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Effects of silicate and phosphate ions on the formation of ferric oxide hydroxide particles

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The effects of silicate and phosphate ions on the formation of α- and β-FeOOH particles were studied. The formation and crystallization of α-FeOOH particles were inhibited by both the anions, and their particle size decreased with increasing concentration of the anions added. This inhibition was caused not only by complexing with ferric ions but also by adsorption on the particle surface. For α-FeOOH the amorphous particles were formed at a higher concentration of these anions. On the other hand, in the case of β-FeOOH the effects of both the anions were little, especially for silicate ions. This difference between α- and β-FeOOH particles could be explained by the difference between their preparation pH. The α-FeOOH particles prepared in the presence of these anions showed a microporosity.

1. Introduction

Numerous studies have been done on the preparation method of the ferric oxide hydroxide particles which are uniform in both shape and size [1–10]. In these studies, the composition and morphology of these solids depended on the concentration of the ferric ion, pH, temperature and solvents. Moreover, recently it has been reported that the anions in the solutions play an important role in affecting the nature of the resulting precipitates. In a previous work, we investigated the effects of citrate ions, possessing a high affinity to ferric ions by chelate formation, on the formation and surface properties of α- and β-ferric oxide hydroxides (α- and β-FeOOH, respectively) particles [11]. It was characteristic of the results that some chelating agents have a great affinity on the formation of β-FeOOH particles and cause the selective adsorption of water molecules on the amorphous particles prepared in the presence of more than 10 mol % citrate ions. On the other hand, the effects of phosphate and silicate ions on the crystallization of amorphous ferric hydroxide to α-FeOOH and α-Fe_2O_3 have been reported by several workers [12–15]. However, there has been little investigation of the effects of inorganic anions on both the formation and properties of α-FeOOH. This study describes the influence of the silicate and phosphate ions on the formation and the surface properties of α- and β-FeOOH particles. The results of this study should contribute to controlling the shape and size of ferric oxide hydroxide particles and producing pigments and high-quality powders for magnetic recording.

2. Experimental procedure

The preparations of α- and β-FeOOH were performed as described previously [11]; α-FeOOH particles were prepared by adding 1.0 mol dm^{-3} sodium hydroxide solution to 0.1 mol dm^{-3} ferric nitrate solution containing different amounts of sodium silicate (SiO_2:Na_2O = 3.22:1) or sodium phosphate (Na_3PO_4) up to pH 12 in a polypropyrene screw-capped vessel at room temperature. The resulting precipitates were aged at 30 °C and pH 12 for various periods from 1–10 days. The ageing time of α-FeOOH particles described in this paper was 4 days, unless otherwise stated. The β-FeOOH particles were prepared by the forced hydrolysis of 0.1 mol dm^{-3} ferric chloride solution containing various amounts of sodium silicate or sodium phosphate; 500 ml solution in a 1 dm^3 screw-capped Pyrex bottle were aged in a forced-convection oven with air turbulent circulation at 100 °C for 5 h. The pH of the resulting suspensions was lower than unity at room temperature. The concentration of the anions added was changed from 0 to 2 mol % silicate or phosphate ions to iron ions for the α- and β-FeOOH particles. All the resulting precipitates were thoroughly washed with water and dried in air at 70 °C for 16 h.

The crystal structures and crystallinity of the prepared powders were examined by means of X-ray diffraction (XRD). The average crystallite sizes, L, of the particles were calculated from XRD data using the Scherrer equation. The shape and size of the particles were inspected by TEM. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) measurements were made using a thermal analysis apparatus in air at a heating rate of 5 °C min^{-1}. The specific surface area of the powders was measured using the nitrogen BET method with an automatic volumetric apparatus. Before nitrogen adsorption, the samples were treated under a vacuum of 10^{-2} Pa at 100 °C for 2 h.

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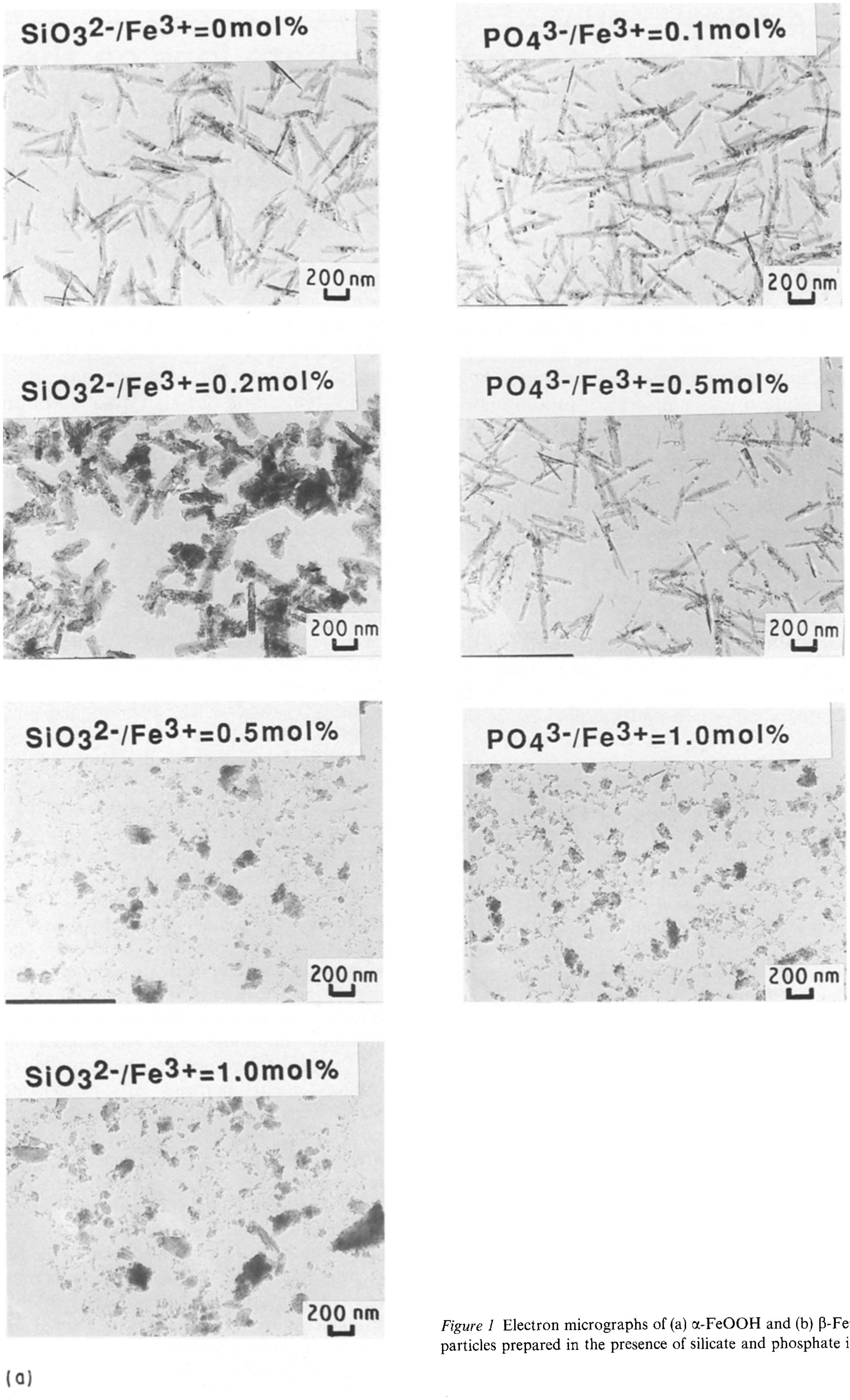


