© *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57, 2820—2823 (1984)* [Vol. 57, No. 10

Cadmium(II)-, Magnesium(II)-, and Zinc(II)-bearing Ferrites Formed from γ-FeOOH at Various Reaction pH's

Kazuo ITO,[*,†] Yutaka TAMAURA, and Takashi KATSURA
Department of Chemistry, Tokyo Institute of Technology Ookayama, Meguro-ku, Tokyo 152

(Received November 21, 1983)

The reaction of γ-FeOOH with the metal (Cd(II), Mg(II), or Zn(II)) and Fe(II) ions in solution gave the metal ion-bearing ferrites without oxidation. The ferrites obtained were the stoichiometric Mg(II)- and Zn(II)-bearing ferrites [$Mg_{0.27}Fe_{2.73}O_{4.00}$ (pH 10.6), $Zn_{0.38}Fe_{2.61}O_{4.00}$ (pH 10.5)] at pH 7.5—11.4, and the nonstoichiometric Cd(II)-bearing ferrites [$Cd_{0.19}Fe_{2.68}O_{4.00}$ (pH 10.2)] at pH 7.5—10.5 (25 °C). The Cd(II)- and Mg(II)-ion content in the ferrites increases with an increase in the reaction pH, but the Zn(II)-ion content is almost constant at pH 7.5—10.5. This pH dependence of the metal-ion content in the ferrites agrees with that of the fractional adsorption of these metals on γ-FeOOH. This suggests that only the adsorbed metal ions are incorporated into the ferrites. The pH dependence of these metal-ion contents in the air-oxidation reaction is also similar to that in the transformation reaction from γ-FeOOH. This transformation reaction seems to be one process in the air-oxidation reaction.

The formation of metal ion-bearing ferrites in solution by the air-oxidation of a $Fe(OH)_2$ suspension in the presence of other metal ions at temperatures above 60°C has previously been studied.[1–11] The reaction pH affects the amount of metal ions incorporated into the ferrites.[5–7] Recently, we found that γ-FeOOH is transformed to Fe_3O_4 in the presence of the Fe(II) ion.[12,13] This transformation reaction is triggered by the adsorption of the Fe(II) ion on γ-FeOOH.[13] In the presence of Fe(II) and Zn(II) ions, γ-FeOOH is transformed to Zn(II)-bearing ferrites.[14] We proposed that the Zn(II) ions were adsorbed on γ-FeOOH and subsequently incorporated to form the Zn(II)-bearing ferrites.[14,15] It seems likely that any ferrite would be formed from γ-FeOOH in the presence of Fe(II) and other metal ions. In the present experiment, we have investigated the formation of Cd(II)-, Mg(II)-, and Zn(II)-bearing ferrites from γ-FeOOH at various reaction pH's; we will also discuss briefly the pH effect of the metal-ion contents in the ferrites, in relation to the adsorption of the metals on γ-FeOOH.

Experimental

Chemicals. All the chemicals used in the present work were of an analytical grade, and the chemical solutions were prepared by the use of distilled water. The NaOH solution was prepared by the use of distilled water through which nitrogen gas had been passed to remove any dissolved oxygen. The γ-FeOOH was prepared according to a method described previously.[13]

Apparatus. The reaction vessel which had been used in a previous paper was adopted.[1]

