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Structural properties of precipitates formed by hydrolysis of Fe^{3+} ions in aqueous solutions containing NO_3^- and Cl^- ions

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The structural properties of precipitates formed by hydrolysis of Fe^{3+} ions in aqueous solutions, containing NO_3^- and Cl^- ions, were investigated. The reactions of hydrolysis were performed in glass autoclaves at 120 °C. X-ray diffraction showed that α-FeOOH and α-Fe_2O_3 were present in hydrolytical products formed in solutions containing NO_3^- ions, while β-FeOOH and α-Fe_2O_3 were typical hydrolytical products in solutions containing Cl^- ions. In the mixed $Fe(NO_3)_3 + FeCl_3$ solutions, the phase composition of the hydrolytical products was determined by the concentration of the dominant Fe(III)-salt. Fourier transform infrared spectroscopy and Mössbauer spectroscopy were also used for the structural characterizations of the hydrolytical products. Transmission electron microscopy showed a diversity of shapes of the particles, which depended strongly on the experimental conditions. All types of particle, observed by transmission electron microscopy, were interpreted.

1. Introduction

The properties of advanced oxide ceramics, including catalysts, pigments and ferrites, strongly depend on the preparation procedures and the characteristics of raw materials. It is known that the best properties of these materials can be obtained when the morphology and size of primary particles are well controlled. Preparation of magnetic iron oxides with known size and morphology of particles is important in the production of magnetic components for application in different electronic devices. The hydrolysis of metal ions is a very useful method for the preparation of metal oxide particles with defined chemical and physical properties.

The process of hydrolysis of Fe^{3+} ions in aqueous solutions depends on many factors, including pH, temperature, time of hydrolysis, electrolytic composition of aqueous solution, etc. For the same experimental conditions different hydrolytic products have been formed depending on the nature of the anion present in the Fe(III)-salt. For instance, Music *et al.* [1] investigated the formation of iron(III) oxyhydroxides and oxides by the hydrolysis of iron(III)-salt solutions at elevated temperatures. In the nitrate and chloride solutions, the hydrolysis of Fe^{3+} ions began with the formation of simple hydroxy complexes, and this step was followed by their polymerization. The hydroxy polymers in the nitrate solution were not presumed to include the nitrate ions in the polymer chain, whereas the polymers formed in chloride solution contained some chloride ions in place of OH^- ions. The next step in the precipitation process was the formation of oxo-bridges and the development of α-FeOOH or β-FeOOH structures. In the $Fe_2(SO_4)_3$ solution the formation of the $FeSO_4^+$ complex suppressed the polymerization process and the formation of Fe(III) oxyhydroxides and oxides. Basic iron(III) sulphates were formed instead.

Murphy *et al.* [2] found α-FeOOH, goethite, in the precipitate after hydrolysis of the $Fe(NO_3)_3$ or $Fe(ClO_4)_3$ solution, while β-FeOOH, akaganeite, was hydrolytical product in the $FeCl_3$ solution. γ-FeOOH, lepidocrocite, as hydrolytical product was detected at certain experimental conditions, i.e., in 0.0165 M $Fe(NO_3)_3$ and in 0.1 or 0.0165 M $Fe(ClO_4)_3$ solutions. β-FeOOH colloids showed a tendency to form Schiller layers [3]. Lorenz & Kempe [4] investigated the hydrolysis of 0.3 M $(Fe_{1-x}M_x)Cl_3$ solutions at 90 °C, $M = Al^{3+}, Cr^{3+}$ or Ga^{3+}, and $0 \leqslant x \geqslant 0.5$. The substitution Fe for M in β-FeOOH increased in the order $Al^{3+} < Cr^{3+} < Ga^{3+}$, and the maximum substitution value of 40 mol % Fe in the case of Ga was obtained.

Matijević & Scheiner [5] investigated conditions for the preparation of monodispersed sols using hydrolysis of Fe(III)-salt solutions. A small addition of phosphate or hypophosphate ions to the $FeCl_3$ solution, before the hydrolysis of Fe^{3+} ions started, had a significant effect on the resulting particle shape [6]. Hamada *et al.* [7] found monodispersed α-Fe_2O_3 (haematite) particles in the form of two linked spheres, after the hydrolysis of the $FeCl_3$–glycine solutions at 98–100 °C, without precipitation of β-FeOOH as a transition phase. A forced hydrolysis of $FeCl_3$–glycine in 2-propanol/water medium generated β-FeOOH,

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which further converted to cuboidal haematite particles.

The effect of the long-range order of an associated surfactant was used to control the size of β-FeOOH particles, which were generated by heating the $FeCl_3$ solution containing surfactant [8]. The time for preparation of β-FeOOH particles was short, 5 min to 1 h, in relation to the time for the preparations previously described.

