]$.

$$d[Fe_{sup}{}^{2+}]/dt = -k_1'[Fe_{sup}{}^{2+}] + k_{-1}[Fe^{2+}-\mathrm{s}\{\gamma\text{-FeO(OH)}\}] \tag{3}$$

When t = 0—2 min in Figure 1, the decrease in amount of γ-FeO(OH) is very small (curve D); the adsorption site number for iron(II) ion on γ-FeO(OH) seems to be constant. Therefore, application of equation (3) to the adsorption of iron(II) ion on γ-FeO(OH) is valid in this time interval. The magnitudes of k_1' and k_{-1} were evaluated in t = 0—2 min

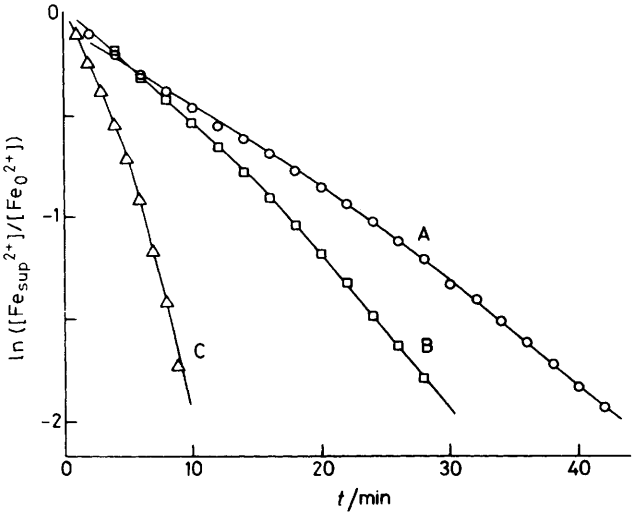

Figure 2. Relationship between ln ($[\mathrm{Fe_{sup}}^{2+}]/[\mathrm{Fe_0}^{2+}]$) and reaction time for pH 8.0 (curve A), 8.2 (B), and 8.4 (C)

using equation (3). In this time interval, the increase in amount of Fe_3O_4 is very small (curve C). Thus, the decrease of iron(II) ion in the supernatant when $t = 0$—2 min (curve A) is taken as that due to adsorption of iron(II) ion on γ-FeO(OH). As a first approximation, k_1 was estimated from the gradient of the tangent of curve A at $t = 0$ ($k_1' = 0.11$ min^{-1}). The amount of iron(II) ion adsorbed on γ-FeO(OH) in the time interval is given by equation (4), where $[\mathrm{Fe_0}^{2+}]$ is the $[\mathrm{Fe_{sup}}^{2+}]$ at $t = 0$. Upon integration of equation (3), we obtain equation (5).

$$[\mathrm{Fe_0}^{2+}] - [\mathrm{Fe_{sup}}^{2+}] = [\mathrm{Fe^{2+}}-\mathrm{s}\{\gamma\text{-FeO(OH)}\}] \quad (4)$$

$$\ln\left\{\frac{(k_1' + k_{-1})[\mathrm{Fe_{sup}}^{2+}] - k_{-1}[\mathrm{Fe_0}^{2+}]}{k_1'[\mathrm{Fe_0}^{2+}]}\right\} = -(k_1' + k_{-1})t \quad (5)$$

With $[\mathrm{Fe_{sup}}^{2+}] = 6 \times 10^{-4}$ mol dm^{-3} at $t = 2$ min and $k_1' = 0.11$ min^{-1}, from equation (5) $k_{-1} = 1.7 \times 10^{-4}$ min^{-1} which is very low compared with k_1' in equation (3) and can be neglected. Equation (3) can be reduced to equation (6). Thus,

$$\mathrm{d}[\mathrm{Fe_{sup}}^{2+}]/\mathrm{d}t = -k_1'[\mathrm{Fe_{sup}}^{2+}] \quad (6)$$

the adsorption step of iron(II) ion on γ-FeO(OH) can be expressed by the first-order reaction (6) if the adsorption site number for iron(II) ion on γ-FeO(OH) is kept constant during the reaction.