Procedure. After adding a M(II) (M=Cd, Mg, or Zn)-ion solution (0.02 dm³, 0.27 mol/dm³, pH 3.0) to the γ-FeOOH suspension (0.75 dm³, pH 4.0), nitrogen gas was passed through for 2 h to remove any dissolved oxygen and carbon dioxide. $FeCl_2$ solution (0.02 dm³, 0.54 mol/dm³. pH 3.0) was then added to the suspension, and the pH was raised to the desired value. When the pH became the desired value (7.5—11.4), the reaction was initiated and the reaction pH became lower. The reaction pH was kept constant by adding an alkaline solution. During the reaction, nitrogen gas was passed through the suspension to prevent any oxidation reaction. After the reaction has continued for 60 h (25°C), the reaction suspension was centrifuged at 4000 rpm under a nitrogen atmosphere. The precipitate was then washed with an acetate buffer solution (pH 4.1, 0.05 mol/dm³) to isolate the products by dissolving the unreacted Fe(II) and M(II) ions. The precipitate was washed further with distilled water and then with acetone to remove the water as completely as possible. The washing water and acetone had been deaerated by passing nitrogen gas through to prevent oxidation. Finally, the precipitate was dried under a nitrogen atmosphere (room temperature). The products thus obtained were examined by means of X-ray diffractometry, IR spectroscopy, and Mössbauer spectroscopy.

Metal-ion Adsorption on γ-FeOOH. Into a 1.0-dm³ polyethylene beaker, 0.8 dm³ of a γ-FeOOH suspension containing the M(II) ion (iron of γ-FeOOH: 10 mmol, M(II)-ion concentration: 5×10^{-5} mol/dm³, NaCl concentration: 6×10^{-5} mol/dm³) was transferred. The suspension temperature was maintained at 25±0.2°C, and nitrogen gas was passed through the suspension to remove the carbon dioxide and to stir the suspension. When the suspension pH became constant after adding an alkaline solution, 0.01 dm³ of the suspension was taken out by means of a syringe and immediately filtered using a Millipore filter (pore size; 220 nm). The M(II)-ion concentration in the filtrate was measured by means of an atomic-absorption method (Varian Techtron, AA 875 type).

Chemical Analysis. The Fe(II) and Fe_{total} concentrations were determined by the 2,2′-bipyridyl method.[16] When the Fe_{total} was determined, the Fe(III) ion was reduced to the Fe(II) ion with hydroxylamine.

Results and Discussion

X-Ray Diffraction Patterns, IR and Mössbauer Spectra, Chemical Compositions and Lattice Constants. In the present study, the mole ratio among the Fe(II) ion, the M(II) ion (M=Cd, Mg, or Zn), and γ-FeOOH (as Fe) in the initial suspension was fixed at 1:2:2. This reaction was initiated by adding the Fe(II) ion. However, the reaction rate was extremely slow at pH values below 7, and no reaction at all occurred at pH values below 6.5. Therefore, in the present paper, no data will be given for pH values below 6. As has been reported previously,[13] the Fe(II) ion is adsorbed on γ-FeOOH at pH values above around 6.8, and the γ-FeOOH is transformed to Fe_3O_4 by the adsorption of the Fe(II) ion on γ-FeOOH. These results suggest that

---

[†] Present address: Toshiba Corporation, R & D Center, 1 Komukai, Saiwai-ku, Kawasaki 210

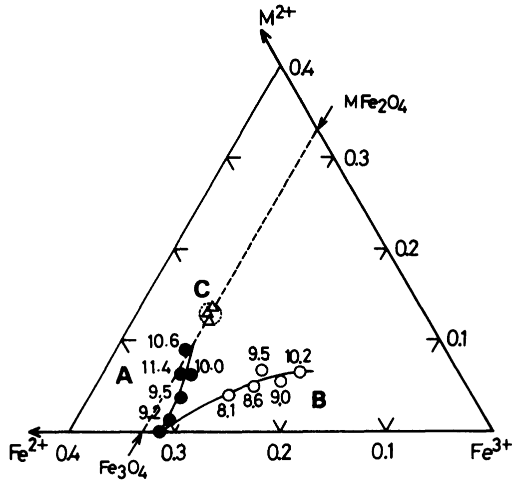

Fig. 1. Ternary diagram showing the chemical compositions of Mg(II)-bearing ferrites(A), Cd(II)-bearing ferrites(B), and Zn(II)-bearing ferrites(C). The values given at the points indicate the reaction pH. M^{2+} means the metal ions of Mg(II), Cd(II), or Zn(II).

the reaction in the present work also proseeds by means of the adsorption of the Fe(II) ion on γ-FeOOH. In the X-ray diffraction patterns of the products, only the peaks of the spinel-type compound appeared. In the IR spectra, no bands of γ-FeOOH or other iron (III) oxides were observed, but bands of ferrites were observed. These results indicate that the γ-FeOOH was completely transformed to ferrites. All the lines of the Mössbauer spectra were assigned to ferrites, as will be described below.

