Formation of Oxidized Molybdenum-bearing Ferrites, $Fe_{2.95-x}Mo_xO_4$ (x = 0.03—0.30) in Aqueous Suspensions by Air Oxidation, and Valence State of Molybdenum

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

Oxidized molybdenum-bearing ferrites (Mo : $Fe_{tot.}$ mol ratios 0.012—0.114 : 1) have been formed by air oxidation of iron hydroxide suspensions, which were prepared in the presence of molybdenum(VI) ions at initial Mo : $Fe_{tot.}$ mol ratios of 0.015—0.300 : 1, at pH 9.0, and 65 °C. The molybdenum content in the centre part of the ferrite particles was found to be very low. *X*-Ray photoelectron spectra of the Mo $3d_{\frac{5}{2}}$ electrons (229.7—230.0 eV) from the molybdenum-bearing ferrites have suggested that Mo is in the valence state of +4 in a lattice of the spinel type.

We have reported previously[1] that molybdenum-bearing ferrites, $Fe_{3-x}Mo_xO_4$ (x = 0.04—0.19), are formed by air oxidation of iron(II) hydroxide suspensions prepared in the presence of molybdenum(III) ions, at initial Mo : $Fe_{tot.}$ mol ratios of 0.032—0.326 : 1, pH 9.0, and 65 °C.

In iron(II) hydroxide suspensions at pH 9.0 and 65 °C, molybdenum(VI) ions are reduced by Fe^{II} and precipitated as molybdenum (average valency 3.5) hydroxides. On standing of such suspensions, under nitrogen at pH 9.0 and 65 °C, molybdenum-bearing ferrites are not formed.[2]

In this paper we report the formation of molybdenum-bearing ferrites by air oxidation of iron hydroxide suspensions, prepared in the presence of molybdenum(VI) ions. The valence state of the Mo in such ferrites was also investigated by *X*-ray photoelectron spectroscopy (x.p.s.).

Experimental

Reagents.—A sodium hydroxide solution of molybdenum(VI) was prepared by dissolving molybdenum trioxide in 2 mol dm^{-3} sodium hydroxide solution. A hydrochloric acid solution of iron(II) chloride and a 2 mol dm^{-3} sodium hydroxide solution were prepared as described by Kanzaki *et al.*[1]

Procedure.—A Dewar-type reaction vessel described by Kaneko and Katsura[3] was used. 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. A hydrochloric acid solution of iron(II) chloride (0.043 16 mol of iron) and a sodium hydroxide solution of molybdenum(VI) were then added. The total volume of the mixture was 0.200 dm^3, and the total amount of chloride ion was 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 under nitrogen for 1 h with stirring at 65 °C. We call this suspension the 'initial suspension,' in which molybdenum(VI) ions are reduced by Fe^{II} and precipitated as molybdenum (average valency 3.5) hydroxide. Then, a mixture of air and nitrogen gas was passed at a rate of 0.2 dm^3 min^{-1} (air : N_2 ratio = 0.1 : 1) through the suspension. The subsequent procedures were the same as those described previously.[1]

The average valency of Mo in the hydroxide precipitate from the initial suspension was estimated by extrapolation of the linear plot of the molybdenum(VI) content in the supernatant against the Mo : $Fe_{tot.}$ mol ratio in the suspension to the intercept on the mol ratio axis. At this Mo : $Fe_{tot.}$ mol ratio, all of the molybdenum(VI) ions added to the suspension are reduced by the Fe^{II} to give the molybdenum hydroxide precipitate.

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

r_{Mo} in the initial suspension	Internal field of hyperfine pattern (kOe)* A	B	C
0	499 ± 4	467 ± 4	
0.060	492 ± 8	456 ± 8	
0.100	488 ± 8	451 ± 8	
0.300	482 ± 8	452 ± 8	406 ± 8

* Oe = 1 000/4π A m^{-1}.