TABLE I Experimental conditions for the precipitation of hydrolytical products of Fe^{3+} ions

Sample	Chemical composition of aqueous solution	Temperature (°C)	Time of hydrolysis (hours)	pH of mother liquor
HP1	0.2 M $Fe(NO_3)_3$	120	24	0.38
HP2	0.2 M $Fe(NO_3)_3$	120	72	0.15
HP3	0.2 M $FeCl_3$	120	24	0.67
HP4	0.2 M $FeCl_3$	120	72	0.62
HP5	0.2 M $FeCl_3$ 0.1 M HCl	120	24	0.67
HP6	0.2 M $FeCl_3$ 0.1 M HCl	120	72	0.37
HP7	0.1 M $FeCl_3$ 0.1 M $Fe(NO_3)_3$	120	24	0.51
HP8	0.1 M $FeCl_3$ 0.1 M $Fe(NO_3)_3$	120	72	0.37
HP9	0.15 M $FeCl_3$ 0.05 M $Fe(NO_3)_3$	120	24	0.51
HP10	0.15 M $FeCl_3$ 0.05 M $Fe(NO_3)_3$	120	72	0.43
HP11	0.05 M $FeCl_3$ 0.15 M $Fe(NO_3)_3$	120	24	0.52
HP12	0.05 M $FeCl_3$ 0.15 M $Fe(NO_3)_3$	120	72	0.40

In the present paper the results are reported of an investigation of the hydrolysis of Fe^{3+} ions in aqueous solutions containing nitrate and chloride anions. The aim of this work was to obtain more information about the influence of two concurrent anions on the structure and shape of particles generated by hydrolysis of Fe^{3+} ions in aqueous solutions.

2. Experimental procedure

In all experiments, analar grade chemicals and doubly distilled water were used. The experiments of forced hydrolysis of Fe(III)-salt solutions were performed in glass autoclaves (Schott, Germany) at 120 °C. Experimental conditions for the hydrolysis of Fe^{3+} ions are described in Table I. The precipitates were washed with doubly distilled water from mother liquor using an ultra-speed centrifuge.

X-ray powder diffraction (XRD) measurements were performed at room temperature using a Philips counter diffractometer with monochromatized CuK_{α} radiation (graphite monochromator). ^{57}Fe Mössbauer spectra were recorded using standard Mössbauer equipment. Mössbauer spectra were fitted using the SIRIUS program. I.r. spectra were recorded at room temperature, in the range 200–4000 cm^{-1}, using an i.r. spectrometer 580 B (Perkin-Elmer). Fourier transform (FT) i.r. spectra were recorded with a Perkin-Elmer spectrometer, model 1720x, in the range 370–4000 cm^{-1}. The FT-IR spectrometer was coupled with a personal computer loaded with the i.r. Data Manager (IRDM) program. The samples were pressed into KBr discs using spectroscopically pure KBr.

TABLE II Phase analysis of the precipitates formed by hydrolysis of Fe^{3+} ions

Sample	XRD analysis (approximate molar fraction)	FT-IR analysis
HP1	α-$Fe_2O_3^{\Delta}$ + α-FeOOH* (3/4) (1/4)	α-Fe_2O_3 + α-FeOOH (dominant)
HP2	α-$Fe_2O_3^{\Delta}$ + α-FeOOH* (3/4) (1/4)	α-Fe_2O_3 + α-FeOOH (dominant)
HP3	β-FeOOH* + α-Fe_2O_3 (few %)	β-FeOOH + αFe_2O_3 (dominant)
HP4	α-$Fe_2O_3^{*}$ + β-FeOOH* (3/5) (2/5)	α-Fe_2O_3 + β-FeOOH (dominant)
HP5	β-FeOOH** + α-$Fe_2O_3^{\Delta}$ (3/4) (1/4)	β-FeOOH + α-Fe_2O_3 (dominant)
HP6	α-Fe_2O_3**	α-Fe_2O_3 + α-FeOOH (small amount)
HP7	β-FeOOH* + α-$Fe_2O_3^{\Delta}$ + α-FeOOH* (4/9) (4/9) (1/9)	β-FeOOH + α-Fe_2O_3 + α-FeOOH
HP8	α-$Fe_2O_3^{*}$	α-Fe_2O_3 + α-FeOOH (small amount)
HP9	β-FeOOH* + α-$Fe_2O_3^{\Delta}$ (5/6) (1/6)	β-FeOOH + α-Fe_2O_3 (dominant)
HP10	α-$Fe_2O_3^{*}$	α-Fe_2O_3 + α-FeOOH (small amount)
HP11	α-$Fe_2O_3^{\Delta}$	α-Fe_2O_3 + α-FeOOH (small amount)
HP12	α-$Fe_2O_3^{\Delta}$ + α-FeOOH* (9/10) (1/10)	α-Fe_2O_3 + α-FeOOH (small amount)

* Little broadened diffraction lines; ** broadended diffraction lines; $^{\Delta}$ sharp diffraction lines.

Transmission electron microscopy (TEM) of all samples was performed with electron microscope EM 10, produced by Opton.

