THERMAL DECOMPOSITION OF SYNTHETIC AKAGANEITE (β-FeOOH)

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(Received 29 October 1981)

ABSTRACT

The thermal decomposition of synthetic akaganeite (β-FeOOH) has been investigated using differential thermal analysis, thermogravimetry, electron microscopy and X-ray diffraction. The results show that β-FeOOH undergoes a dehydroxylation reaction at 250–300°C in common with other polymorphs of FeOOH, but unlike them undergoes a strongly exothermic peak after dehydroxylation. The size and temperature of this peak is strongly dependent on the atmosphere surrounding the sample and appears to be associated with the loss of chloride, an unavoidable impurity in the synthetic material. Morphological and chemical data suggest that a process of chemical transport occurs during thermal decomposition in a nitrogen atmosphere.

INTRODUCTION

Although the thermal decomposition of α- and γ-FeOOH has been extensively investigated, relatively few studies of β-FeOOH have been made and considerable uncertainty exists in the interpretation of the mode of decomposition of this compound [1]. Possibly the main reason for this is that insufficient attention has been paid to characterising the synthetic product. Some time ago, Mackenzie [2] suggested that the chloride content of synthetic samples may play a significant role in the thermal decomposition of β-FeOOH, a suggestion which has only recently been confirmed by the work of Ishikawa and Inouye [3]. In addition, Ellis et al. [4] have shown that many of the reports of chloride-free β-FeOOH, synthesised by the hydrolysis of aqueous $FeCl_3$ solution, could be in error because of chloride loss during dissolution in open containers with concentrated nitric acid. Because of these uncertainties, particular attention has been paid to the fate of sorbed chloride in this study of the thermal decomposition of β-FeOOH.

EXPERIMENTAL

Materials

Sample 1 was prepared from an aqueous 0.4 M solution of iron(III) chloride which was aged for 7 days at room temperature, hydrolysed for 7 days at 70°C, and

the precipitate allowed to settle before decanting the clear supernatant liquid. After washing with deionised water until peptisation occurred, the sediment was transferred to Visking cellulose dialysis tubing and dialysed against deionised water for 14 days. A small aliquot of this suspension was retained for electron microscopy and the remainder was dried on a water bath and lightly ground to pass 100 mesh.

Sample 2 was obtained from a partially neutralised, aqueous solution of iron(III) chloride (OH/Fe molar ratio = 2.00), aged for 48 h at room temperature, hydrolysed at 70°C for 7 days, and then washed, dialysed, dried and ground in a similar manner to sample 1.

Methods

Differential thermal analysis (DTA) was carried out using a DuPont 900 Differential Thermal Analyser equipped with the high temperature (1200°C) cell, 25 mg samples being heated at a rate of $20 \, K \, min^{-1}$ in an atmosphere of nitrogen or oxygen flowing at $100 \, cm^3 \, min^{-1}$.

Differential scanning calorimetry (DSC) curves were obtained using a Perkin-Elmer DSC-2 equipped with a katharometer for evolved gas detection. A sample weight of 10 mg was used with a heating rate of $10 \, K \, min^{-1}$ and a nitrogen flow rate of $100 \, cm^3 \, min^{-1}$.

A Stanton Redcroft TG 750 thermobalance was used for thermogravimetry. A 10 mg sample was heated at $10 \, K \, min^{-1}$ in an atmosphere of nitrogen or oxygen flowing at $30 \, cm^3 \, min^{-1}$.

X-Ray diffraction patterns of the samples (rolled in Durafix cement) were obtained on a Debye–Scherrer camera using iron-filtered Co K_α radiation.

Samples for electron–optical examination were dispersed ultrasonically in double-distilled water and dried on carbon-coated support grids for examination on an AEI EM6 instrument.

Approximately 10 mg of each sample were dissolved in 5 ml of 20% H_2SO_4 in a sealed tube by heating to 50–60°C for 30 min and aliquots taken to determine the iron [5] and chloride [6] contents of the original sample.

CHARACTERISATION OF SYNTHETIC PRODUCTS

X-Ray diffraction of both samples shows that the only crystalline phase present is β-FeOOH and from electron micrographs there is no evidence of poorly ordered material. In addition, both samples have the same morphology but in sample 1 the square rod-like crystals are about 400 nm long by 14 nm wide whereas in sample 2 they are much smaller, about 50 nm long and 6 nm wide. The chloride contents of samples 1 and 2 are 2.9 and 3.8%, respectively, giving unit cell formulae of $Fe_8O_{7.4}OH_{8.6}Cl_{0.6}$ and $Fe_8O_{7.1}OH_{8.9}Cl_{0.9}$. In deriving these formulae, the excess negative charge arising from the incorporation of chloride ions in the structure is satisfied by the protonation of an equivalent number of oxide ions.