Chemical Analysis.—The molybdenum content was determined by spectrophotometry using 1,2-dimercapto-4-methylbenzene.[4] The sum of the iron(II) and molybdenum(≤V) contents was determined by titration[3,5] with standard potassium dichromate solution. Molybdenum(≤V) ions are oxidized by an excess of iron(III) in acidic solution to Mo^{VI}, that is, their content is determined from the iron(II) formed. The sum of the iron and molybdenum contents was also determined by titration with standard potassium dichromate solution, after reduction by zinc amalgam to Fe^{II} and Mo^{III} and then oxidation of Mo^{III} to Mo^{VI} by an excess of Fe^{III}.

Results and Discussion

Formation of Molybdenum-bearing Ferrites in Iron Hydroxide Suspensions at Initial Mo : $Fe_{tot.}$ *Mol Ratios* (r_{Mo}) = 0—0.300 : 1.—Figure 1 shows the Mössbauer spectra at room temperature of the precipitates taken from the suspensions upon completion of the oxidation reaction. At r_{Mo} = 0 [spectrum (*a*)], which corresponds to Fe_3O_4, the usual two, six-line hyperfine absorption pattern is seen. In spectra (*b*), (*c*), and (*d*) (r_{Mo} = 0.060, 0.100, and 0.300 : 1), the peaks of the spinel-type compounds broaden and the resolution deteriorates. In addition, new peaks, which are assigned to the six-line hyperfine pattern C by a least-squares fit,[6] appear to the right of peaks B_1 and B_2 in spectrum (*d*). The internal fields of the six-line hyperfine absorption patterns A and B decrease with increasing r_{Mo} (Table). These results suggest that, at higher r_{Mo} values, spinel-type compounds having higher molybdenum contents