3. Results and discussion

The results of phase analysis of the precipitates, formed by hydrolysis of Fe^{3+} ions in aqueous solutions containing NO_3^- and Cl^- ions, are given in Table II. There is good agreement between XRD and FT-IR analysis of the precipitates, expect that FT-IR spectra of samples HP6, HP8, HP10, and HP11 showed, in addition to α-Fe_2O_3, the presence of small amount of α-FeOOH. Determination of α-FeOOH and α-Fe_2O_3 in the natural sample was discussed in previous paper [9]. Figs 1 and 2 show characteristic XRD powder patterns of samples HP1, HP5 and HP6.

In the solution containing equivalent amounts of NO_3^- and Cl^- ions, after 24 h of hydrolysis at 120 °C, β-FeOOH (4/9), α-Fe_2O_3 (4/9) and α-FeOOH (1/9)

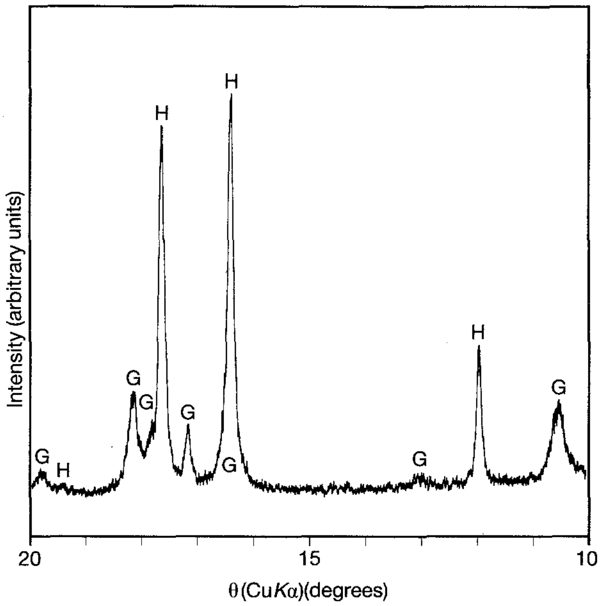

Figure 1 Characteristic part of X-ray powder diffraction pattern of sample HP1, recorded at room temperature. G, α-FeOOH; H, α-Fe_2O_3.

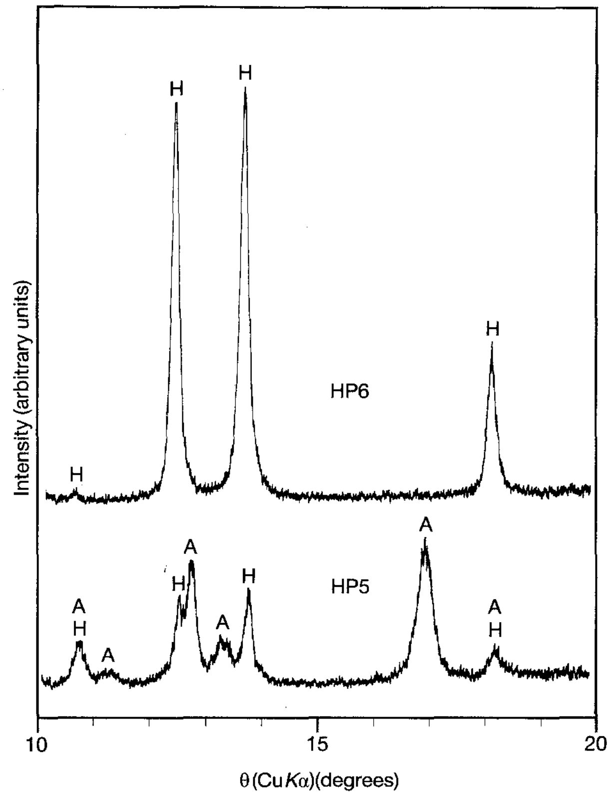

Figure 2 Characteristic parts of X-ray powder diffraction pattern of samples HP5 and HP6, recorded at room temperature. A, β-FeOOH; H, α-Fe_2O_3.

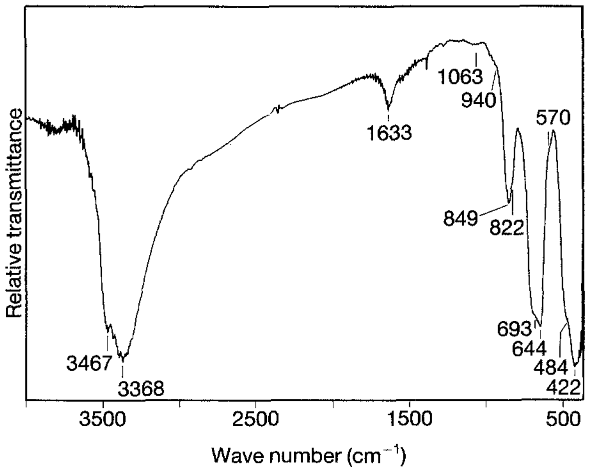

Figure 3 Fourier transform i.r. spectrum of sample HP3, recorded at room temperature.

