Formation of Molybdenum-bearing Ferrites, $Fe_{3-x}Mo_xO_4$ (x = 0.04—0.19), in Aqueous Suspension by Air Oxidation

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Molybdenum-bearing ferrites (Mo : $Fe_{tot.}$ mol ratios 0.015—0.069 : 1) have been formed by air oxidation of iron(II) hydroxide suspensions, which were prepared in the presence of Mo^{III} ions, at Mo : $Fe_{tot.}$ mol ratios of 0.032—0.326 : 1 in the initial suspensions, at pH 9.0 and 65 °C. Lattice constants of the Mo-bearing ferrites, $Fe_{3-x}Mo_xO_4$, were found to increase linearly with increasing values of x. This relationship agrees with that of stoicheiometric Mo-bearing ferrites.

The formation of ferrites by air oxidation of aqueous iron(II) hydroxide suspensions containing other metal ions has already been investigated in our laboratory.[1-7] Titanium-bearing ferrites (oxidized) are formed at Ti^{IV} : $Fe_{tot.}$ mol ratios of 0—0.5 : 1 in the initial suspension, at pH 9.0 and 65 °C.[6] At low vanadium(IV) concentrations in the initial suspension, stoicheiometric vanadium-bearing ferrites are formed at pH 11.0 and 65 °C, but at higher concentrations, α-FeO(OH) is formed together with vanadium-bearing ferrites having a higher vanadium content.[7] In the case of chromium(III), $Cr_{0.42}Fe_{2.56}O_{4.00}$ is obtained by nitrate oxidation of an aqueous suspension at pH 7.0 and 80 °C.[8]

In this paper, we report the formation of molybdenum-bearing ferrites by air oxidation of iron(II) hydroxide suspensions, which were prepared in the presence of Mo^{III} ions.

Experimental

Reagents.—A hydrochloric acid solution of molybdenum(III) chloride (0.432 mol dm^{-3}) was prepared from a 5 mol dm^{-3} hydrochloric acid solution of a molybdic acid by a conventional electrolytic reduction method,[9] but platinum electrodes were used. A hydrochloric acid solution of iron(II) chloride was prepared from iron metal just before use. A 2 mol dm^{-3} sodium hydroxide solution was prepared by dissolving sodium hydroxide in distilled water freed from carbon dioxide and oxygen.

Apparatus.—A Dewar-type reaction vessel described previously [1] was used.

Procedure.—Distilled water and sodium chloride were transferred to the reaction vessel and nitrogen gas was bubbled into the rapidly stirred solution for 1 h to remove the dissolved CO_2 and oxygen. Hydrochloric acid solutions of iron(II) chloride (0.043 16 mol of iron) and molybdenum(III) chloride were then added. The volume of the solution was set to 0.200 dm^3, and the total concentration of chloride ion was fixed (0.33 mol). The pH was adjusted to 9.0 by using 2 mol dm^{-3} sodium hydroxide solution and the suspension was left to stand for 1 h with stirring under nitrogen at 65 °C (we call this suspension the ' initial suspension '). Then, air-mixed nitrogen gas was passed at a rate of 0.2 dm^3 min^{-1} (air : N_2 flow ratio = 0.1 : 1) through the suspension in place of nitrogen gas. Subsequent procedures were the same as those described by Kaneko and Katsura.[1]

After completion of the oxidation reaction, some of the molybdenum was present as Mo^{VI} in the supernatant and some Mo was present as a molybdenum hydroxide or a spinel-type compound. The pH of the suspension was raised to 11.0 by adding 2 mol dm^{-3} sodium hydroxide solution, left to stand for 2 h with passage of air at 0.2 dm^3 min^{-1} at 65 °C, and then washed twice with distilled water by centrifugation. The precipitate thus obtained is referred to as ' the product '. By this aeration, molybdenum hydroxide dissolves completely as the Mo^{VI} ion.

During the aeration (pH 11.0 and 65 °C), the spinel-type compounds are slightly oxidized to the γ-Fe_2O_3 type. Therefore, the lattice constants and Mössbauer spectral parameters of spinel-type compounds were estimated from the *X*-ray powder diffraction patterns and Mössbauer spectra of the precipitates taken from the suspension, after completion of the oxidation reaction.

Preliminary experiments were carried out in order to establish the most suitable pH value of the reaction suspension from which the Mo-bearing ferrites could be readily obtained. At pH 8.0—10.0, the product was the Mo-bearing ferrite and substantial Mo was present in the Mo-bearing ferrite at pH 9.0. At pH 11.0, α-FeO(OH) was formed. In this study, therefore, the oxidation reaction was carried out at pH 9.0.