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

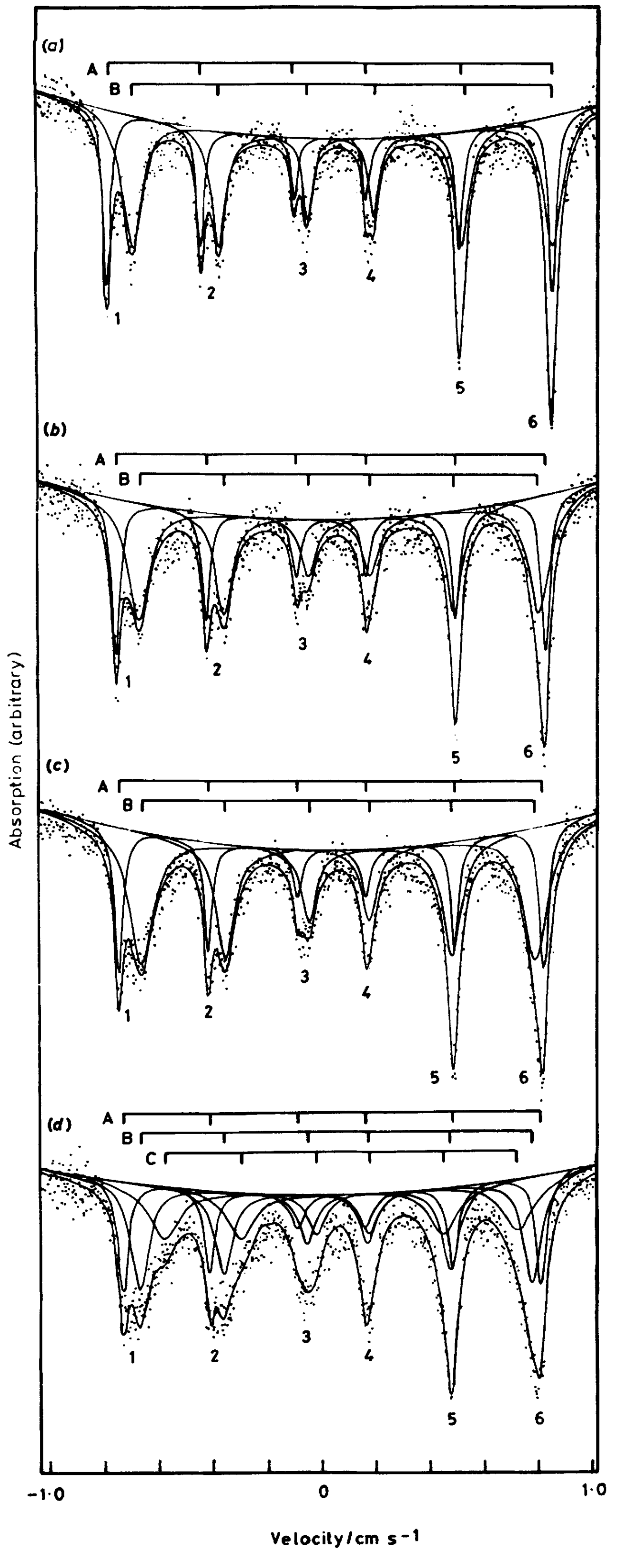

Figure 1. Mössbauer spectra at room temperature of the precipitates obtained after completion of the air-oxidation reactions at initial Mo:Fe$_{tot.}$ mol ratios (r_{Mo}) of 0 (*a*), 0.060 (*b*), 0.100 (*c*), and 0.300 (*d*). Solid lines represent least-squares fit; A, B, and C patterns are indicated

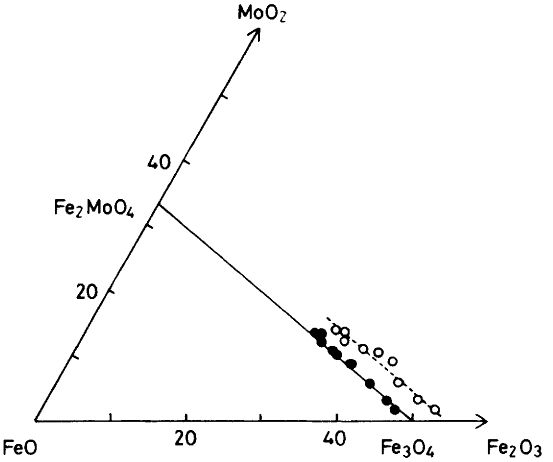

Figure 2. Average chemical composition of molybdenum-bearing ferrites obtained by air-oxidation reactions (○) and upon heating these ferrites at 1 200 °C for 2 h under the oxygen pressure appropriate for formation of stoicheiometric molybdenum-bearing ferrites (●), expressed in terms of FeO, Fe_2O_3, and MoO_2. The value for a solid solution of Fe_3O_4–Fe_2MoO_4 is given by the straight line

are formed.[1,6] The lattice constants of the spinel-type compounds increased with increasing r_{Mo},[7] and chemical analysis of such compounds separated from the molybdenum hydroxide precipitate upon aeration at pH 11.0 and 65 °C[1] showed that the molybdenum content (Mo:Fe$_{tot.}$ mol ratio) increased from 0.012 to 0.114:1 with increasing r_{Mo} from 0.015:1 to 0.300:1. These results suggest that the spinel-type compounds are molybdenum-bearing ferrites.

The average chemical compositions of the molybdenum-bearing ferrites were calculated from the iron(II) contents (Fe^{II}:Fe$_{tot.}$ mol ratio) as estimated by use of equation (1). After

Iron(II) content = [Content of (Fe^{II} + Mo$^{\leq V}$) in the suspension after completion of the oxidation reaction] − [(content of Mo in the Mo-bearing ferrite) × 2] − [(content of Mo in the hydroxide precipitate after completion of the oxidation reaction) × 2.5] (1)