Figure 1 Electron micrographs of (a) α-FeOOH and (b) β-FeOOH particles prepared in the presence of silicate and phosphate ions.

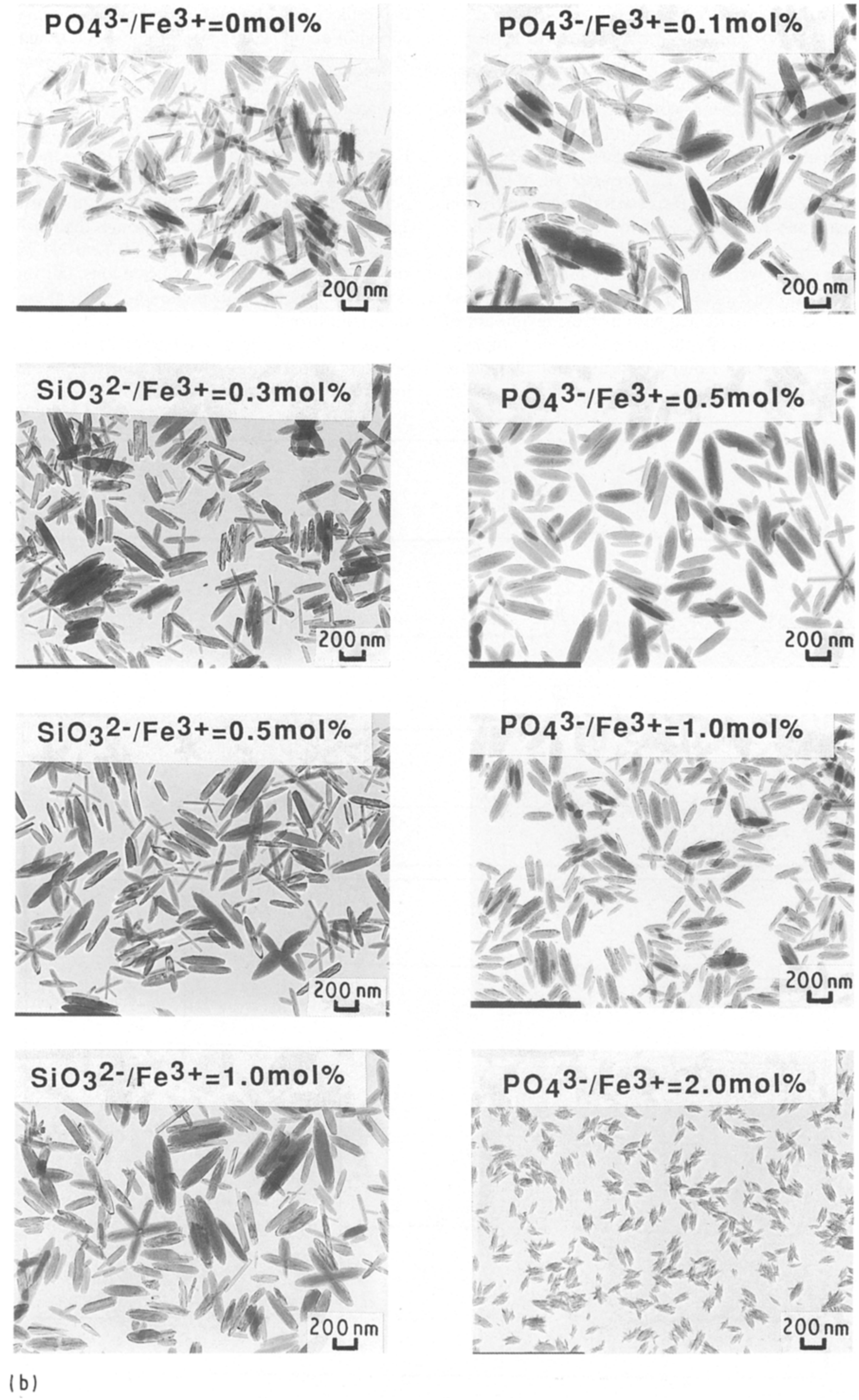


Figure 1 Continued

3. Results and discussion

3.1. Effects of silicate and phosphate ions on particle formation

The electron micrographs of α- and β-FeOOH particles prepared at various concentrations of the anions added are shown in Fig. 1a and b, and the XRD patterns of these particles are shown in Fig. 2a and b. As can be seen in Fig. 1a, the size of α-FeOOH particles decreased with increase in the concentration of silicate and phosphate ions up to 0.5 and 1 mol %, respectively, and above these concentrations very fine particles only were formed. The diffraction peaks characteristic of α-FeOOH, depicted in Fig. 2a, also diminished and broadened with increasing amount of both anions, and finally the particles became amorphous above 0.5 and 1 mol % silicate and phosphate ions, respectively. These XRD results correspond with