Figure 1 shows the chemical compositions of the ferrites formed at various reaction pH's. The values given at the points for Curves A and B are the reaction pH values. The small region denoted by C represents the chemical compositions of the Zn(II)-bearing ferrites. The Zn(II) ion contents in the ferrites remain nearly constant at various reaction pH values, and their compositions are included in the small region. The straight line (broken line) connecting Fe_3O_4 and MFe_2O_4 corresponds to the stoichiometric chemical compositions of M(II)-bearing ferrites ($M_{1-x}Fe_{2+x}O_4$). As can be seen from Fig. 1, the chemical compositions of the Zn(II)- and Mg(II)-bearing ferrites (A and C) are nearly stoichiometric, but those of the Cd(II)-bearing ferrites (B) deviate fairly much from stoichiometry [$Cd_{0.19}Fe_{2.68}O_{4.00}$ (pH 10.2)]. The deviation increases with an increase in the Cd(II)-ion content in the ferrite. This suggests that vacant sites of the Cd(II)-bearing ferrites increase with an increase in the Cd(II) content in the ferrites. The nonstoichiometric Cd(II)-bearing ferrites were also formed in the air-oxidation reaction,[6] so the Cd(II)-bearing ferrites seem to be oxidized easily. These may cause the nonstoichiometry of the Cd(II)-bearing ferrites. The relationship between the M(II)-ion content in the ferrites and the reaction pH will be described later.

Figure 2 gives the room-temperature Mössbauer spectra of the M(II)-bearing ferrites with the highest M(II)-ion content. Spectrum a corresponds to the Fe_3O_4 formed from γ-FeOOH. The spectra of the Fe_3O_4 and the Mg(II)-bearing ferrites show two distinct hyperfine patterns; one is due to the tetrahedral Fe(III) ions (A site), and the other, to the octahedral Fe(III) and Fe(II) ions (B site). The line intensities at the B site for the Mg(II)-bearing ferrites are lower than those for the Fe_3O_4. This indicates that the Mg(II) ion is incorporated into the B site of the ferrites. The spectrum of the Zn(II)-bearing ferrite (Spectrum c) shows two broadened Zeeman patterns and a quadrupole doublet. Dobson *et al.*[17] reported that the Zn(II)-bearing ferrite ($Zn_{0.6}Fe_{2.4}O_{4.0}$) formed by a solid-state reaction had a similar pattern in its spectrum. The Zn(II)-bearing ferrites from γ-FeOOH seem to have the same ionic distribution as those produced by the soild-state reaction. The spectra of the Cd(II)-bearing ferrites (Spectrum d) show six broadened absorption lines. This broadening may come from the nonstoichiometry and/or the Cd(II)-ion incorporation into the spinel structure.