completion of the oxidation reaction at pH 9.0 and 65 °C all the iron was incorporated in the molybdenum-bearing ferrites. The first term in equation (1) represents the sum of the contents of Fe and Mo in the molybdenum-bearing ferrites and the molybdenum hydroxide precipitate. The second and third terms represent the amounts of Fe^{III} reduced by Mo in the molybdenum-bearing ferrites and hydroxide precipitate, respectively. As described later, x.p.s. suggested that the valence state of Mo in the molybdenum-bearing ferrites is +4. During the oxidation reaction, the average valency of Mo in the hydroxide precipitate was assumed to be that of Mo in the hydroxide precipitate contained in the initial suspension (3.5). Figure 2 (open circles) shows the average chemical compositions for the ternary system FeO, Fe_2O_3, and MoO_2. As shown, the average chemical compositions of the molybdenum-bearing ferrites formed in the iron hydroxide suspension upon air oxidation are 10—15% lower in FeO than those of stoicheiometric molybdenum-bearing ferrites. After complete dissolution of the molybdenum hydroxide precipitate in the suspension upon aeration at pH 11.0 and 65 °C, the molybdenum-bearing ferrites obtained were heated at 1 200 °C for 2 h under the oxygen pressure appropriate for preparation of stoicheiometric molybdenum-bearing ferrites.[6] The molybdenum-bearing ferrites are thus reduced and the average chemical compositions move along the oxygen reaction lines

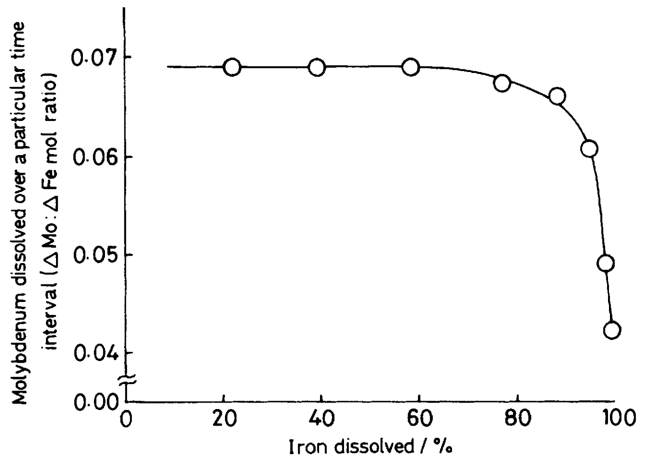

Figure 3. Release of Mo and Fe during the dissolution of molybdenum-bearing ferrite particles obtained by air-oxidation at an initial Mo:$Fe_{tot.}$ mol ratio 0.100:1

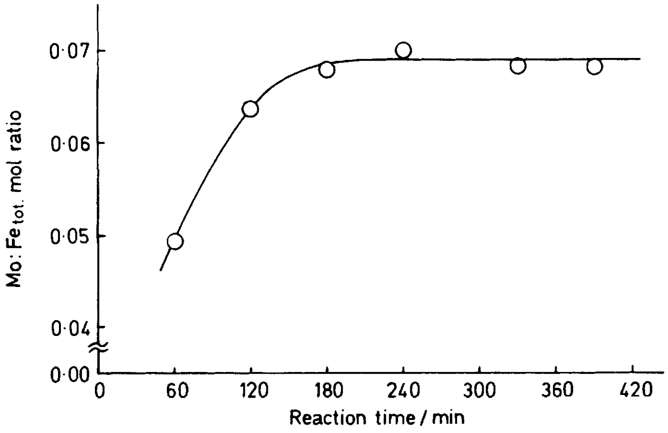

Figure 4. Change of Mo:$Fe_{tot.}$ mol ratio in the molybdenum-bearing ferrites formed during the air-oxidation reaction at an initial Mo:$Fe_{tot.}$ mol ratio of 0.100:1

(which are parallel to the FeO—Fe_2O_3 line) to points on the Fe_3O_4—Fe_2MoO_4 line (Figure 2, closed circles). These facts suggest that oxidized molybdenum-bearing ferrites, of composition $Fe_{2.95-x}Mo_xO_4$ (x = 0.03—0.30), are formed upon air oxidation of iron hydroxide suspensions, in the presence of molybdenum(VI) ions.

