Mössbauer Spectra at 77 K of Products formed during Transformation of $Fe(OH)_2$ to Fe_3O_4 in Aqueous Suspension by Air Oxidation

Tadao Kanzaki* and Takashi Katsura
Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Mössbauer spectra at 77 K of the products formed during the aerial oxidation of aqueous iron(II) hydroxide suspensions, combined with *X*-ray powder diffraction and electron micrograph data have suggested that at pH 9.0, $Fe(OH)_2$ and Fe_3O_4 are formed. [During the initial stage, iron(III) hydroxide oxide, γ-FeO(OH), is also formed.] It has been also suggested that at pH 7.0, only 'green rust II' is formed in the second stage, followed by the formation of Fe_3O_4, while the content of Fe^{2+} ion in the supernatant gradually decreases. The Mössbauer data suggest that the $Fe^{II}:Fe^{III}$ mol ratio in green rust II is 2:1.

The formation of Fe_3O_4 in aqueous iron(II) hydroxide suspensions was first studied by Feitknecht.[1] Bernal *et al.*[2] studied the process crystallographically and proposed a scheme for the formation process. Misawa *et al.*[3] presented a systematic diagram of the formation process, in which both dissolved and solid species are included. Kiyama[4] studied the optimum conditions for the formation of Fe_3O_4 by air oxidation of aqueous iron(II) hydroxide suspensions and reported that in neutral suspensions, Fe_3O_4 is formed *via* 'green rust II' or a mixture of green rust II and $Fe(OH)_2$, but in alkaline suspension, Fe_3O_4 is formed directly. On the other hand, Bohnsack[5] proposed the formation of Fe_3O_4 through γ-FeO(OH). Recently, Tamaura *et al.*[6] reported that the formation of Fe_3O_4 by aerial oxidation of aqueous iron(II) hydroxide suspensions proceeds in three stages: (*i*) formation of iron(III) oxides [amorphous γ-FeO(OH)] and slower formation of Fe_3O_4; (*ii*) rapid formation of Fe_3O_4; and (*iii*) linear formation of Fe_3O_4.

In this paper, we have measured Mössbauer spectra at 77 K of the products formed during the air oxidation of an aqueous iron(II) hydroxide suspension as a first step in the study of the mode of formation of Fe_3O_4.

Experimental

Reagents.—Analytical grade reagents were used. Sodium hydroxide solutions were prepared by dissolving sodium hydroxide in distilled water free from carbon dioxide and oxygen.

Procedure.—A Dewar-type reaction vessel with a capacity of 2 dm^3 and with a glass cover was used. The construction of the reaction vessel was the same as that employed previously.[7] Distilled water, 0.5 mol dm^{-3} sulphuric acid solution, and sodium sulphate were transferred to the reaction vessel and nitrogen gas was bubbled into the rapidly stirred (600 r.p.m.) solution for 1 h to remove the dissolved CO_2 and oxygen. Then iron(II) sulphate heptahydrate (120 g; 0.4316 mol of iron) was added. The pH was adjusted to 9.0 or 7.0 by using both 2 and 5 mol dm^{-3} sodium hydroxide solutions. The volume of the suspension was set to 2.00 dm^3, and the total concentration of sulphate ion was fixed (0.375 mol dm^{-3}). The suspension was left to stand under nitrogen for 1 h while stirring at 65 °C. Air was passed at a rate of 0.2 dm^3 min^{-1} through the suspension. During the oxidation, the pH was kept constant at 9.0 or 7.0 by the addition of 0.2 or 2 mol dm^{-3} sodium hydroxide solution respectively. Subsequent procedures were the same as those described by Kaneko and Katsura.[7] The oxidation reactions were complete after *ca.* 600 min and only Fe_3O_4 ($Fe^{II}:Fe_{tot.}$ mol ratio = 0.333:1) was formed. At a particular reaction time, nitrogen gas was passed for 10 min through the suspension in place of air and then an aliquot of the suspension was removed using a glass syringe. These suspension samples were examined by chemical analysis, Mössbauer spectra, electron micrograph and *X*-ray powder diffraction measurements.