As seen by curve D in Figure 1, when the reaction proceeds beyond $t = 2$ min, the amount of γ-FeO(OH) decreases with reaction time, but *ca.* 70% of the γ-FeO(OH) remains untransformed at $t = 8$ min. On the other hand, *ca.* 80% of the iron(II) ion in the supernatant was consumed during the 8 min (curve A). Thus, the reaction for the consumption of iron(II) ion in the supernatant proceeded fairly rapidly but a considerable amount of the γ-FeO(OH) remained untransformed. This suggests that the adsorption site number for Fe^{2+} on γ-FeO(OH) can be taken as nearly constant in the time interval t 0—8 min, if the adsorption site number is large compared with the concentration of the iron(II) ion. In general, the adsorption capacity of the iron oxides for metal ions is high.[16] Thus, equation (6) can be applied to the adsorption of iron(II) ion on γ-FeO(OH) when $t = 0$—8 min and pH = 8.4.

Figure 2 shows the relationship between ln ($[\mathrm{Fe_{sup}}^{2+}]/[\mathrm{Fe_0}^{2+}]$) and t for pH 8.0 (curve A), 8.2 (B), and 8.4 (C), where the adsorption site number for the iron(II) ion on γ-FeO(OH) is taken as nearly constant. As the reaction proceeds, each curve changes linearly, then curves, and then again changes linearly. The first straight line in the curve can be explained by equation (6) of the adsorption of iron(II) ion on γ-FeO(OH). The region where the reaction is expressed by equation (6) will be designated as stage I, and the region where the second straight line appears as stage II.

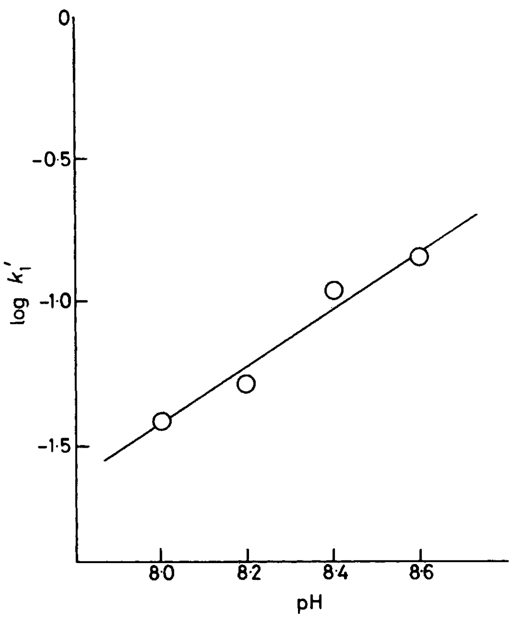

Figure 3. Relationship between log (k_1'/min^{-1}) and reaction pH

The appearance of the second straight line with a higher slope than that of the first suggests that a second reaction, which consumes the iron(II) ion of the supernatant and also seems to be represented by a first-order process, becomes prominent in stage II, and that the second reaction and the adsorption reaction of iron(II) ion on γ-FeO(OH) take place in parallel. If the second reaction is expressed by equation (7)

$$\mathrm{d}[\mathrm{Fe_{sup}}^{2+}]/\mathrm{d}t = -k_3'[\mathrm{Fe_{sup}}^{2+}] \quad (7)$$

the rate of decrease of iron(II) ion in the supernatant in stage II will be given by equation (8). This expresses the first-order

$$\mathrm{d}[\mathrm{Fe_{sup}}^{2+}]/\mathrm{d}t = -k_1'[\mathrm{Fe_{sup}}^{2+}] - k_3'[\mathrm{Fe_{sup}}^{2+}] \quad (8)$$

reaction where both adsorption of iron(II) ion on γ-FeO(OH) and the second reaction which consumes the iron(II) ion take place. The straight line in stage II may be expressed by equation (8), and the slope given by the rate constant $-(k_1' + k_3')$. As seen by curve A in Figure 1, the amount of Fe_3O_4 increases with t, and *ca.* 30% of the Fe_3O_4 which would have been formed if the reaction was completed, was formed when $t = 8$ min. The adsorption reaction of the iron(II) ion on Fe_3O_4 becomes more prominent in stage II. This reaction may be represented by equation (7).

When the logarithmic values of k_1' (obtained from the slopes of the straight lines in stage I of Figure 2) were plotted against the reaction pH, a straight line of slope *ca.* 1.0 was obtained (Figure 3). This suggests that one OH^- is involved in the adsorption step of iron(II) ion on γ-FeO(OH) or that one proton is released during the course of the adsorption step. On the other hand, the overall reaction for the transformation of