Distribution of Molybdenum Ions in the Molybdenum-bearing Ferrite Particles.—In order to determine this distribution, the particles obtained by air oxidation of an iron hydroxide suspension at r_{Mo} = 0.100:1 were dissolved in 1.0 mol dm^{-3} hydrochloric acid solution (sodium chloride concentration 1 mol dm^{-3}) and the amounts of Mo and Fe dissolved with time were determined. From these data, the percentage of the total Fe dissolved at a particular time and the amount of Mo dissolved over a particular time interval (ΔMo:ΔFe mol ratio) were calculated and are plotted in Figure 3. The abscissa of this plot also represents the percentage dissolution of a particle from its surface towards the centre.[8] Figure 3 shows that the molybdenum content in the centre of the molybdenum-bearing ferrite particle is very low.

The molybdenum-bearing ferrites formed during the oxidation reaction were separated by dissolving the hydroxides of Mo and Fe with 0.5 mol dm^{-3} hydrochloric acid solution (sodium chloride concentration 1 mol dm^{-3}) under nitrogen (dissolution time 1 h). During the dissolution process, 10% of the ferrite particles were also dissolved from the surface towards the centre, but as shown in Figure 3 the average chemical composition of the particle was unaltered, within experimental error. The molybdenum contents (Mo:$Fe_{tot.}$ mol ratio) in the molybdenum-bearing ferrites are plotted against the oxidation reaction time in Figure 4. The Mo:$Fe_{tot.}$ mol ratio increases abruptly at the beginning of the oxidation reaction and then reaches a constant value. Electron micrographs of molybdenum-bearing ferrites formed at the beginning of the oxidation reaction showed that the particle size was very small. These results suggest that the distribution of Mo in the molybdenum-bearing ferrite particle described above is closely related to the process of formation of the ferrite.

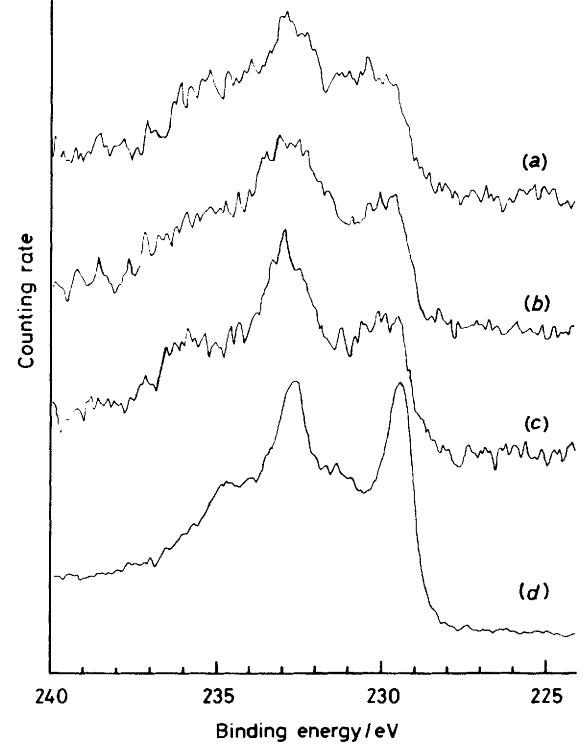

Figure 5. X.p.s. spectra of the Mo 3*d* electrons from the molybdenum-bearing ferrite obtained by the air-oxidation reaction at an initial Mo:$Fe_{tot.}$ mol ratio of 0.100:1 (*a*), after sputtering with Ar^+ ions, for 1 (*b*) and 2 h (*c*), and from MoO_2 (*d*)

The Valence State of Molybdenum in the Molybdenum-bearing Ferrite.—It was suggested previously[6] that Mo is in the valence state of +4 in the lattice of molybdenum-bearing ferrites formed in a solid state reaction. We have investigated the valence state of Mo in the present molybdenum-bearing ferrites by *X*-ray photoelectron spectroscopy (x.p.s.).