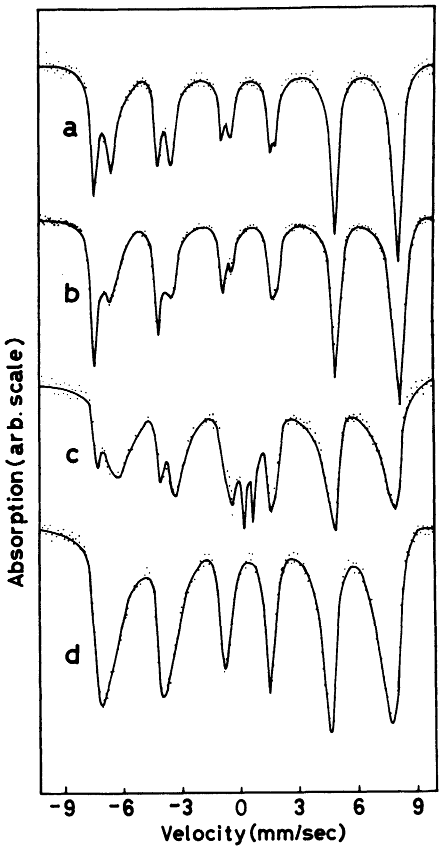

Fig. 2. Room temperature Mössbauer spectra of magnetite formed from γ-FeOOH(a), Mg(II)-bearing ferrite (b), Zn(II)-bearing ferrite (c), and Cd(II)-bearing ferrite (d). The chemical compositions of the ferrites are $Fe_{2.93}O_{4.00}$ (a), $Mg_{0.27}Fe_{2.73}O_{4.00}$ (b), $Zn_{0.38}Fe_{2.61}O_{4.00}$ (c), and $Cd_{0.19}Fe_{2.68}O_{4.00}$ (d) respectively.

The lattice constant of the Zn(II)-bearing ferrite with the highest Zn(II) content in Fig. 1 ($Zn_{0.38}Fe_{2.61}O_{4.00}$) was 0.8416 nm. This higher value of the lattice constant than that of Fe_3O_4 (0.8397 nm)[18] confirms the incorporation of the Zn(II) ion into the lattice point by replacing the Fe(II) ion in Fe_3O_4 with the Zn(II) ion. The lattice constant of the Mg(II)-bearing ferrite with the highest Mg(II)-ion content in Fig. 1 ($Mg_{0.27}Fe_{2.73}O_{4.00}$)

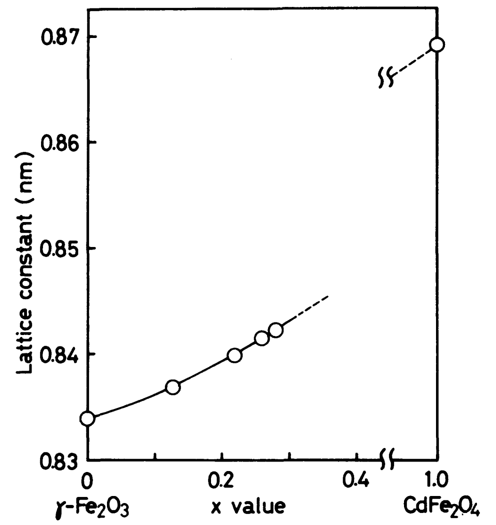

Fig. 3. The relationship between the lattice constants and the x values of the completely oxidized Cd(II)-bearing ferrites. The x values represent the mole ratio of $CdFe_2O_4$ to ($CdFe_2O_4$+γ-Fe_2O_3).

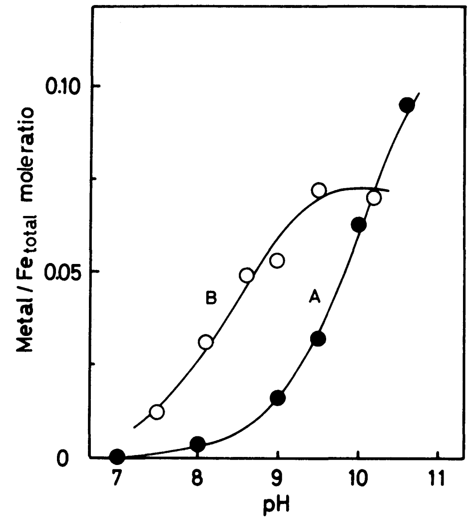

Fig. 4. pH dependence on the metal ion contents incorporated into Mg(II)-bearing ferrites (A) and Cd(II)-bearing ferrites (B).