the results of TEM. On the other hand, no remarkable effects of anions are seen on the β-FeOOH particles. The rod-like particles were formed on adding up to 1 mol % silicate ions (Fig. 1b) and no remarkable change in the XRD patterns was observed (Fig. 2b). In the case of phosphate ions, large needle-like β-FeOOH particles were formed up to 0.5 mol % and their sizes decreased above 1 mol %. But the sharp-pointed needle-like particles were still formed at 2 mol % phosphate ions, even though their sizes were small. The peaks characteristic of β-FeOOH were not changed by the addition of silicate ions, but the addition of >1 mol % phosphate ions made these peaks weak and broad.

Fig. 3 shows the DTA curves of the α-FeOOH powders prepared at various concentrations of silicate ions. The endothermic peak at 200–300 °C, being

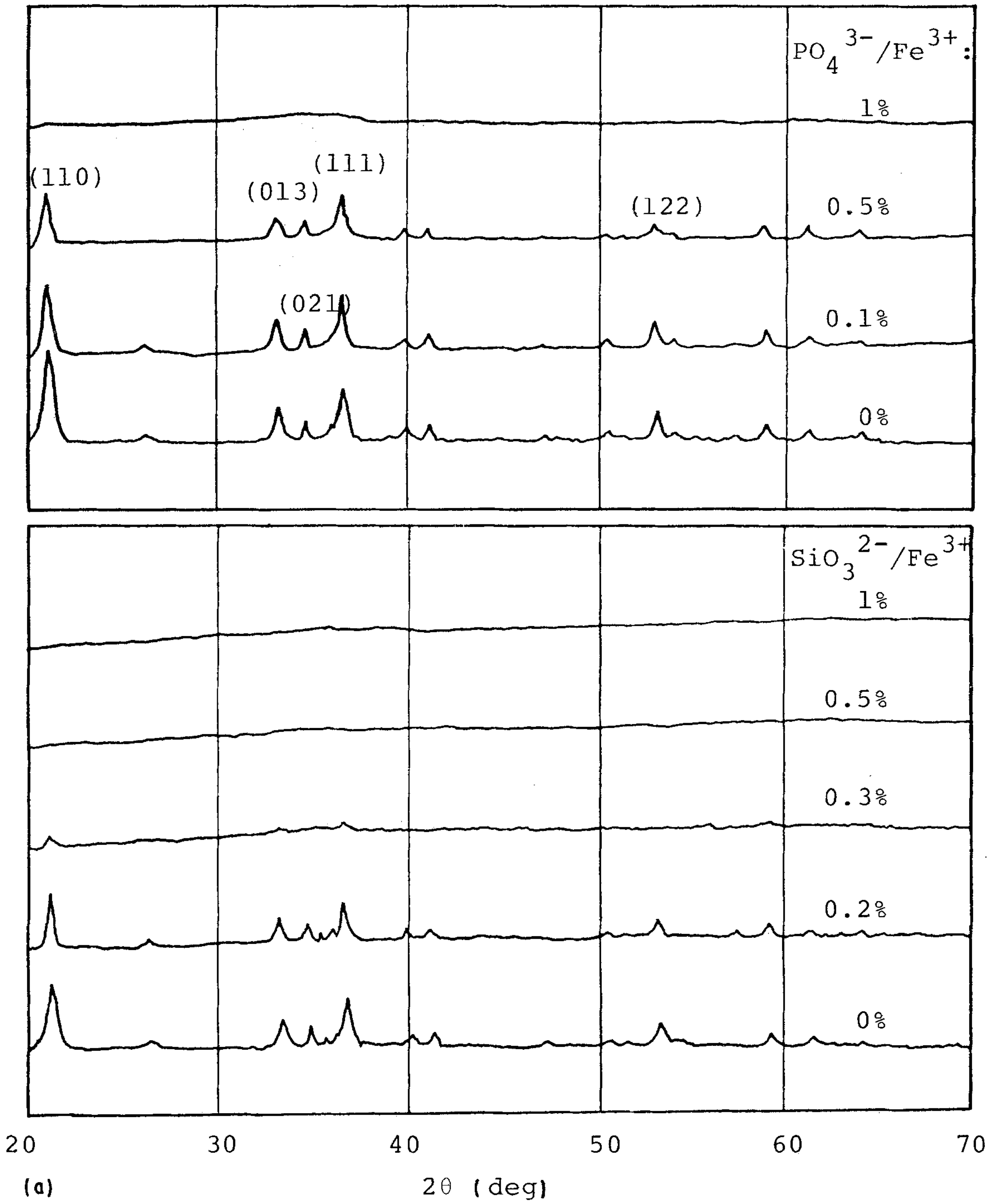


Figure 2 XRD patterns for (a) α-FeOOH and (b) β-FeOOH particles, formed with different amounts of added silicate and phosphate ion