Chemical Analysis.—The Mo content was determined by spectrophotometry with 1,2-dimercapto-4-methylbenzene. The sum of the Fe and Mo content was determined by titration [1,10] with potassium dichromate standard solution.

Results and Discussion

The Figure shows the Mössbauer spectra at room temperature of the precipitates taken from the suspensions, after completion of the oxidation reactions [Mo : $Fe_{tot.}$ mol ratios (r_{Mo}) of 0—0.326 : 1 in the initial suspension at pH 9.0 and 65 °C]. In the Mössbauer spectrum at $r_{Mo} = 0$ [spectrum (*a*)], which corresponds to Fe_3O_4, the usual two, six hyperfine absorption pattern is seen. In spectra (*b*), (*c*), and (*d*) (r_{Mo} of 0.120, 0.216, and 0.326 : 1 respectively), the peaks of the spinel-type compound broaden and resolution deteriorates. In spectrum (*d*) ($r_{Mo} = 0.326 : 1$), the absorption around the Doppler velocity of 0 cm s^{-1} becomes more intense. Abe [11] studied the Mössbauer spectra of the stoicheiometric Mo-bearing ferrites obtained by a solid-state reaction. He reported a similar broadening of the Mössbauer lines and the absorption around the Doppler velocity of 0 cm s^{-1} at higher Mo contents. This broadening and the absorption around 0 cm s^{-1} seem to arise because the Mo ion is substituted for iron in the spinel-type compound. The Mössbauer spectral parameters (internal field) determined for the A- and B-sites are summar-

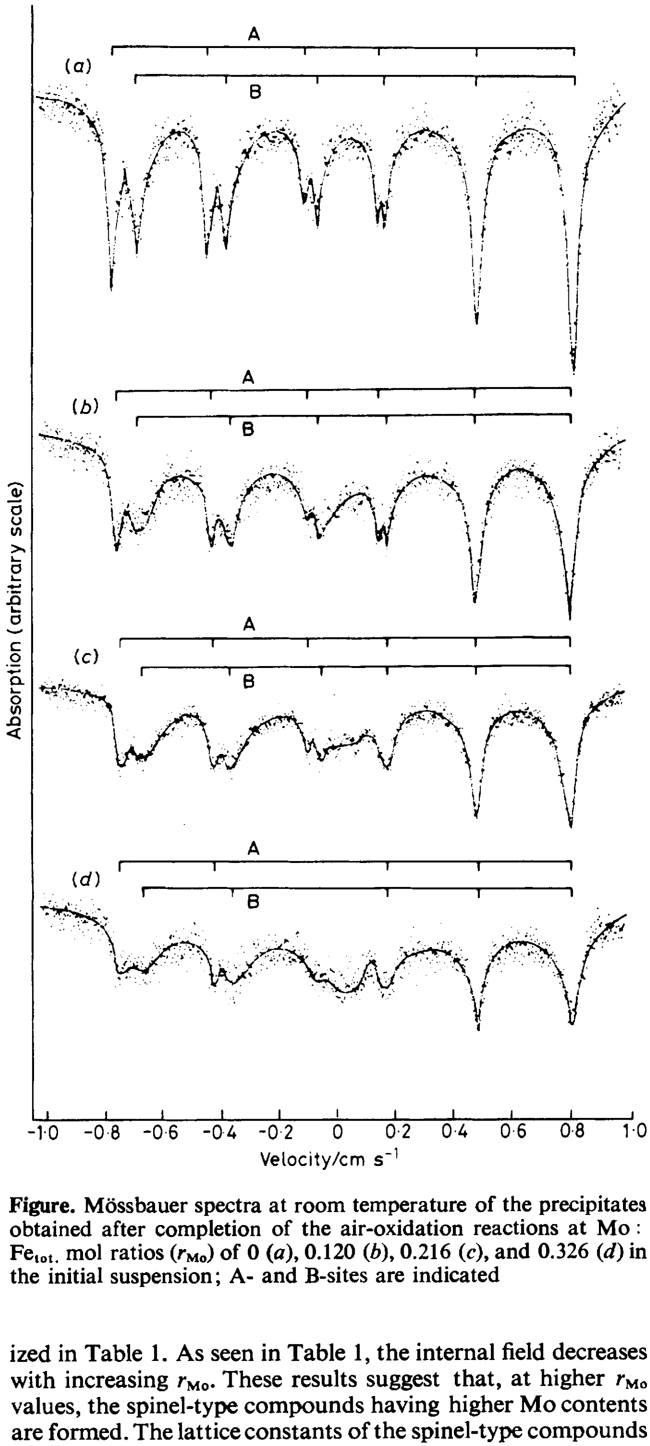

Figure. Mössbauer spectra at room temperature of the precipitates obtained after completion of the air-oxidation reactions at Mo : Fe$_{tot.}$ mol ratios (r_{Mo}) of 0 (*a*), 0.120 (*b*), 0.216 (*c*), and 0.326 (*d*) in the initial suspension; A- and B-sites are indicated