RESULTS

The DTA curves obtained in a nitrogen atmosphere are similar to those given by Mackenzie and Berggren [1], showing a multiple endothermic effect in the temperature range 150–300°C and a sharp exothermic effect at higher temperatures (Fig. 1). For sample 1, a double endothermic peak at 185 and 270°C, due to dehydroxylation, is obtained in addition to a sharp exothermic peak at 455°C and a minor effect at 685°C. The curve for sample 2, however, exhibits a more complex endothermic peak system with a low temperature peak at 100°C, due to the loss of adsorbed water, and the main dehydroxylation endotherm comprising at least two overlapping peaks at 180 and 250°C. In this case, the exothermic peak is at a slightly lower temperature of 420°C.

The power-compensation DSC curve for sample 2 indicates that the complex endothermic peak system in the temperature range 120–350°C is, in fact, composed of four overlapping peaks (Fig. 2); the same degree of resolution is not obtained for sample 1. Qualitative tests established that the evolved gas was water vapour and, since the shape of the evolved gas detection curve parallels that of the DSC curve, water is evolved during each of the four peaks. The three small peaks at about 147, 177 and 209°C are similar in many respects to those that have been observed on the dehydroxylation curves of synthetic goethite (α-FeOOH) and assigned to surface dehydroxylation reactions [8]. Treatment of the samples with H_3PO_4, known to be strongly adsorbed by α-FeOOH as a bidentate ligand [9], causes these peaks on the curve for β-FeOOH to disappear, again bearing out the striking similarity between the two minerals.
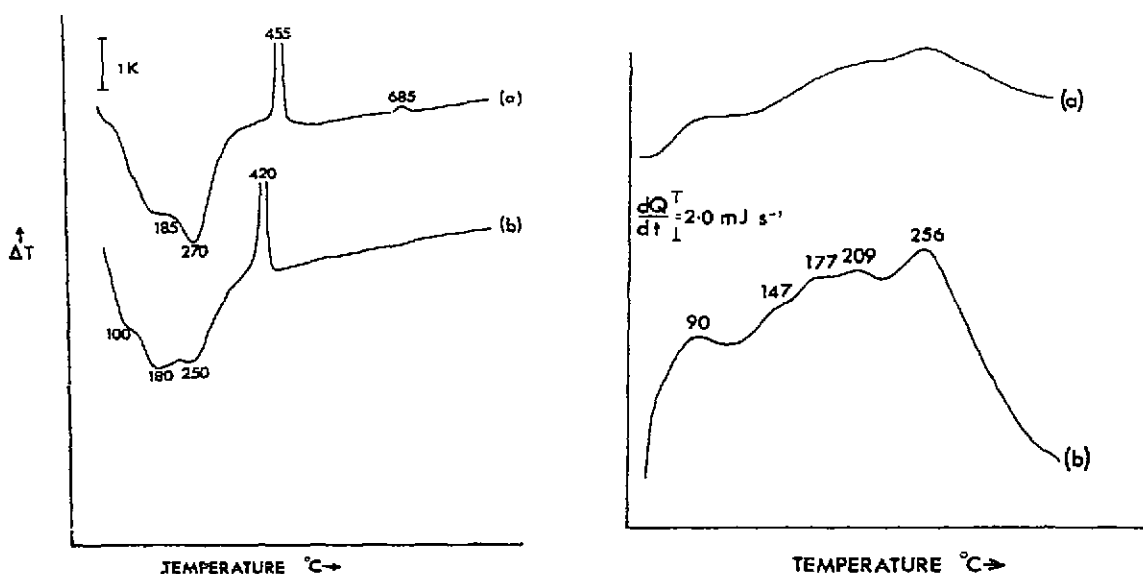
Fig. 1. DTA curves obtained in a nitrogen atmosphere for (a) sample 1 and (b) sample 2.

Fig. 2. Power compensation DSC curve of (b) sample 2 and (a) simultaneous evolved gas detection curve.

The DTA curves obtained in an oxygen atmosphere are significantly different from those obtained in an atmosphere of nitrogen. In particular, the sharp exotherm observed in nitrogen occurs at a higher temperature in both instances (Fig. 3), particularly for sample 1 where the increase in peak temperature is 245°C; the peak is also markedly broadened. The peak system representing dehydroxylation is not greatly altered, although the relative sizes of some peaks vary slightly.