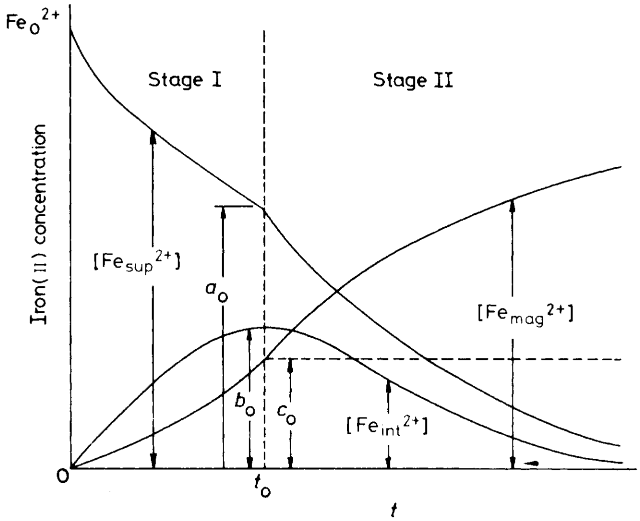

Figure 4. Schematic diagram of the time variation of the concentrations of iron(II) ion of the supernatant of the reaction suspension, $[Fe_{sup}^{2+}]$, of the intermediate, $[Fe_{int}^{2+}]$, and of Fe_3O_4, $[Fe_{mag}^{2+}]$

γ-FeO(OH) to Fe_3O_4 can be written as equation (9). Thus, two protons are released when the transformation reaction is completed. Since one proton is released in the adsorption step (as mentioned above) the reaction can be represented by the reactions (10) and (11) where $-s'\{\gamma\text{-FeO(OH)}\}$ is the surface of γ-FeO(OH) after the transformation reaction.

$$Fe^{2+} + 2\ \gamma\text{-FeO(OH)} \longrightarrow Fe_3O_4 + 2\ H^+ \qquad (9)$$

$$Fe^{2+} + -s\{\gamma\text{-FeO(OH)}\} \longrightarrow Fe^{2+}-s\{\gamma\text{-FeO(OH)}\} + H^+ \qquad (10)$$

$$Fe^{2+}-s\{\gamma\text{-FeO(OH)}\} \longrightarrow Fe_3O_4 + H^+ + -s'\{\gamma\text{-FeO(OH)}\} \qquad (11)$$

In general, when bivalent cations are adsorbed on iron oxides, about two protons are released.[14] However, in the case of the adsorption of the iron(II) ion on γ-FeO(OH) only one proton is released, and subsequently one more proton will be released during the course of the transformation of the Fe^{2+} adsorbed intermediate, $Fe^{2+}-s\{\gamma\text{-FeO(OH)}\}$, to Fe_3O_4.

Transformation of the Intermediate, $Fe^{2+}-s\{\gamma\text{-FeO(OH)}\}$, *to* Fe_3O_4.—As suggested above, one more proton will be released in the subsequent transformation reaction of the intermediate to Fe_3O_4. We studied the pH dependence of the rate constant (k_2) in this transformation step to see whether or not one more proton is released. From the fact that all of the iron(II) ion was transformed to Fe_3O_4, the reverse reaction seems to be neglected; the intermediate is considered to decompose into Fe_3O_4 in the first-order reaction. Thus, all the reactions involved may be represented by the first-order reactions, shown by sequence (12).

$$Fe_{sup}^{2+} \xrightarrow{k_1} Fe^{2+}-s\{\gamma\text{-FeO(OH)}\} \xrightarrow{k_2} Fe_3O_4 + -s'\{\gamma\text{-FeO(OH)}\} \qquad (12)$$

When the reaction proceeds to stage II, the second reaction, the adsorption reaction of iron(II) ion on Fe_3O_4 and represented by a first-order process, becomes prominent and the adsorption of the iron(II) ion takes place on both γ-FeO(OH) and Fe_3O_4. In stage I, since the second reaction seems to be negligible, the adsorption reaction of iron(II) ion on γ-FeO(OH) is prominent. Thus variations in the concentration of iron(II) ions in the supernatant, intermediate, and Fe_3O_4 with reaction time are schematically represented by Figure 4, if it is assumed that the second reaction is initiated at time t_0.