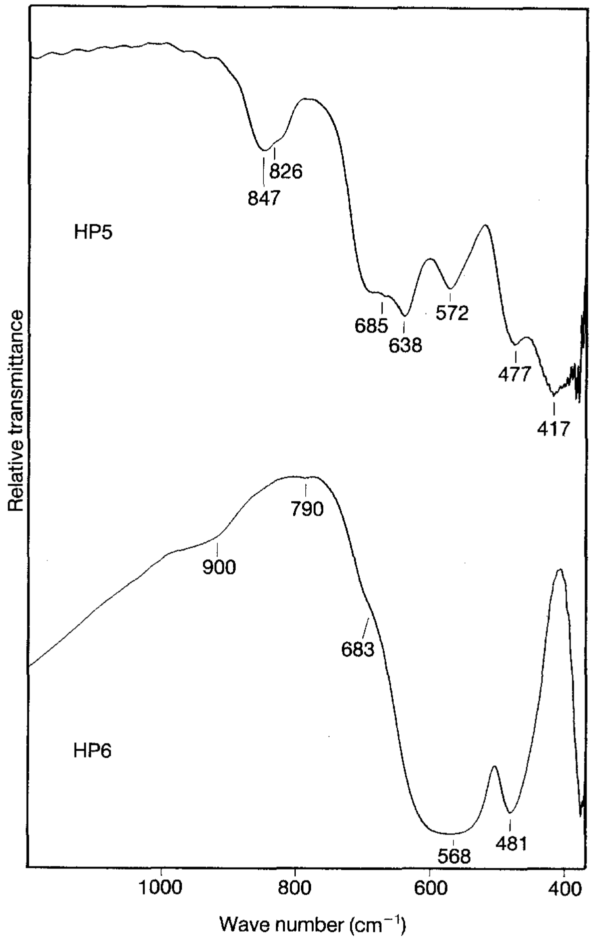

Figure 4 Fourier transform i.r. spectra of samples HP5 and HP6, recorded at room temperature.

were formed (sample HP7), while after 72 h of hydrolysis, only α-Fe_2O_3 (sample HP8) was detected by XRD. The FT-IR spectrum of sample HP8 additionally showed the presence of small amount of α-FeOOH. In a solution of 0.15 M $FeCl_3$ + 0.05 M $Fe(NO_3)_3$, after 24 h of hydrolysis at 120 °C, β-FeOOH (5/6) and α-Fe_2O_3 (1/6) were formed (sample HP9), while after 72 h of hydrolysis, β-FeOOH was not detected in the precipitate (sample HP10). β-FeOOH was also not detected in samples HP11 and HP12 formed by hydrolysis of 0.05 M $FeCl_3$ + 0.15 M $Fe(NO_3)_3$ solution.

The characteristic results obtained by FT-IR spectroscopy are shown in Figs 3–5. Fig. 3 shows the FT-IR spectrum of sample HP3, characterized with three spectral regions. A very strong and broad band with transmittance minima at 3467 and 3368 cm^{-1} can be ascribed to OH stretching vibrations. The band at 1638 cm^{-1} corresponds to the H–O–H bending mode, and indicates the presence of molecular water in the sample. Dominant bands at 849, 822 cm^{-1} and 693, 644 cm^{-1} can be ascribed to β-FeOOH. These i.r. bands, characteristic for β-FeOOH, have also been recorded by other researchers [10, 11]. The presence of a very small amount of α-Fe_2O_3 in sample HP3 can be suggested on the basis of shoulders at ≈ 570 and 484 cm^{-1}.

Fig. 4 shows FT-IR spectra of samples HP5 and HP6. In sample HP5, β-FeOOH can be identified on the basis of bands at 847, 826 cm^{-1} and 685, 638 cm^{-1}. The bands at 572 and 477 cm^{-1} can be ascribed to α-Fe_2O_3. With a prolonged time of hydrolysis, β-FeOOH further transformed to α-Fe_2O_3, which is illustrated in the FT-IR spectrum of sample HP6. The bands of very weak intensities, observed at 900 and 790 cm^{-1}, can be ascribed to small amount of α-FeOOH.

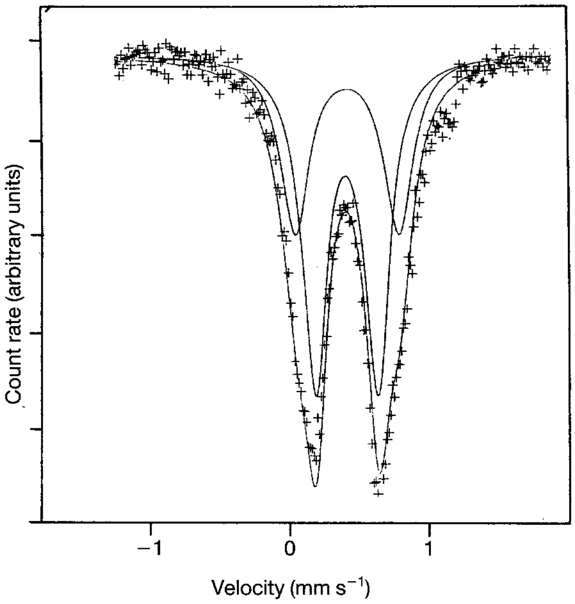

Figure 6 ^{57}Fe Mössbauer spectrum of β-FeOOH, recorded at room temperature.