Mössbauer Spectroscopic Measurements.—The suspension sample was transferred, under nitrogen gas, dropwise to a simple acrylate resin cell, at room temperature and was frozen by putting the cell on a copper plate immersed in liquid nitrogen for 1 min. The cell provided a cylindrical space for the sample 16 mm diameter and 2.5 mm deep. The frozen sample was covered with an acrylate resin plate and wrapped in aluminium foil. Under dried nitrogen gas, the cell was then attached to the cell holder cooled to between 0 and −10 °C in a cryostat. The cryostat was evacuated and the sample was then cooled using liquid nitrogen. This attachment process was completed rapidly to avoid melting of the frozen sample and formation of frost in the cryostat. The possibility of chemical change of the suspension sample during the freezing and attachment to the cryostat was not examined, but it is considered unlikely. Iron-57 Mössbauer spectra at 77 K were obtained by using ^{57}Co radiation with an electromechanical transducer operating in a constant acceleration mode in conjunction with a 512 channel analyser. The velocity scale was calibrated using the hyperfine spectra at room temperature of a natural α-iron foil, which also served as the isomer shift reference.

X-Ray Powder Diffraction and Electron Micrograph Measurements.—The suspension sample was sealed in a centrifuge tube under nitrogen and centrifuged. The precipitate thus obtained was coated on a glass plate and sealed by Scotch mending tape (3 M Co., U.S.A.; cellophane tape) under nitrogen. The *X*-ray powder diffraction pattern was obtained with Fe-K_α radiation. An electron micrograph of the precipitate was obtained by rapidly dispersing the suspension sample on a sample holder.

Chemical Analysis.—The amounts of iron(II) and iron(III) were determined by titration[7] with 0.021189 mol dm^{-3} potassium permanganate standard solution.

Results and Discussion

Electron micrographs were taken of the precipitates formed during the oxidation reaction at pH 9.0 and 7.0. In the suspension before oxidation at pH 9.0, translucent square crystals are formed. *X*-Ray powder diffraction measurements on the precipitate indicated that they are $Fe(OH)_2$. In the initial

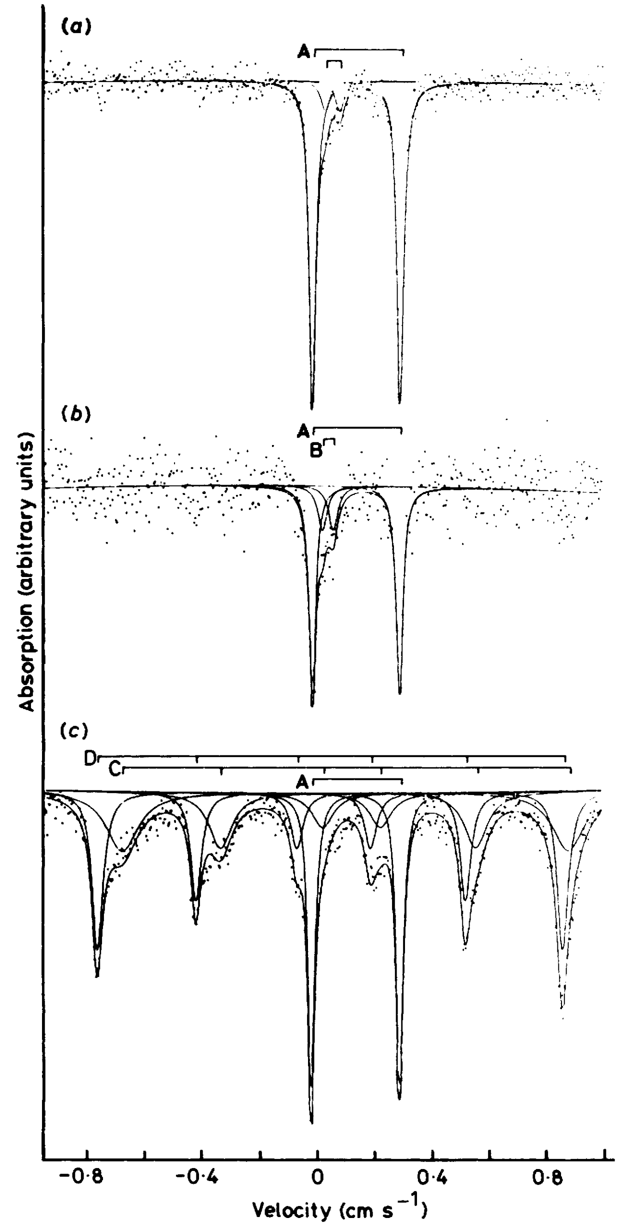

Figure 1. Mössbauer spectra at 77 K of the suspension at an Fe^{II}:$Fe_{tot.}$ mol ratio of 0.987 : 1, (*a*) before the oxidation reaction at pH 9.0, and of suspensions of Fe^{II}:$Fe_{tot.}$ mol ratios of 0.864 (*b*) and 0.528 : 1 (*c*) during the oxidation reaction. Solid lines represent the least-squares fit; patterns A, B, C, and D are indicated