was 0.8388 nm, slightly lower than that of Fe_3O_4. The lattice constant of $MgFe_2O_4$ (0.8387 nm)[19] is near to that of Fe_3O_4; therefore, the lattice constant probably is not so greatly changed by replacing the Fe(II) ion in Fe_3O_4 with the Mg(II) ion. The Cd(II)-bearing ferrites were nonstoichiometric; they formed a solid solution among Fe_3O_4, γ-Fe_2O_3,and $CdFe_2O_4$, so the lattice constant is determined by means of these three components. To simplify the analysis of the lattice constants, the component number of the nonstoichiometric Cd(II)-bearing ferrites in Fig. 1 was reduced to two (a solid solution between γ-Fe_2O_3 and $CdFe_2O_4$) by oxidizing the ferrites. The Cd(II)-bearing ferrites are readily oxidized at 150 °C for 2 d, since their particle size is small (100—200 nm). Figure 3 shows the relationship between the lattice constant and the mole fraction x of the $CdFe_2O_4$ component in the solid solution between γ-Fe_2O_4 and $CdFe_2O_4$. The lattice constant of γ-Fe_2O_3 and $CdFe_2O_4$ were determined by Schrader and Büttner[20] and by Roberts and Merwin[21] respectively. The lattice constants of the oxidized Cd(II)-bearing ferrites fall between those of γ-Fe_2O_3 and $CdFe_2O_4$. This confirms the incorporation of the Cd(II) ion into the lattice structure of the ferrites.

pH Effect of M(II)-ion Contents in Ferrites. Figure 4 shows the relationship between the Mg(II) and Cd(II) ion contents in the ferrites, and the reaction pH. As may be seen in Fig. 4, the Mg(II) (Curve A)- and Cd(II) (Curve B)-ion contents increase with an increase in the reaction pH. The Zn(II)-ion content remained almost constant, as has been mentioned above. Next, we compared this result (Fig. 4) with the adsorption of M(II) on γ-FeOOH at various pHs. Figure 5 shows the relationship between the fractional adsorption of M(II) and the solution pH. Curves A, B, and C are fractional adsorptions of Mg(II), Cd(II), and Zn(II) respectively. All of them increase from near nil to near 100% with an increase in the pH. The pH regions of the pH-adsorption edges (the sharp rise of the curves) for Zn(II), Cd(II), and Mg(II) increase in this order. Over the pH values from pH 7 to 11, where the ferrites are formed from γ-FeOOH, this adsorption behavior is quite similar to the incorporation profiles against the pH. The pH regions of the pH-adsorption edges fit those of the pH-incorporation edges for the Cd(II) and Mg(II) ions (Fig. 4). Measures, the adsorbed amount and the incorporated amount of Zn(II) both remain constant in this pH region. This strongly suggests that the metals are adsorbed on γ-FeOOH, and then subsequently incorporated to form the metal ion-bearing ferrites. The air oxidation of an $Fe(OH)_2$ suspension containing metal ions brings about the formation of the metal ion-bearing ferrites.[1—11] In previous reports,[12—15] we have suggested that the air-oxidation reaction involves a process in which the γ-FeOOH-layer is formed on the Fe_3O_4 by the oxidation of the adsorbed Fe(II) ion. The Fe_3O_4 particles will grow by the repetition of these processes during the air oxidation. When the other metal ion is present in the reaction suspension, the metal ion will be adsorbed along with the Fe(II) ion on the γ-FeOOH-layer, and the γ-FeOOH will be transformed into the metal