Table 1. Internal field estimated from the Mössbauer spectra at room temperature of the precipitates obtained after completion of the oxidation reactions

r_{Mo} in the initial suspension	Internal field (kOe) *	
	A-site	B-site
0	499 ± 5	467 ± 5
0.120	490 ± 5	467 ± 7
0.216	488 ± 5	461 ± 7
0.326	485 ± 10	457 ± 10

* Oe = 1 000/4π A m^{-1}.

Table 2. Chemical composition of the Mo-bearing ferrites

Initial suspension	Mo-bearing ferrites	
r_{Mo}	r_{Mo}	Chemical composition
0.032	0.015	$Fe_{2.96}Mo_{0.04}O_{4.00}$
0.065	0.026	$Fe_{2.92}Mo_{0.08}O_{4.00}$
0.120	0.036	$Fe_{2.90}Mo_{0.10}O_{4.00}$
0.216	0.052	$Fe_{2.85}Mo_{0.15}O_{4.00}$
0.326	0.069	$Fe_{2.81}Mo_{0.19}O_{4.00}$

ized in Table 1. As seen in Table 1, the internal field decreases with increasing r_{Mo}. These results suggest that, at higher r_{Mo} values, the spinel-type compounds having higher Mo contents are formed. The lattice constants of the spinel-type compounds increased with increasing r_{Mo}. Katsura *et al.*[12] reported that the lattice constants of the stoicheiometric Mo-bearing ferrites, $Fe_{3-x}Mo_xO_4$ from a solid-state reaction increased linearly with increasing values of x. Chemical analysis of the products shows that the Mo content (Mo : Fe$_{tot.}$ mol ratio) of the spinel-type compounds increases from 0.015 to 0.069 on increasing the Mo : Fe$_{tot.}$ mol ratios in the initial suspensions from 0.032 to 0.326 (Table 2). These results suggest that the spinel-type compounds are the Mo-bearing ferrites.

The chemical compositions of the Mo-bearing ferrites estimated from the Mo : Fe$_{tot.}$ mol ratios of the ferrites, assuming that the chemical compositions were stoicheiometric, are given in Table 2. The lattice constants of the Mo-bearing ferrites, $Fe_{3-x}Mo_xO_4$, increased linearly with increasing values of x. This relationship agrees with that of stoicheiometric Mo-bearing ferrites reported by Katsura *et al.*[12]

References

1 K. Kaneko and T. Katsura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 747.
2 K. Kaneko, K. Takei, Y. Tamaura, T. Kanzaki, and T. Katsura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1080.
3 T. Kanzaki, J. Nakajima, Y. Tamaura, and T. Katsura, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 135.
4 Y. Tamaura and T. Katsura, *J. Chem. Soc., Dalton Trans.*, 1980, 825.
5 K. Ito, T. Kanzaki, Y. Tamaura, and T. Katsura, *J. Chem. Soc., Dalton Trans.*, 1981, 2217.
6 T. Katsura, Y. Tamaura, and G. S. Chyo, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 96.
7 Y. Tamaura, S. Mechimonchit, and T. Katsura, *J. Inorg. Nucl. Chem.*, 1981, **43**, 671.
8 Y. Tamaura, U. Rasyid, and T. Katsura, *J. Chem. Soc., Dalton Trans.*, 1980, 2125.
9 'Inorganic Syntheses,' ed. J. C. Bailar, jun., McGraw-Hill Book Co. Inc., New York, 1953, vol. 4, p. 97.
10 JIS M 8131, investigated by Japanese Industrial Standards Committee, Japanese Standards Association, Tokyo, 1962.
11 M. Abe, Ph.D. Thesis, Tokyo Institute of Technology, Tokyo, Japan, 1972.
12 T. Katsura, M. Wakihara, S. Nara, and T. Sugihara, *J. Solid State Chem.*, 1975, **13**, 107.

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