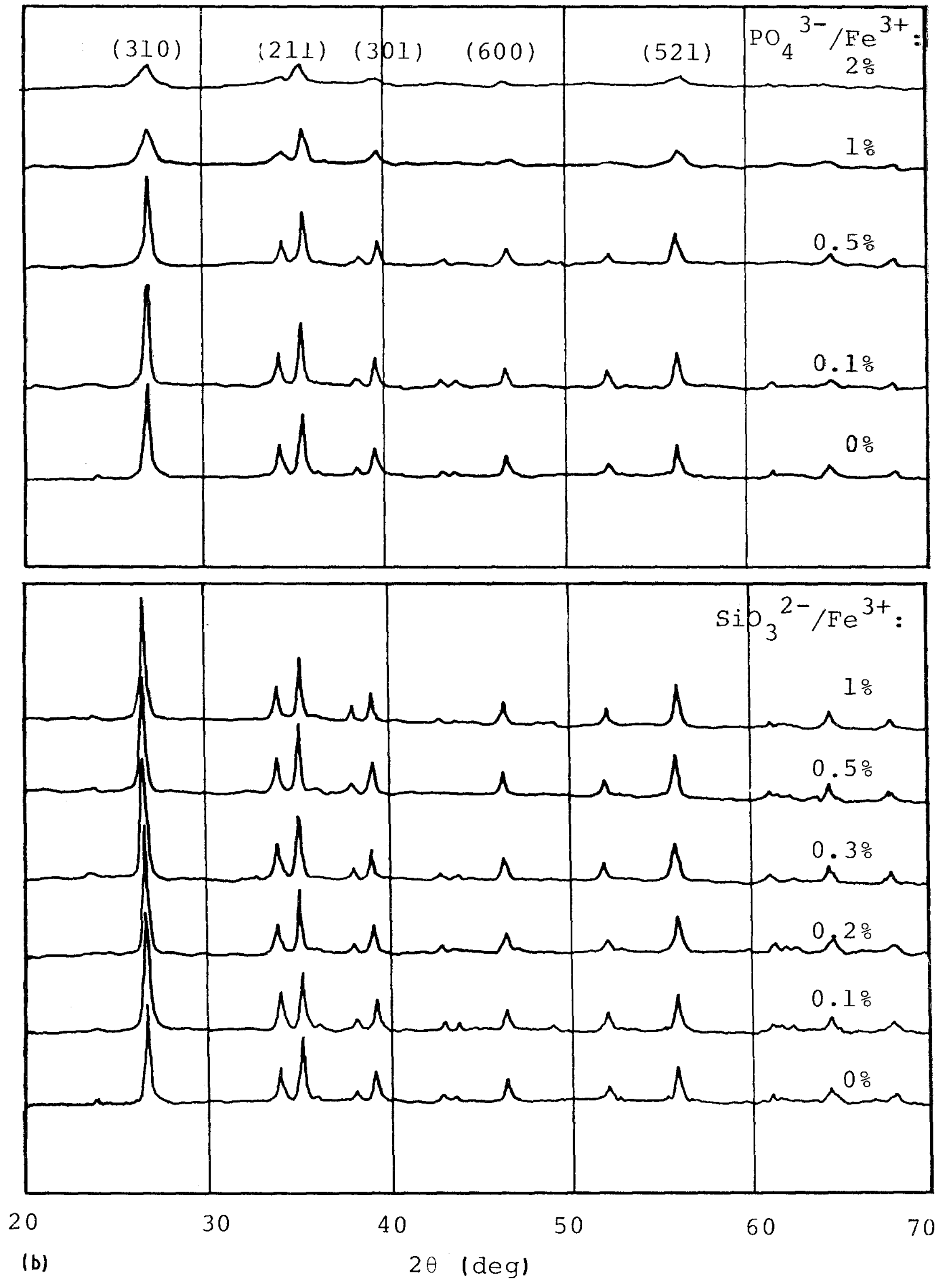


Figure 2 Continued

derived from the phase transformation from α-FeOOH to α-Fe_2O_3, became small on increasing the concentration of silicate ions. Simultaneously, the endothermic peak at 50–70 °C and the exothermic peak at 440–550 °C became progressively greater and shifted to higher temperatures as the amount of silicate ions increased. The former and latter peaks are ascribed to the elimination of adsorbed and/or bound water and the crystallization from the amorphous phase to α-Fe_2O_3, respectively [11, 16]. Similar results were obtained for the DTA curves of α-FeOOH particles formed in the presence of phosphate ions. This result evidently suggests that the growth and crystallization of α-FeOOH particles are obstructed by these anions. On the other hand, the DTA curves of β-FeOOH produced with 1 mol % silicate ions have an endothermic peak at 300 °C and a small exothermic peak at 550 °C, as indicated with a dashed line in Fig. 3. This result indicates that well-crystallized large β-FeOOH particles were still formed in the presence of 1 mol % silicate ions.

Fig. 4 shows the weight loss values of the samples between 100 and 300 °C obtained from TG measurement as a function of added anion concentration. This