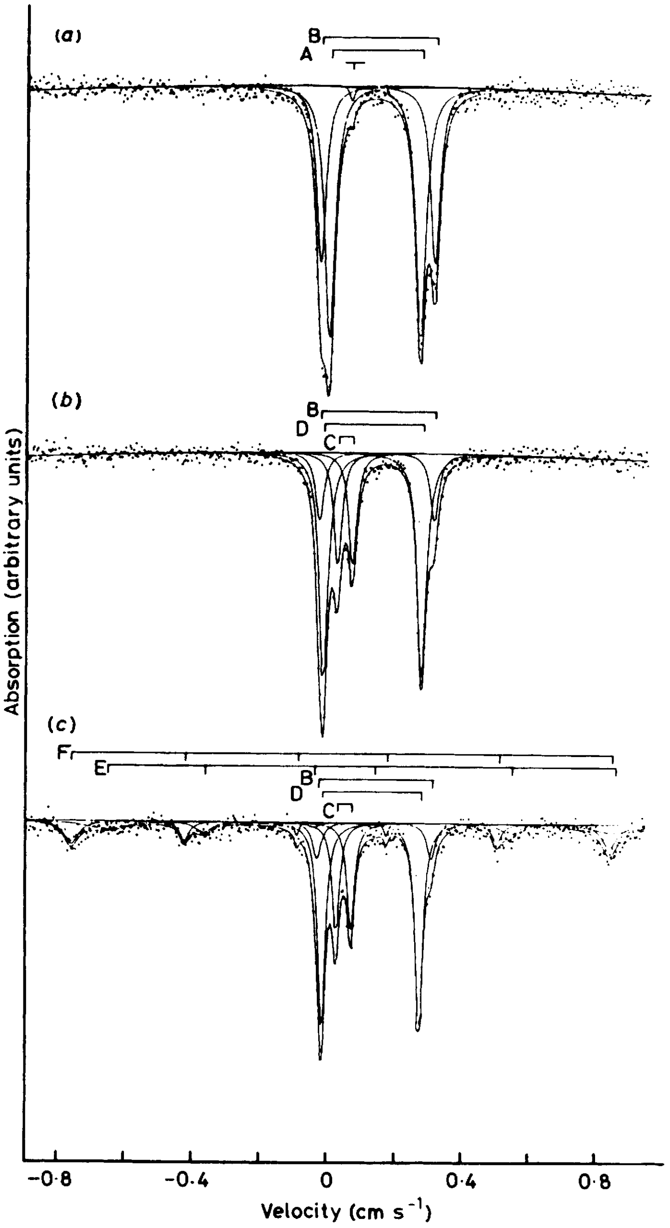

Figure 2. Mössbauer spectra at 77 K of the suspension at an Fe^{II}:$Fe_{tot.}$ mol ratio of 0.986 : 1, (*a*) before the oxidation reaction at pH 7.0, and of suspensions of Fe^{II}:$Fe_{tot.}$ mol ratios of 0.751 (*b*) and 0.623 : 1 (*c*) during the oxidation reaction. Solid lines represent the least-squares fit; patterns A, B, C, D, E, and F are indicated

stage of the oxidation reaction, cubic and large needle-like crystals are formed. The cubic crystals were identified as Fe_3O_4 by *X*-ray powder diffraction on the precipitate, but the needle-like crystals were not identified. During the oxidation, the crystals of $Fe(OH)_2$ grow and become opaque. In the suspension before the oxidation reaction at pH 7.0, opaque square crystals are formed. The *X*-ray powder diffraction pattern of the precipitate did not show clear lines of $Fe(OH)_2$. It has been reported that during the titration of Fe^{2+} ion in sulphate solution with sodium hydroxide solution, $Fe(OH)_2$ precipitates at the point of first precipitation (pH 8.10, 20 °C)[8] and this suggests that the opaque square crystals are indeed $Fe(OH)_2$. In the initial stage of the oxidation, hexagonal plate-like crystals are formed from the $Fe(OH)_2$. *X*-Ray powder diffraction measurements on the precipitate indicated that the hexagonal plate-like crystals are green rust II.[2,9] In the second stage of the oxidation reaction, only the hexagonal plate-like crystals of green rust II are seen and the crystals grow as the oxidation proceeds. In the third stage cubic crystals of Fe_3O_4 appear.