Thermogravimetry, carried out in a nitrogen atmosphere, indicates a continuous weight loss from sample 1 between room temperature and 800°C and, despite the slight inflection at about 240°C, it is difficult to subdivide the total weight loss of 19.3% [Fig. 4, curve (a)]. The curve for sample 2, however, differs in that, after an initial weight loss similar to sample 1 in the interval 20–420°C, an extremely rapid weight loss of 3.8% occurs at 420°C [Fig. 4, curve (b)]. This reaction is probably associated with the sharp exothermic peak on the DTA curve and it is noteworthy that at this temperature brown fumes were evolved from the sample and a red sublimate formed in the cooler parts of the balance assembly. The total weight loss observed for sample 2 was 21.3%. When the samples were evacuated over phosphorus pentoxide to remove adsorbed water before heating on the thermobalance, the weight losses were reduced to 14.4 and 18.8%, respectively.

The phase changes occurring during heating have been studied using X-ray diffraction and it was found that upon heating to 550°C in a nitrogen atmosphere, i.e. beyond the temperature of the sharp exothermic peak on the DTA curve, the only product detectable was well-crystallised hematite. The major crystalline phase present on heating to 420°C was also hematite but this was accompanied by a more
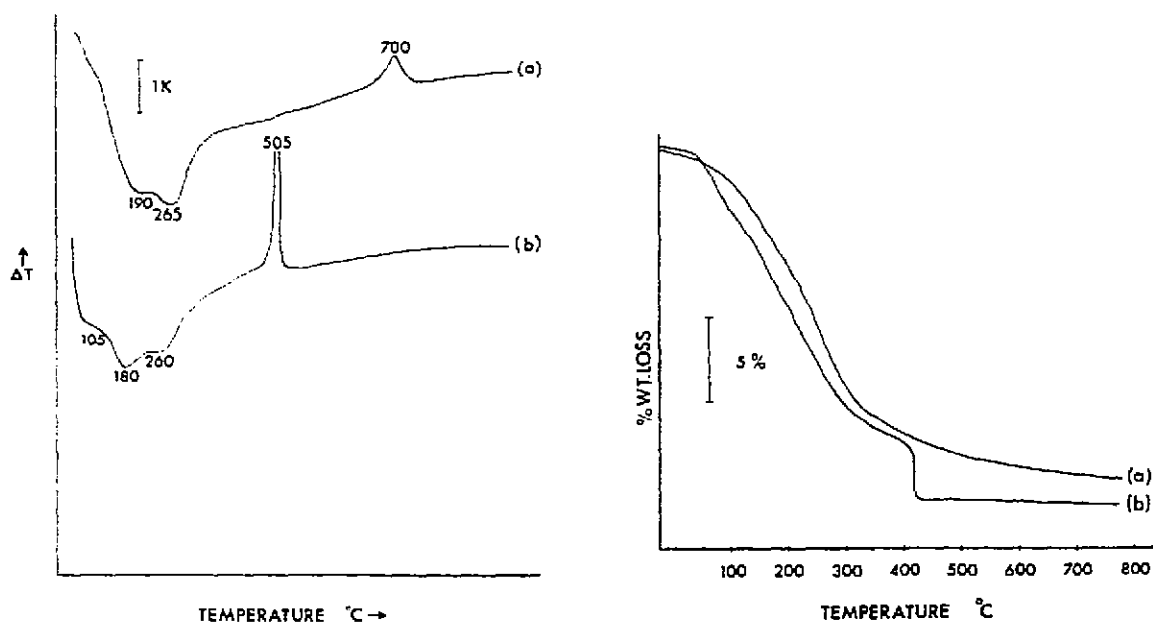

Fig. 3. DTA curves obtained in an oxygen atmosphere for (a) sample 1 and (b) sample 2.

Fig. 4. TG curves for (a) sample 1 and (b) sample 2.