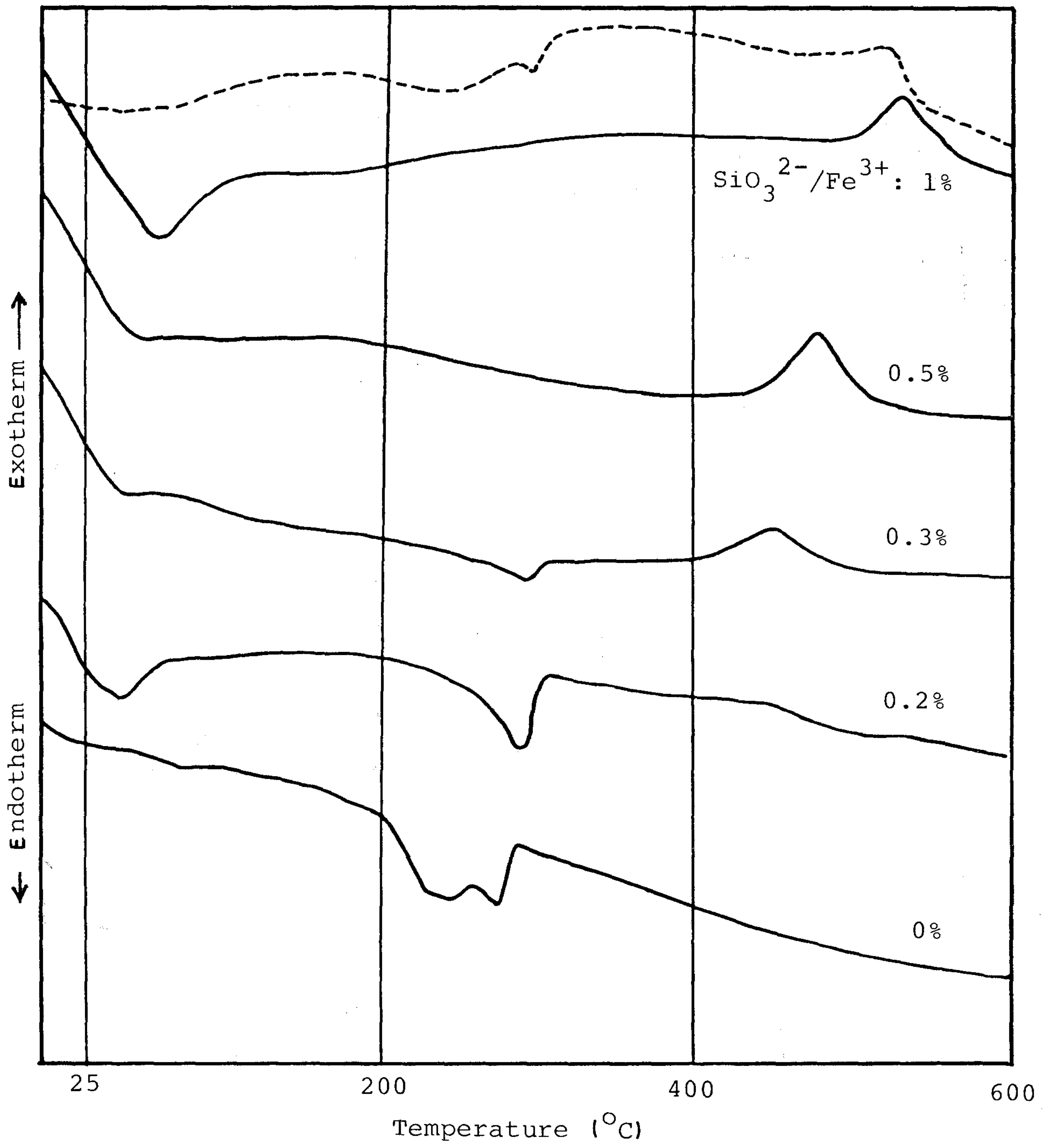


Figure 3 DTA curves of α-FeOOH particles formed with different amounts of silicate ions. (– – –) Result with β-FeOOH particles prepared in the presence of 1 mol % silicate ions.

weight loss is caused by the phase transformation of α- and β-FeOOH to α-Fe_2O_3. The weight loss values of α-FeOOH decreased drastically with increasing concentration of both anions (Fig. 4a). In the case of β-FeOOH, the weight loss values remained almost constant at slightly more than the theoretical dehydration value of 10.1% except for the powder prepared at 2 mol % phosphate ions.

To develop a better understanding of the effects of anions on the formation and crystallization of α- and β-FeOOH, the average crystallite sizes, L, of the (0 2 1) and (1 1 0) planes of α-FeOOH, (L_{021} and L_{110}), and the L_{310} of β-FeOOH were calculated from the XRD patterns. The L values of α- and β-FeOOH particles are shown as a function of added anion concentration in Fig. 5a and b, respectively. The L_{110} value of α-FeOOH remained constant up to 0.2 and 0.5 mol % silicate and phosphate ions added, respectively, and abruptly decreased above these concentrations, though the decrease in L_{021} started from a low concentration for both anions. This result suggests that the particle growth of α-FeOOH along the long axis (*c*-axis) is hindered, while the size along the short axis (*b*-axis) remains constant up to the corresponding mole per cent, because the L_{110} and L_{021} values of α-FeOOH are the measure of the width and length of the long rectangular α-FeOOH plate particles, respectively [17]. In contrast, the L_{310} of β-FeOOH in Fig. 5b rapidly decreased with increase in the concentration of phosphate ions. It can be considered from this result that the particle growth of β-FeOOH along *a*- and *b*-axes is hindered by phosphate ions, because

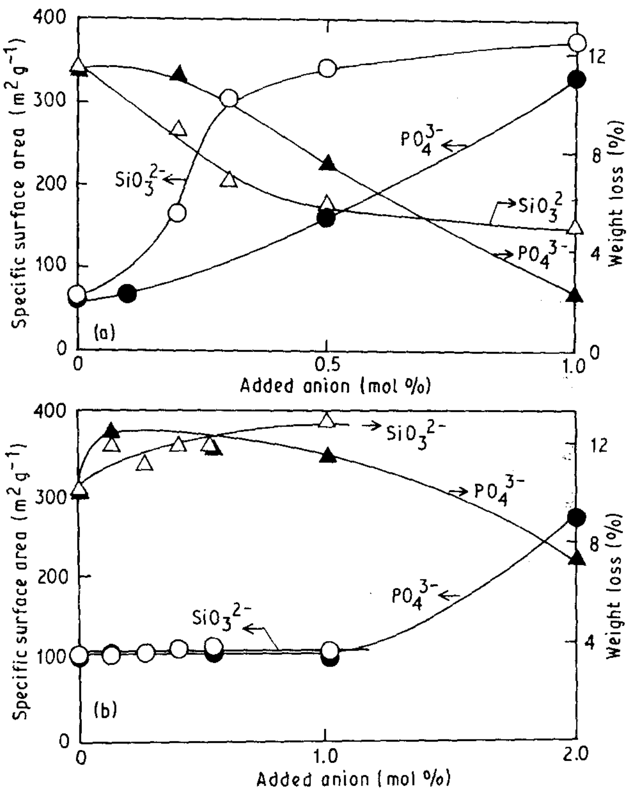


Figure 4 The change of specific surface area, S_n, and weight loss as a function of added anions for (a) α-FeOOH and (b) β-FeOOH.