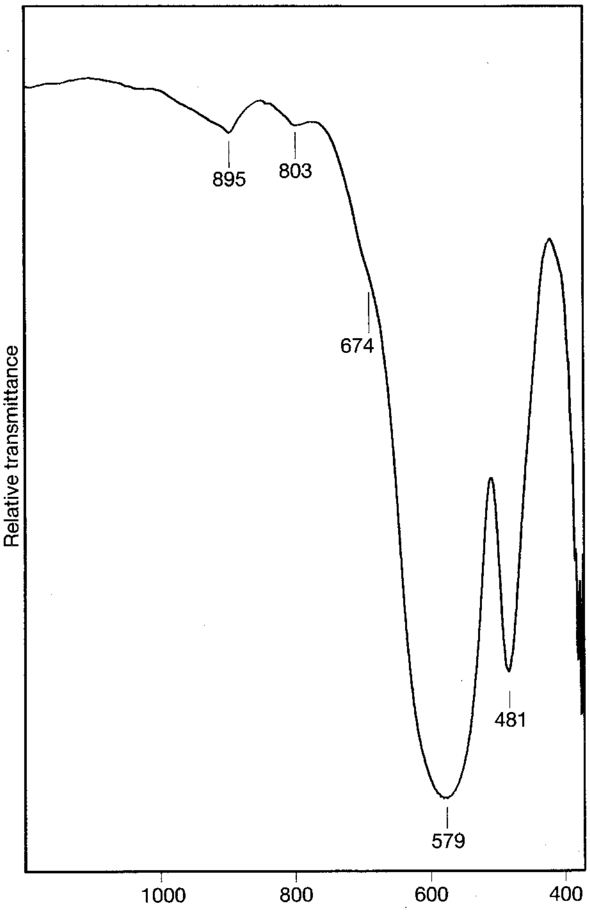

Figure 5 Fourier transform i.r. spectrum of sample HP12, recorded at room temperature.

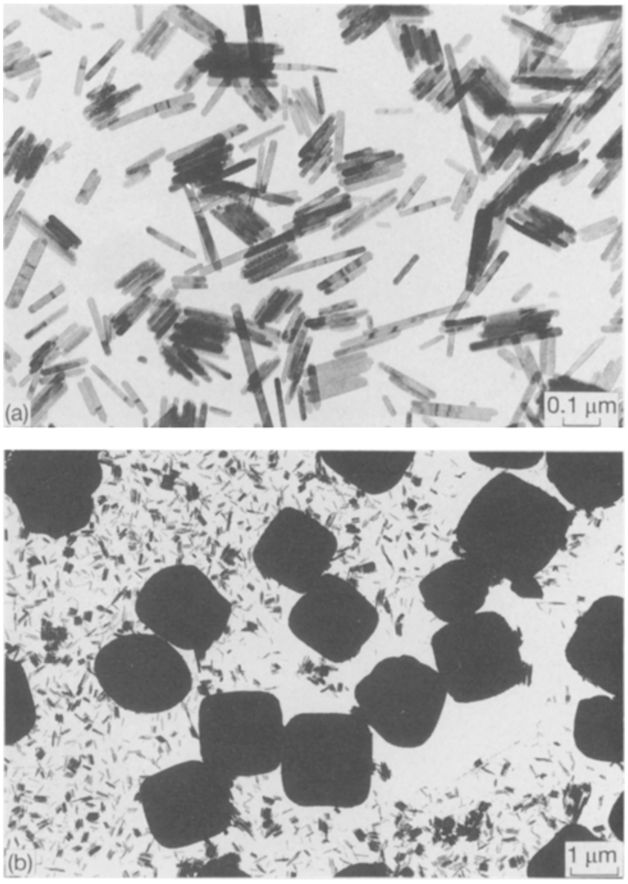

Figure 7 Transmission electron micrographs of the precipitates formed by hydrolysis of 0.2 M $FeCl_3$ solution at 120 °C, (a) after 24 h (sample HP3); (b) after 72 h (sample HP4).

Fig. 5 shows an FT-IR spectrum of sample HP12. At 895 and 803 cm^{-1}, two bands of small intensities are observed. These bands correspond to Fe–O–H bending vibrations in α-FeOOH, and they are usually used for detection of α-FeOOH in the samples of a complex phase composition. A very strong band at 579 cm^{-1} and a strong band at 481 cm^{-1} indicate that α-Fe_2O_3 is a dominant phase in the precipitate. The nature of i.r. bands, corresponding to α-Fe_2O_3, was discussed in previous papers [12, 13].