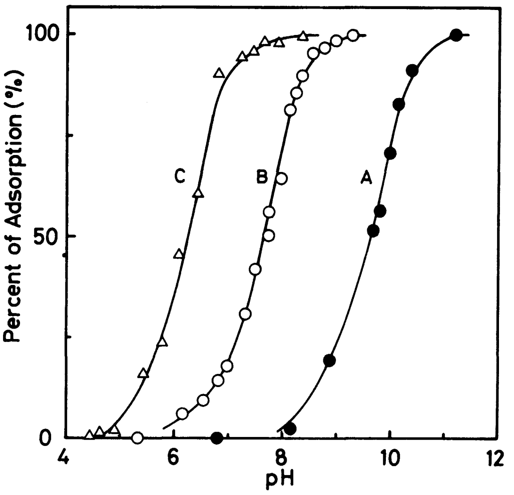

Fig. 5. Fractional adsorption of Mg(II) (A), Cd(II) (B), and Zn(II) (C) on γ-FeOOH as a function of pH.

ion-bearing ferrites on the surface. For Cd(II), Mg(II), and Zn(II) ions, the pH dependence of their contents, as incorporated into the ferrites in the air-oxidation reaction(5–7), is very similar to the results in the present study (Fig. 4 and 5). These results suggest the validity of the above discussion.

References

1) T. Katsura, Y. Tamaura, and G. S. Chyo, *Bull. Chem. Soc. Jpn.*, **52**, 96 (1979).

2) Y. Tamaura and T. Katsura, *J. Chem. Soc., Dalton*, **1980**, 825.

3) Y. Tamaura, S. Mechaimonchit, and T. Katsura, *J. Inorg. Nucl. Chem.*, **43**, 671 (1981).

4) Y. Tamaura, U. Rasyid, and T. Katsura, *J. Chem. Soc., Dalton*, **1980**, 2125.

5) K. Kaneko and T. Katsura, *Bull. Chem. Soc. Jpn.*, **52**, 747 (1979).

6) K. Kaneko, T. Takei, Y. Tamaura, T. Kanzaki, and T. Katsura, *Bull. Chem. Soc. Jpn.*, **52**, 1080 (1979).

7) T. Kanzaki, J. Nakajima, Y. Tamaura, and T. Katsura, *Bull. Chem. Soc. Jpn.*, **54**, 135 (1981).

8) K. Ito, T. Kanzaki, Y. Tamaura, and T. Katsura, *J. Chem. Soc., Dalton*, **1981**, 2217.

9) T. Kanzaki, H. Furukawa, and T. Katsura, *J. Chem. Soc., Dalton*, **1983**, 1197.

10) Y. Tamaura, T. Kanzaki, and T. Katsura, Proc. Third Int. Conf. on Ferrites, Kyoto (1980), p. 15.

11) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **51**, 134 (1978).

12) Y. Tamaura, P. V. Buduan, and T. Katsura, *J. Chem. Soc., Dalton*, **1981**, 1807.

13) Y. Tamaura, K. Ito, and T. Katsura, *J. Chem. Soc., Dalton*, **1983**, 189.

14) K. Ito, Y. Tamaura, and T. Katsura, *J. Chem. Soc., Dalton*, **1983**, 987.

15) Y. Tamaura, Y. Kobori, and T. Katsura, *Nippon Kagaku Kaishi*, **1983**, 1433.

16) I. Iwasaki, T. Katsura, T. Ozawa, M. Mashima, H. Haramura, and B. Iwasaki, *Bull. Volc. Soc. Jpn., Ser. II*, **5**, 75 (1960).

17) D. C. Dobson, J. W. Linnett, and M. M. Rahman, *J. Phys. Chem. Solids*, **31**, 2727 (1970).

18) X-ray Data Card, 19-629, Powder Diffraction File, Joint Committee on Powder Diffraction Standards (JCPDS).

19) P. P. Kirichok, L. G. Kustovskii, G. S. Podvalnykh, M. A. Shamanov, and V. P. Bibik, *Bull. Acad. Sci. USSR, Phys. Ser.*, **38**, 618 (1974).

20) R. Schrader and G. Büttner, *Z. Anorg. Allg. Chem.*, **320**, 205 (1963).

21) H. S. Roberts and H. E. Merwin, *Am. J. Sci.*, **21** 145 (1931).