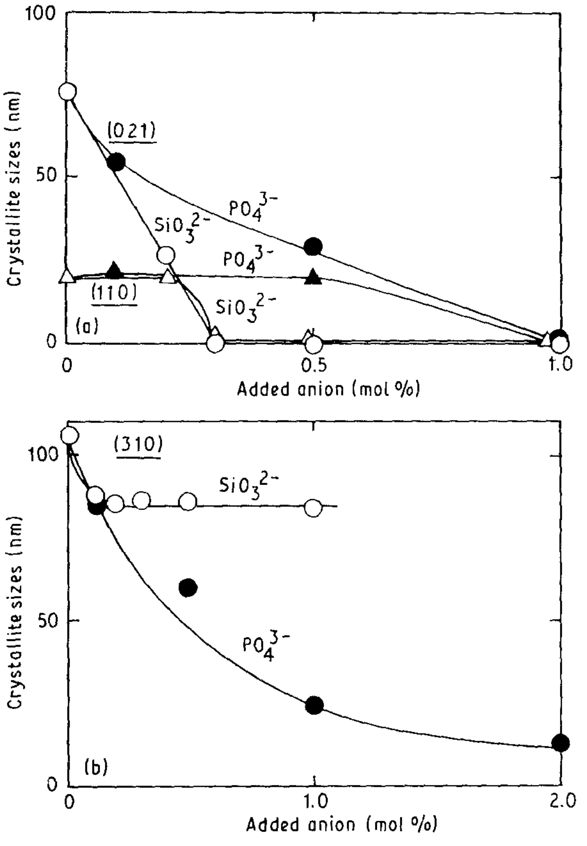


Figure 5 The change of crystallite size as a function of added anions for (a) α-FeOOH and (b) β-FeOOH.

the L_{310} value corresponds to the particle width of the crystalline rod-like β-FeOOH particles elongating along the *c*-axis [18]. However, on adding silicate ions, these effects were not remarkable; the L_{310} of β-FeOOH decreased slightly in the low concentration region and then remained constant, as is seen in Fig. 5b. These results can be supported by the morphology change of the particles in the transmission electron micrographs (Fig. 1).

These different effects of both the anions between α- and β-FeOOH would be due to the difference between the preparation pH of these particles: because the silicate ions exist as monomers at pH 12 [19], the monomer silicate ions form complexes with ferric ions to prevent the hydrolysis reaction to produce α-FeOOH particles. A similar mechanism can be considered for phosphate ions. On the contrary, it has been reported that a soluble complex of silicate monomer–Fe^{3+} and phosphate monomer–Fe^{3+} exist below pH 3.5 and 1.7 at room temperature, respectively [20, 21]. However, the silicate ions are also polymerized and exist mainly as colloidal particles in equilibrium with $Si(OH)_4$ in the pH region lower than 9 [19], so the concentration of silicate monomer ions is reduced. This polymerization of silicate ions would be accelerated at a high temperature of 100 °C. Therefore, the inhibitory effects of the silicate ions on the hydrolysis reaction for producing β-FeOOH are much less than those of phosphate ions.

It has been found that the crystallization from amorphous ferric hydroxides to α-FeOOH is hindered by silicate and phosphate ions, and this inhibitory effect was explained in terms of the adsorption of these anions on the hydroxides [12–15]. This inhibitory mechanism was verified in this work by the following experiments. Phosphate ions, 0.5 mol %, were added to the suspension containing the pure α-FeOOH particles aged for 1 day and then the suspension was aged at pH 12 and 30 °C for another 6 days. The L_{210} values of α-FeOOH did not vary with this ageing, indicating that the crystallization of α-FeOOH was prevented by the adsorption of phosphate ions on the particle surface. According to our preliminary experiment, the amount of adsorbed phosphate ions on the amorphous ferric hydroxides formed without ageing was 3.2 ions nm^{-2} at 2.0 mol % phosphate ions, pH 12 and 30 °C. This adsorbed amount means that ~ 64% of the particle surface is covered with phosphate ions, because the cross-sectional area of phosphate ions is 0.2 nm^2, calculated from its ionic radius of 0.25 nm. These amorphous ferric hydroxides adsorbing phosphate ions of 3.2 ions nm^{-2} were not crystallized on ageing in the suspension at pH 12 and 30 °C for 20 days. From these results it is clear that phosphate ions interfere with the crystallization of amorphous ferric hydroxides and α-FeOOH through adsorption on these particles.

Fig. 6 shows the L_{021} values of α-FeOOH formed in the presence of phosphate ions as a function of ageing time. As can be seen in this figure, the L_{021} value of $PO_4^{3-}/Fe^{3+} = 1.0$ mol % system abruptly increased after 4 days ageing, while those of $PO_4^{3-}/Fe^{3+} = 0$ and 0.5 mol % systems increased slowly at the beginning of ageing and saturated after 4 days. However, on adding 2 mol % PO_4^{3-} ions, α-FeOOH particles were still not crystallized after ageing for 10 days. This retardation or inhibition

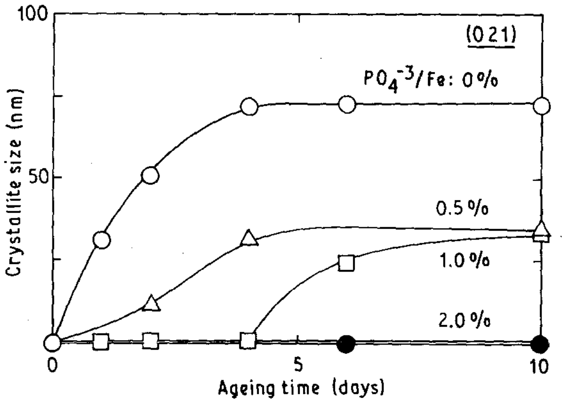


Figure 6 The change of crystallite size of α-FeOOH formed in the presence of various concentrations of phosphate ions as a function of ageing time.

of crystallization evidently suggest that the phosphate ion is an important determining factor of the size and crystallinity of α-FeOOH particles.