Mössbauer spectroscopy has found important applications in the investigation of phase composition, crystallinity, stoichiometry and nuclear magnetic properties of the oxide precipitates, obtained from Fe(II)- and Fe(III)- salt solutions. It has been shown by Mössbauer spectroscopy and XRD that the chemical and structural properties of precipitated oxides formed from $FeSO_4$ solutions [14, 15] are strongly dependent on the $[Fe^{2+}]/[OH^-]$ concentration ratio at the beginning of the precipitation process, and also on the rate of oxygenation, the time of precipitation, the temperature and the kind of alkali (NH_4OH or NaOH) added. The effect of urea on the chemical and structural properties of oxides precipitated from $FeSO_4$ solution has also been investigated [16].

In previous work [1] Mössbauer spectroscopy was used to characterize the products of hydrolysis of 0.1 M solutions of $Fe(NO_3)_3$, $FeCl_3$, $Fe_2(SO_4)_3$ and $NH_4Fe(SO_4)_2$ at 90 °C. The experimental conditions utilized in that work made it possible to follow all transformations in $Fe(NO_3)_3$ and $FeCl_3$ solutions, from iron(III) hydroxy polymers to haematite as the end product. The precipitate, obtained by hydrolysis of 0.1 M $Fe(NO_3)_3$ solution for 80 min at 90 °C and aged for 2 days, showed central quadropole doublet, Q, at room temperature and three relatively well resolved components, M_1, M_2 and M_3, at liquid nitrogen temperature. The parameters of component M_1 (469 kOe) were ascribed to α-FeOOH, while components M_2 and M_3 with small values of hyperfine magnetic field, 416 and 353 kOe, respectively, were ascribed to iron(III) hydroxy polymers. With an increase in the time of hydrolysis of $Fe(NO_3)_3$ solution, α-FeOOH converted to α-Fe_2O_3.

In the present work, we consider the Mössbauer spectrum of β-FeOOH (Fig. 6), which was obtained by slow hydrolysis of 0.1 M $FeCl_3$ solution. Mössbauer spectrum of β-FeOOH recorded at room temperature is characterized with two quadropole doublets having the following parameters: $\Delta_1 = 0.532$ and $\Delta_2 = 0.884$ mm s^{-1}, $\Gamma_1 = 0.256$ and $\Gamma_2 = 0.297$ mm s^{-1}. The area under the peaks corresponding to Q_1 doublet, 61.44%, was calculated, while the isomer shifts of $\delta_1 = 0.381$ and $\delta_2 = 0.393$ mm s^{-1} (relative to α-Fe) were similar. These results evidently indicate the presence of two kinds of iron atoms contributing to the

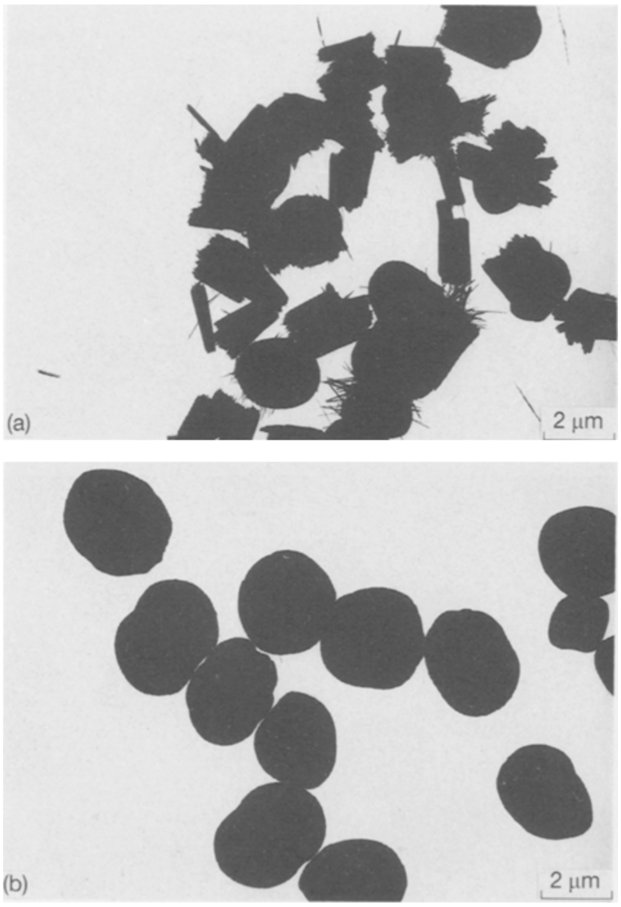

Figure 8 Transmission electron micrographs of the precipitates formed by hydrolysis of 0.2 M $FeCl_3$ + 0.1 M HCl solution at 120 °C, (a) after 24 h (sample HP5); (b) after 72 h (sample HP6).