In stage I, the concentration of the intermediate may be given by equation (13), where x mol dm^{-3} of $[Fe_{sup}^{2+}]$ are transformed into the intermediate, $Fe^{2+}-s\{\gamma\text{-FeO(OH)}\}$;

$$[Fe_{int}^{2+}] = x - [Fe_{mag}^{2+}] \qquad (13)$$

where $[Fe_{int}^{2+}]$ and $[Fe_{mag}^{2+}]$ are the iron(II) ion concentrations of the intermediate and Fe_3O_4, respectively. The rate of formation of Fe_3O_4 is proportional to the concentration of the intermediate, therefore equation (14) applies. Since $x = [Fe_0^{2+}](1 - e^{-k_1't})$, then equation (14) can be rewritten as equation (15). Upon integration ($t = 0$, $[Fe_{mag}^{2+}] = 0$), we obtain equation (16) and the concentration of the intermediate is given by equation (17).

$$d[Fe_{mag}^{2+}]/dt = k_2[Fe_{int}^{2+}] = k_2(x - [Fe_{mag}^{2+}]) \qquad (14)$$

$$d[Fe_{mag}^{2+}]/dt + k_2[Fe_{mag}^{2+}] = k_2[Fe_0^{2+}](1 - e^{-k_1't}) \qquad (15)$$

$$[Fe_{mag}^{2+}] = [Fe_0^{2+}]\,[1 + (k_2e^{-k_1't} - k_1'e^{-k_2t})/(k_1' - k_2)] \qquad (16)$$

$$[Fe_{int}^{2+}] = x - [Fe_{mag}^{2+}] = \frac{[Fe_0^{2+}]k_1'}{k_1' - k_2}(e^{-k_2t} - e^{-k_1't}) \qquad (17)$$

In stage II (Figure 4), when x mol dm^{-3} of $[Fe_{sup}^{2+}]$ is consumed, it is used for adsorption on γ-FeO(OH) (the formation of the intermediate) and for adsorption on Fe_3O_4. Then the concentration of the intermediate is given by equation (18),

$$[Fe_{int}^{2+}] = \frac{k_1'}{k_1' + k_3'}x - [Fe_{mag}^{2+}] + b_0 \qquad (18)$$

since, out of x mol dm^{-3}, a $k_1'/(k_1' + k_3')$ portion is transformed to the intermediate. The intermediate concentration at t_0 (Figure 4) is given by b_0 and t_0 is the time when stage I changes to II. Since $x = a_0[1 - e^{-(k_1' + k_3')(t - t_0)}]$ where a_0 is the Fe_{sup}^{2+} concentration at t_0, then the rate of formation of Fe_3O_4 in stage II is given by equation (19) and then equation (20) applies. Upon integration {$t = t_0$, $[Fe_{mag}^{2+}] = c_0$ (Figure 4)} we obtain equation (21), where $k_4 = k_1' + k_3'$. The concentration of the intermediate is given by equation (22).

$$\frac{d[Fe_{mag}^{2+}]}{dt} = k_2[Fe_{int}^{2+}] = k_2\left(\frac{k_1'}{k_1' + k_3'}x - [Fe_{mag}^{2+}] + b_0\right) \qquad (19)$$

$$\frac{d[Fe_{mag}^{2+}]}{dt} + k_2[Fe_{mag}^{2+}] = \frac{a_0k_1'k_2}{k_1' + k_3'}[1 - e^{-(k_1' + k_3')(t - t_0)}] + b_0k_2 \qquad (20)$$

$$[Fe_{mag}^{2+}] = (b_0 + \frac{a_0k_1'}{k_4})[1 - e^{-k_2(t - t_0)}] + \frac{a_0k_1'k_2}{k_4(k_4 - k_2)}[e^{-k_4(t - t_0)} - e^{-k_2(t - t_0)}] + c_0 \qquad (21)$$

$$[Fe_{int}^{2+}] = b_0 + \frac{a_0k_1'}{k_4}[1 - e^{-k_4(t - t_0)}] - [Fe_{mag}^{2+}] \qquad (22)$$

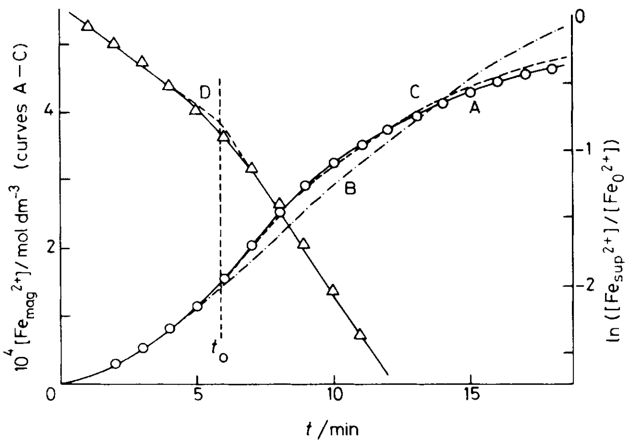

Figure 5. Time variations of iron(II) ion concentration of Fe_3O_4 (experimental data) (curve A), the Fe_3O_4 concentrations evaluated from equation (16) (B) and equation (21) (C), and ln ([Fe_{sup}^{2+}]/[Fe_0^{2+}]) (experimental data) (D)