The surface of molybdenum-bearing ferrite particles obtained upon aeration at pH 11.0 and 65 °C after completion of the oxidation reaction was cleaned by dissolution in 0.5 mol dm^{-3} hydrochloric acid solution for 1 h, and then by twice washing in 0.1 mol dm^{-3} sodium hydroxide solution for 10 min under nitrogen. The γ-Fe_2O_3 and molybdenum oxide films on the surface of the ferrite particles are thus dissolved. After washing in water under nitrogen, the sample was coated on a sample holder for x.p.s. measurement and was dried in vacuum at room

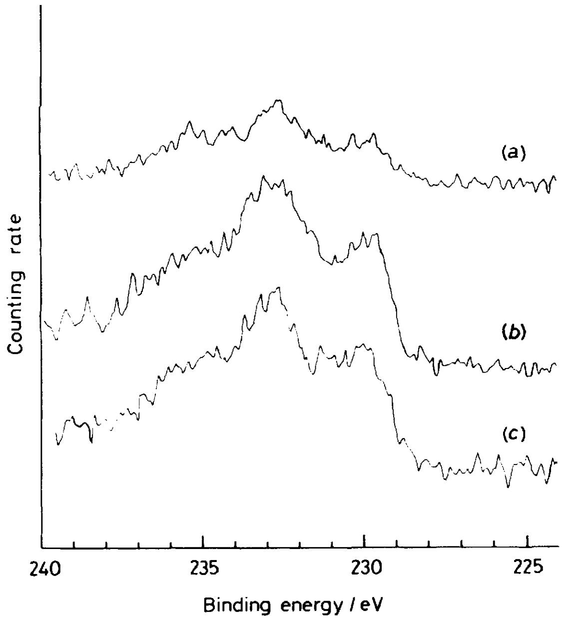

Figure 6. X.p.s. spectra of the Mo $3d$ electrons from the molybdenum-bearing ferrites obtained by air oxidation at initial Mo:$Fe_{tot.}$ mol ratios of 0.060:1 (*a*), 0.100:1 (*b*), and 0.300:1 (*c*). Samples were sputtered with Ar^+ ions for 1 h

temperature. Figure 5 shows the Mo $3d$ x.p.s. spectra for the molybdenum-bearing ferrite formed from the iron hydroxide suspension at $r_{Mo} = 0.100:1$. The spectrum for MoO_2 also is shown [Figure 5(*d*)] as a reference for Mo^{4+}. Spectrum (*a*) shows broad and unresolved peaks, due to Mo^{4+} $3d_{\frac{5}{2}}$ (230.3 eV), Mo^{4+} $3d_{\frac{3}{2}}$ (232.7 eV), Mo^{6+} $3d_{\frac{5}{2}}$ (232.7 eV), Mo^{6+} $3d_{\frac{3}{2}}$ (235.3 eV), and Mo^{5+} $3d$. The spectra (*b*) and (*c*) show the Mo $3d$ spectra for the molybdenum-bearing ferrite sputtered with Ar^+ ions for 1 (*b*) and 2 h (*c*) in the spectrometer to clean the surface. The intensities of the peaks for Mo^{5+} and Mo^{6+} $3d$ electrons decrease and the peaks for Mo^{4+} $3d_{\frac{5}{2}}$ are clearly resolved. This shows that the peaks for Mo^{5+} and Mo^{6+} $3d$ electrons arise from molybdenum-(V) and -(VI) contaminants on the surface of the ferrite samples.

The x.p.s. spectra for the Mo $3d$ electrons from the ferrites (after sputtering with Ar^+ ions for 1 h) formed at $r_{Mo} = 0.060$, 0.100, and 0.300:1 are shown in Figure 6. They show clearly resolved peaks for Mo^{4+} $3d_{\frac{5}{2}}$ electrons (229.7—230.0 eV). The areas of these peaks were estimated as described previously.[6] The peak area ratio standardized to the peak area for the ferrite formed at $r_{Mo} = 0.300:1$ (0.38:0.63:1) was in good agreement with the corresponding ratio of the molybdenum contents (0.40:0.63:1). These facts suggest that the x.p.s. spectra originate from molybdenum ions in a lattice of the spinel type, that is, these ions are in the valence state of +4.

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