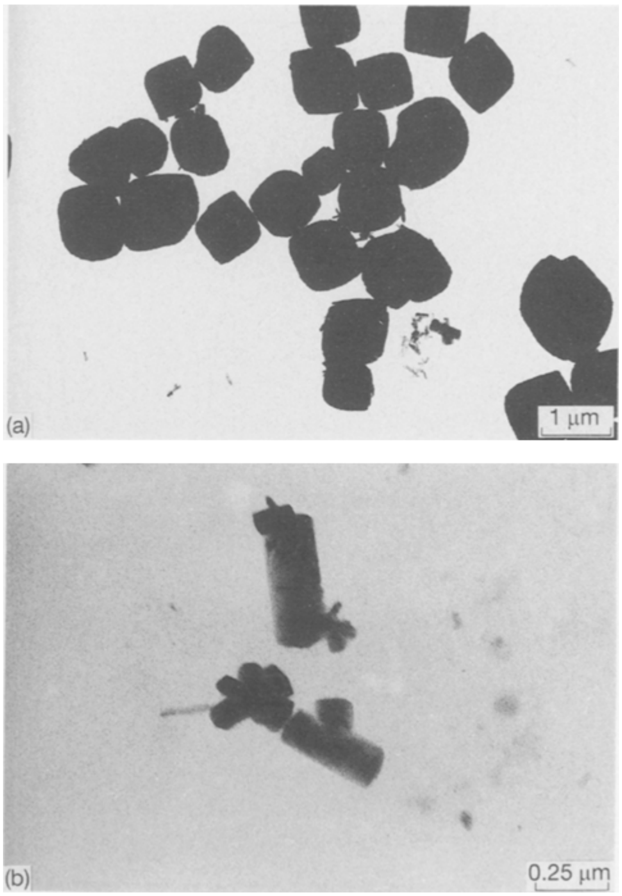

Figure 9 Transmission electron micrographs of the precipitates formed by hydrolysis of 0.1 M $FeCl_3$ + 0.1 M $Fe(NO_3)_3$ solution at 120 °C, (a) after 72 h (sample HP8); (b) enlarged detail showing dendritic nature of α-FeOOH particles in sample HP8.

Mössbauer effect. The nature of these two doublets is not clear. Johnston & Logan [17] suggested that inner doublet in the Mössbauer spectrum of β-FeOOH is a consequence of iron in the structural $O_3(OH)_3$ octahedron, whereas the outer doublet is a consequence of iron in the tunnels, i.e. the chain of cavities along the *c*-axis of the hollandite-like structure. Childs *et al.* [18] proposed that iron in the $O_3(OH)_3$ octahedron is responsible for the inner doublet, whereas iron in the $O_2(OH)_4$ octa-hedron is responsible for the outer doublet. This conclusion is supported by Chambaere *et al.* [19]. The appearance of the outer doublet in the Mössbauer spectrum of β-FeOOH was also interpreted in terms of a chlorine substituted octahedron, $O_3(OH)_2Cl$ [20].

The results of the TEM investigation showed different shapes of colloidal particles, and the characteristic results obtained by this technique, can be summarized as follows. Fig. 7 shows particles obtained by hydrolysis of 0.2 M $FeCl_3$ solution at 120 °C. Fig. 7a shows separated and enlarged β-FeOOH particles, obtained after 24 h (sample HP3). These particles are in the form of rods (cigar-shaped) and show a tendency to form a lateral array of the particles. After 72 h of hydrolysis of 0.2 M $FeCl_3$ solution at 120 °C, α-Fe_2O_3 became the dominant phase in sample HP4 (Fig. 7b). In Fig. 7b, α-Fe_2O_3 particles are cuboids and some of them ellipsoids, while small rods corresponding to β-FeOOH are also visible. Addition of 0.1 M HCl to the 0.2 M $FeCl_3$ solution affected the shape of the particles.