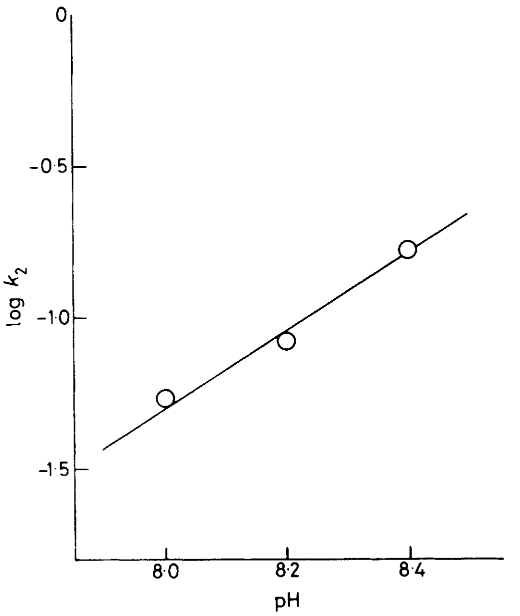

Figure 6. Relationship between log (k_2/min^{-1}) and reaction pH

Table. Values of k_2 calculated from equations (16) and (21) for pH 8.4 at t = 1—13 min

	k_2/min^{-1} (pH 8.4)	
t/min	equation (16)	equation (21)
1	(0.2)	—
2	(0.2)	—
3	(0.2)	—
4	0.18	—
5	0.18	—
6 (t_0)	0.18	—
7	—	(0.1)
8	—	0.17
9	—	0.18
10	—	0.18
11	—	0.17
12	—	0.17
13	—	0.16

The k_2 values can be calculated for each point from equation (16) for stage I, and equation (21) for stage II using [Fe_{mag}^{2+}] for each point in Figure 5 at pH 8.4. The k_2 values calculated for pH 8.4 are summarized in the Table. The point t_0 was found from the point where the first and second lines intersect (Figure 5). Values in parentheses in the Table include a higher error, since [Fe_{mag}^{2+}] or [Fe_{mag}^{2+}] − c_0 are very small. As seen in the Table, the k_2 values evaluated for each point are nearly the same with an average of 0.18 min^{-1}. Using k_2 = 0.18 min^{-1}, [Fe_{mag}^{2+}] values for each point were calculated using equations (16) and (21). The calculated results are given by curves B and C, respectively, in Figure 5. Curve A shows the experimental data of [Fe_{mag}^{2+}]. As seen in Figure 5, in stage I (the region before t_0), curve B is well fitted to curve A, and in stage II (the region after t_0), curve C to curve A. This shows that the experimental results are explained approximately by equations (16) and (21) based on the assumption that the second reaction [adsorption reaction of the iron(II) ion on Fe_3O_4] is initiated at t_0. Of course, in practice, the second reaction also takes place in stage I. However, the reaction is neglected in stage I, but becomes prominent in stage II.

The k_2 values for pH 8.0 and 8.2 were evaluated in a similar manner to give 0.05 and 0.08 min^{-1} respectively. When the logarithmic values of k_2 are plotted against reaction pH, a straight line with a slope of 1.25 is obtained, as shown by Figure 6. This shows that in the transformation step of the intermediate to Fe_3O_4, one proton is released.

Thus, Fe_3O_4 formation by the reaction between γ-FeO(OH) and iron(II) ion proceeds in two steps: (a) adsorption step of iron(II) ion on γ-FeO(OH) (formation of the intermediate) and (b) the transformation step of the intermediate to Fe_3O_4. When metal ions are adsorbed on the surface of the oxides, hydrolysis of the metal ions takes place.[14] Since one proton is released in the first step its reaction may be written by equation (23). In the second step, the intermediate is transformed to Fe_3O_4 with a release of one proton and can be written by

$$2\ \gamma\text{-FeO(OH)} + Fe^{2+} + H_2O \longrightarrow [\gamma\text{-FeO(OH)}]_2FeOH^+ + H^+ \quad (23)$$

$$[\gamma\text{-FeO(OH)}]_2FeOH^+ \longrightarrow Fe_3O_4 + H_2O + H^+ \quad (24)$$

equation (24). As mentioned previously, the formation of Fe_3O_4 by the transformation of γ-FeO(OH) proceeds *via* a dissolution–precipitation process. Reaction (24) includes this process.

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