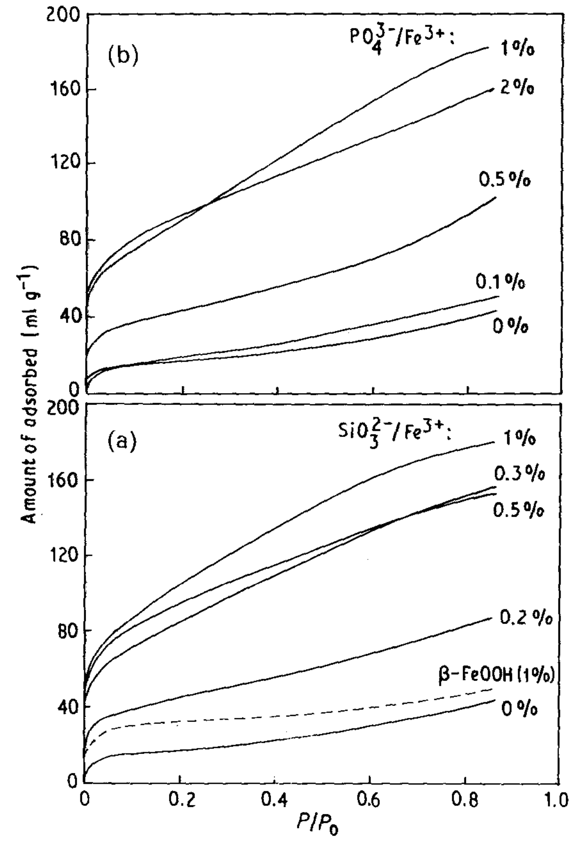


Figure 7 The nitrogen adsorption isotherms on α-FeOOH particles formed in the presence of various concentrations of (a) silicate and (b) phosphate ions. (---) Result for β-FeOOH particles prepared in the presence of 1 mol % silicate ions.

3.2. Surface properties of α- and β-FeOOH particles

The adsorption isotherms of nitrogen on the α-FeOOH particles formed in the presence of silicate and phosphate ions are shown in Fig. 7a and b, respectively. These adsorption isotherms on α-FeOOH changed from Type II to Type I of BDDT classification with increasing concentrations of anions added. The adsorption of nitrogen at low relative pressure also increased with increasing concentration of anions, showing the formation of micropores. However, such large differences in the isotherms were not seen for β-FeOOH. A typical adsorption isotherm for β-FeOOH prepared with 1 mol % silicate added is plotted in Fig. 7a with a dashed line. The specific surface areas of the powders, S_n, calculated using the BET equation, are also shown in Fig. 4, together with the weight loss values from TG measurement. The S_n values of α-FeOOH increased up to 379 and

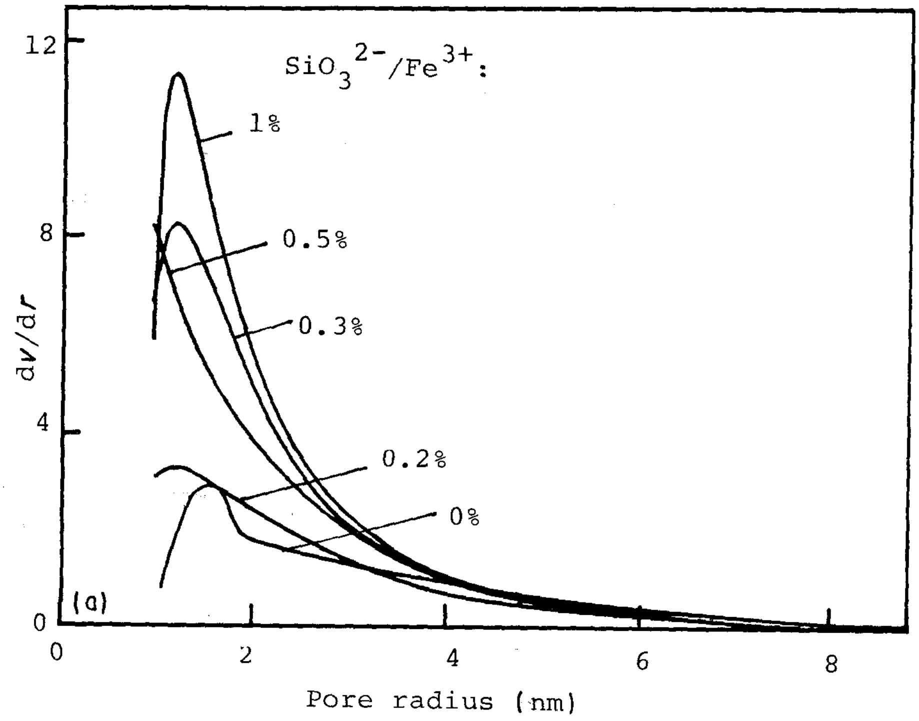
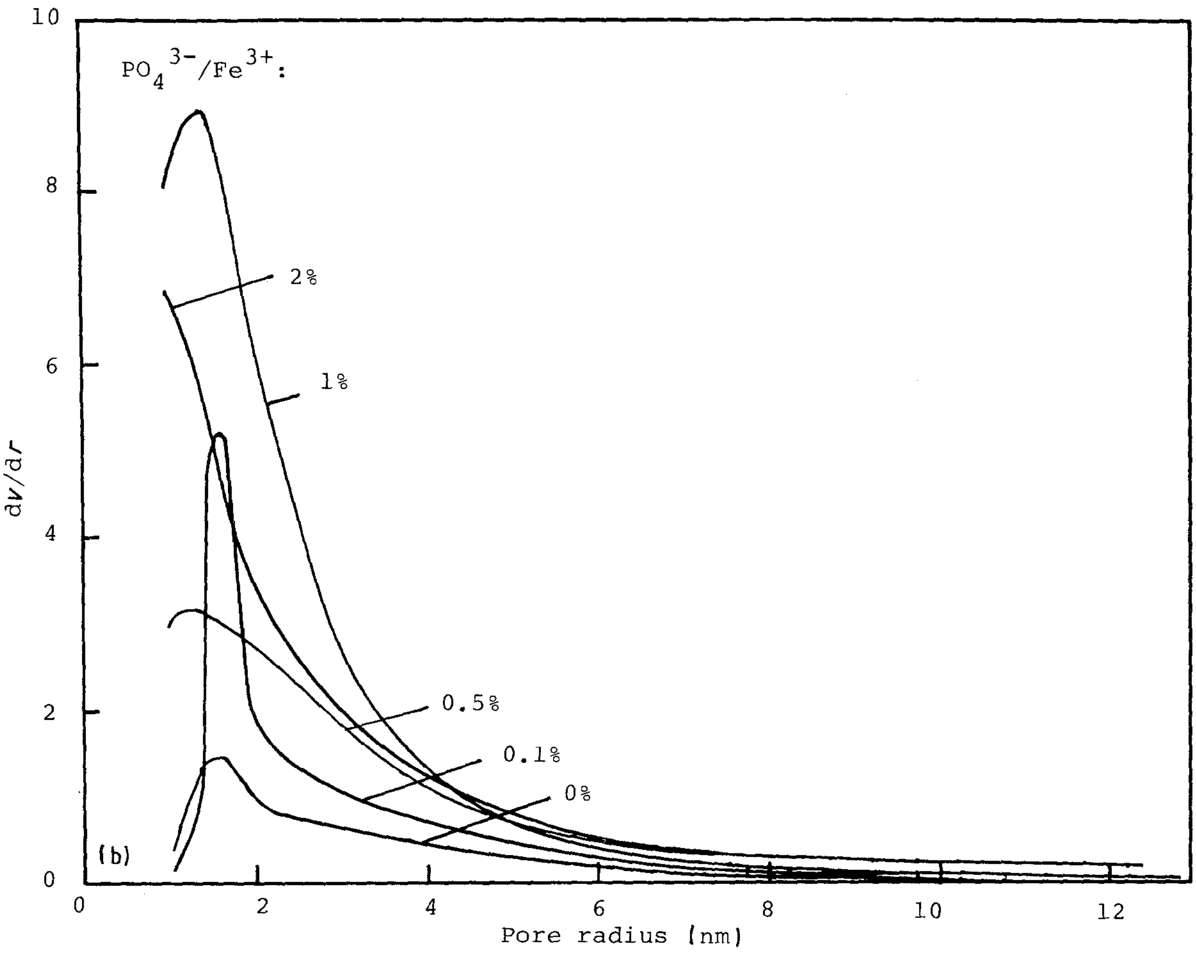