Mössbauer spectra at 77 K of the suspension during the oxidation reaction at pH 9.0 and 7.0 are shown in Figures 1 and 2 respectively. The Mössbauer spectra were analysed by a least-squares fit computer program. It was assumed that: (*a*) the peak shapes are Lorentzian; (*b*) the relationships first peak = second peak for paramagnetic spectra, and first peak = sixth peak, second peak = fifth peak, and third peak = fourth peak for magnetically split spectra hold for the peak area and line half-widths. The initial values of peak position, area and half-width for the least-squares fit were estimated from the Mössbauer spectra by the finite impulse response operator (f.i.r.o.)

Table. $Fe^{II}:Fe_{tot.}$ mol ratios in the suspensions, Mössbauer parameters, and area fractions estimated from the Mössbauer spectra at 77 K

pH	$Fe^{II}:Fe_{tot.}$ Chemical analysis	$Fe^{II}:Fe_{tot.}$ Mössbauer spectra	Mössbauer pattern	δ^a/cm s^{-1}	Δ^a/cm s^{-1}	Internal field^b (kOe)	Area fraction
7.0	0.986	0.991	A	0.134	0.269		0.600
			B	0.142	0.337		0.391
	0.751	0.736	B	0.143	0.340		0.164
			C	0.049	0.044		0.263
			D	0.132	0.291		0.572
	0.623	0.586	B	0.139	0.343		0.080
			C	0.048	0.045		0.213
			D	0.129	0.293		0.405
			E	0.093	−0.010	488	0.302
			F	0.040	−0.001	508	
9.0	0.987	0.888	A	0.131	0.305		0.888
	0.864	0.772	A	0.130	0.306		0.772
			B	0.032	0.037		0.228
	0.528	0.476	A	0.131	0.310		0.215
			C	0.109	0.010	490	0.785
			D	0.048	0.002	514	

^{a} Values with respect to natural α-iron foil; error ±0.002 cm s^{-1}. ^{b} Oe = 1 000/4π A m^{-1}.

method.[10] The results are shown in Figures 1 and 2 by solid lines and the Mössbauer parameters are listed in the Table. The Mössbauer spectrum of the suspension before oxidation at pH 9.0 [Figure 1(*a*)] shows a paramagnetic pattern A arising from the Fe^{2+} ion, and the isomer shift (δ) and quadrupole splitting (Δ) for this spectrum (Table) are in good agreement with published values for $Fe(OH)_2$ (δ 0.115 cm s^{-1}, Δ 0.300 cm s^{-1} at 90 K).[11] This agrees with the results of the *X*-ray powder diffraction and the electron micrograph measurements described above. The Mössbauer spectrum of the suspension at an early stage of the oxidation shows the paramagnetic patterns A and B arising from $Fe(OH)_2$ and Fe^{3+} ion, respectively. Pattern B due to Fe^{3+} ion may be due to the large needle-like crystals in the electron micrograph. The parameters of this spectrum correspond to iron(III) hydroxide oxide [γ-FeO(OH)] (δ 0.030 cm s^{-1}, Δ 0.055 cm s^{-1} at 77 K).[12] The hyperfine pattern for Fe_3O_4 was not analysed, but a few hyperfine peaks were deconvoluted by the f.i.r.o. method. During the course of the oxidation, hyperfine patterns C and D for Fe_3O_4 appear in the Mössbauer spectrum [Figure 1(*c*)]. Hargrove and Kündig[13] reported that the Mössbauer spectrum at 77 K of Fe_3O_4, prepared by a solid-state reaction, yields hyperfine patterns for five sub-lattices. The Mössbauer spectrum at 77 K for Fe_3O_4 formed in aqueous suspension was not completely analysed, although the spectra due to two sub-lattices are shown.