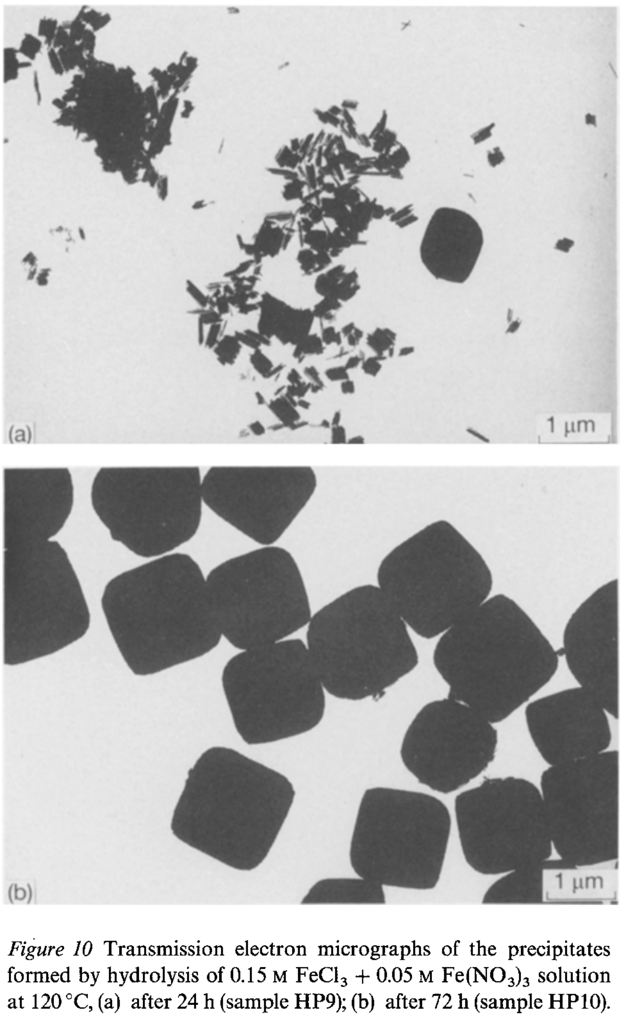

Figure 10 Transmission electron micrographs of the precipitates formed by hydrolysis of 0.15 M $FeCl_3$ + 0.05 M $Fe(NO_3)_3$ solution at 120 °C, (a) after 24 h (sample HP9); (b) after 72 h (sample HP10).

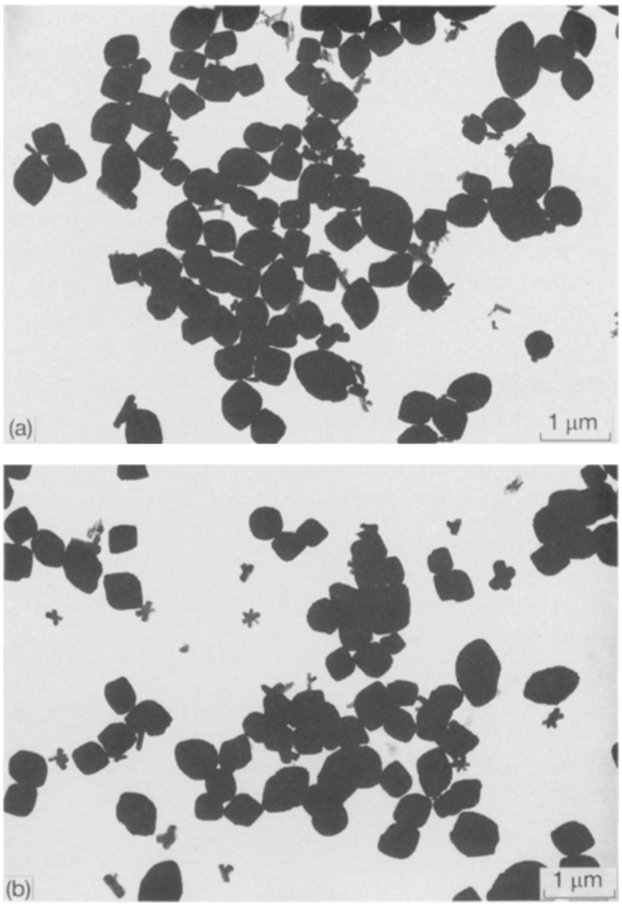

Figure 11 Transmission electron micrographs of the precipitates formed by hydrolysis of 0.05 M $FeCl_3$ + 0.15 M $Fe(NO_3)_3$ solution at 120 °C, (a) after 24 h (sample HP11); (b) after 72 h (sample HP12).

Fig. 8a shows particles, (sample HP5) formed after 24 h of hydrolysis of 0.2 M $FeCl_3$ + 0.1 M HCl solution at 120 °C. β-FeOOH particles are visible as bundles of needles, and their shape is different from that shown in Fig. 7a. After 72 h of hydrolysis of 0.2 M $FeCl_3$ + 0.1 M HCl solution at 120 °C, ellipsoidal α-Fe_2O_3 particles (sample HP6) were also produced (Fig. 8b). Hydrolysis of 0.1 M $FeCl_3$ + 0.1 M $Fe(NO_3)_3$ solution at 120 °C after 72 h generated α-Fe_2O_3 particles which were dominantly cuboids (Fig. 9a). α-FeOOH particles in sample HP8 showed a dendritic nature (Fig. 9b). The measured value of the angle between the main α-FeOOH particle and its dendrite at the coherent boundary is close to 120°; this is in agreement with the calculated value (117.5°) given by Maeda & Hirono [21].

Fig. 10 shows particles obtained by hydrolysis of 0.15 M $FeCl_3$ + 0.05 M $Fe(NO_3)_3$ solution at 120 °C, after 24 h (sample HP9) and after 72 h (sample HP10), respectively. It can be seen in Fig. 10b that monodispersed α-Fe_2O_3 cuboids were obtained. Fig. 11 shows particles generated by hydrolysis of 0.15 M $Fe(NO_3)_3$ + 0.05 M $FeCl_3$ solution at 120 °C after 24 h (sample HP11) and after 72 h (sample HP12). α-Fe_2O_3

particles are dominant; however, many of them have an irregular shape. Star-shaped and X-shaped particles are α-FeOOH.

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