Figure 8 The pore-size distribution of α-FeOOH formed in the presence of different amounts of (a) silicate and (b) phosphate ions.



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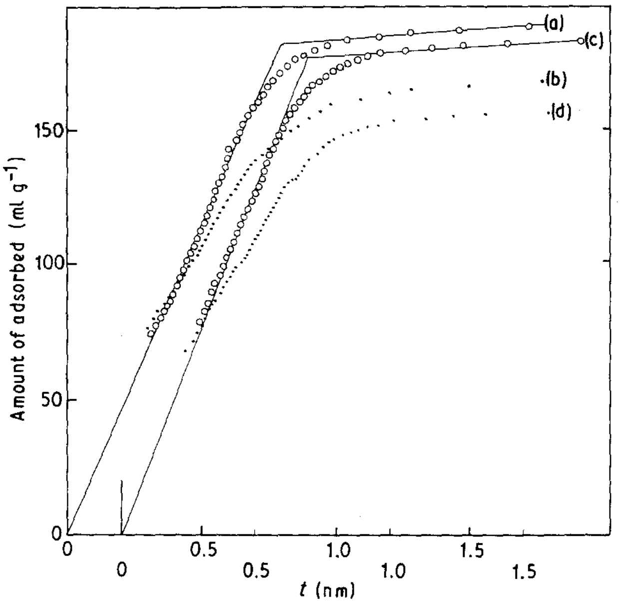

Figure 9 The *t*-plots for α-FeOOH formed in the presence of different amounts of silicate and phosphate ions. PO_4^{3-}/Fe^{3+}: (a) 1%, (b) 2%. SiO_3^{2-}/Fe^{3+}: (c) 1%, (d) 0.5%.

335 $m^2 g^{-1}$ on addition of silicate and phosphate ions, respectively. On the contrary, the values for β-FeOOH remain constant at 100–115 $m^2 g^{-1}$, except when 2 mol % phosphate ions are added.

To clarify the porosity of α-FeOOH prepared in the presence of silicate and phosphate ions, the pore-size distribution and *t*-method analyses were carried out. The pore-size distribution curves, computed from these isotherms using the Cranston–Inkley method [22], of α-FeOOH prepared at various concentrations of silicate and phosphate ions are shown in Fig. 8a and b. The fractions of micro- and mesopores of radius < 1.6 nm increased with increasing concentrations of both anions. The pore-size distribution can be also recognized by the *t*-plot, as shown in Fig. 9. The sharp break points cannot be seen clearly in the *t*-plots of these α-FeOOH particles. The micropore radius distribution can be estimated by the MP method [23] from the curvature between the two straight lines in Fig. 9. The micropore radii so obtained were from 0.7–1.0 nm for Sample a and from 0.6–1.0 nm for Sample c. This result clearly suggests that these α-FeOOH particles possess micropores in addition to mesopores. In our previous work, a similar increase in S_n has been observed for α- and β-FeOOH particles formed in the presence of citrate ions [11]. These particles did not show a clear microporosity but adsorbed water molecules selectively [11]. In this study such selective adsorption was not observed. The adsorptive properties of α- and β-FeOOH prepared in the presence of various anions will be reported in detail in the near future.

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