The Mössbauer spectrum of the suspension before oxidation at pH 7.0 [Figure 2(*a*)] shows paramagnetic patterns A and B arising from Fe^{2+} ion. The value of δ for the pattern A is in good agreement with the value for $Fe(OH)_2$,[11] but Δ is smaller. This deviation may be due to the lower crystallinity of $Fe(OH)_2$ formed at pH 7.0.[14] The values of δ and Δ for pattern B were in good agreement with the values (δ 0.142 cm s^{-1}, Δ 0.341 cm s^{-1}) for the paramagnetic Mössbauer spectrum at 77 K of the supernatant before oxidation at pH 7.0. This suggests that pattern B is due to dissolved Fe^{2+} ion[15] in the suspension. The values of δ and Δ for pattern B are also in good agreement with the values for $FeSO_4 \cdot 7H_2O$.[16,17] In the Mössbauer spectrum of the suspension during the second stage of the oxidation [Figure 2(*b*)], pattern A for $Fe(OH)_2$ disappears and paramagnetic patterns arising from Fe^{3+} ion (C) and Fe^{2+} ion (D) are seen. As described above, only crystals of green rust II are found in the suspension during the second stage. This suggests that the patterns C and D arise from Fe^{3+} and Fe^{2+} ions in the green rust II. As oxidation proceeds, hyperfine patterns E and F for Fe_3O_4 appear [Figure 2(*c*)]. Small paramagnetic patterns due to Fe^{3+} ion in the Mössbauer spectra shown in Figures 1 and 2(*a*) are caused by $Fe(OH)_3$ contamination.

Area fractions were calculated from the peak areas estimated using the least-squares fit by assuming that the non-recoilless fractions for the different spectra are equal (Table). $Fe^{II}:Fe_{tot.}$ mol ratios calculated from the area fractions assuming that one-third of the peak of the hyperfine patterns corresponds to Fe^{2+} ion in Fe_3O_4 are in agreement with the values estimated from the chemical analysis of the suspensions. This suggests that the calculation using the area fractions is valid. The area ratios of the paramagnetic pattern D:C shown in Figure 2(*b*) and (*c*) are equal to 2.17:1 and 1.90:1, respectively; that is, the $Fe^{II}:Fe^{III}$ mol ratio in the green rust II is 2:1. It has been reported that the $Fe^{II}:Fe^{III}$ mol ratio of green rust II is 1:1,[18,19] but recently, Tamaura *et al.*[20] and Shamoto *et al.*[21] reported that the $Fe^{II}:Fe^{III}$ mol ratio of green rust II is 2:1. This work confirms the latter ratio using a non-destructive method.

Tamaura *et al.*[20] and Shamoto *et al.*[21] also reported that sulphate ion is present in green rust II ($Fe^{II}:Fe^{III}:SO_4$ = 2:1:1). The mol ratio of dissolved Fe^{2+} ion to total iron in the suspension ($Fe^{2+}{}_{dissol.}:Fe_{tot.}$) during the oxidation reaction at pH 7.0 was calculated from the results of chemical analysis and the amount of sodium hydroxide consumed on the assumption that the $Fe^{II}:Fe^{III}:SO_4$ mol ratio in the green rust II formed in the suspension is equal to 2:1:1. The amount of Fe_3O_4 formed in the suspension with an $Fe^{II}:Fe_{tot.}$ mol ratio of 0.623:1 was obtained from the value of the area fraction for Fe_3O_4 (0.302). The $Fe^{2+}{}_{dissol.}:Fe_{tot.}$ mol ratios estimated are 0.539, 0.210, and 0.120:1 in the suspensions with $Fe^{II}:Fe_{tot.}$ mol ratios of 0.986, 0.751, and 0.623:1, respectively. These values are approximately equal to the values of the area fractions for the paramagnetic pattern B arising from the dissolved Fe^{2+} ion (Table). The ratio of the $Fe^{2+}{}_{dissol.}:Fe_{tot.}$ mol ratios, 1:0.39:0.22, is in good agreement with that of the area fractions, 1:0.42:0.21. Thus, the Mössbauer spectroscopic measurements at 77 K provide some information on the products formed during the air oxidation of aqueous iron(II) hydroxide suspensions.

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