poorly ordered phase which may be structurally related to β-FeOOH [Fig. 5(a)]. In an oxygen atmosphere, the products obtained on heating to 420 and 550°C are significantly different from those obtained in nitrogen; in particular, only two diffuse reflections that may be associated with hematite can be seen (214 and 300).
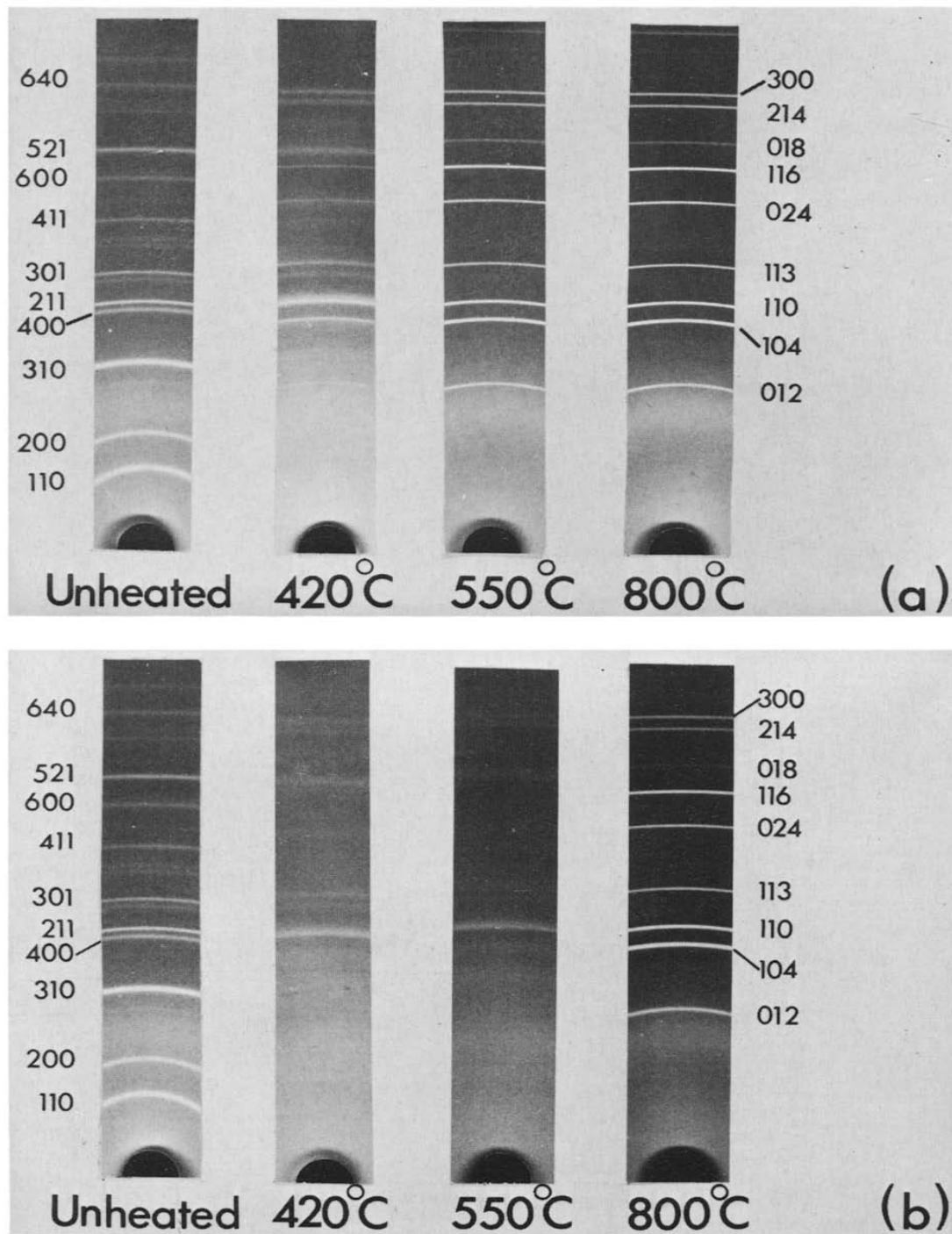

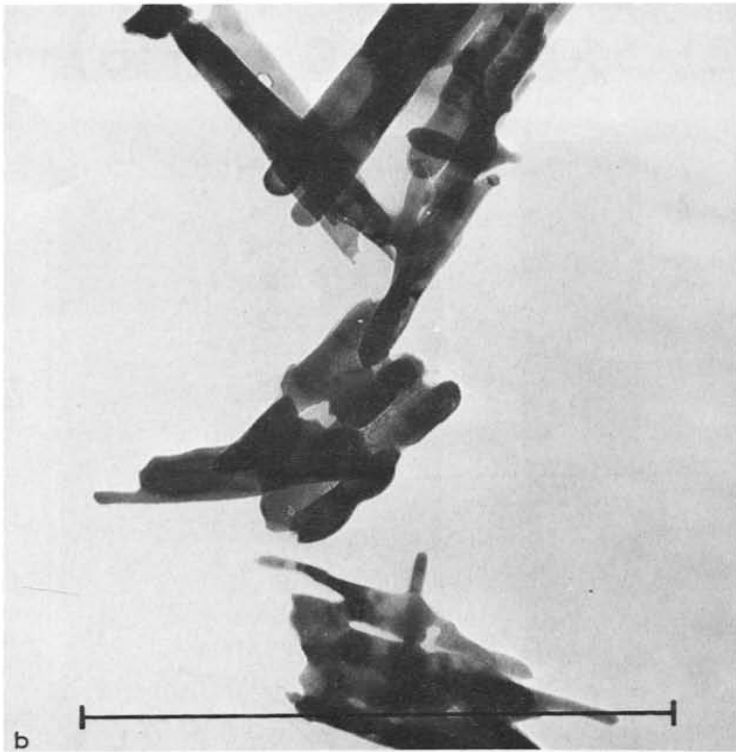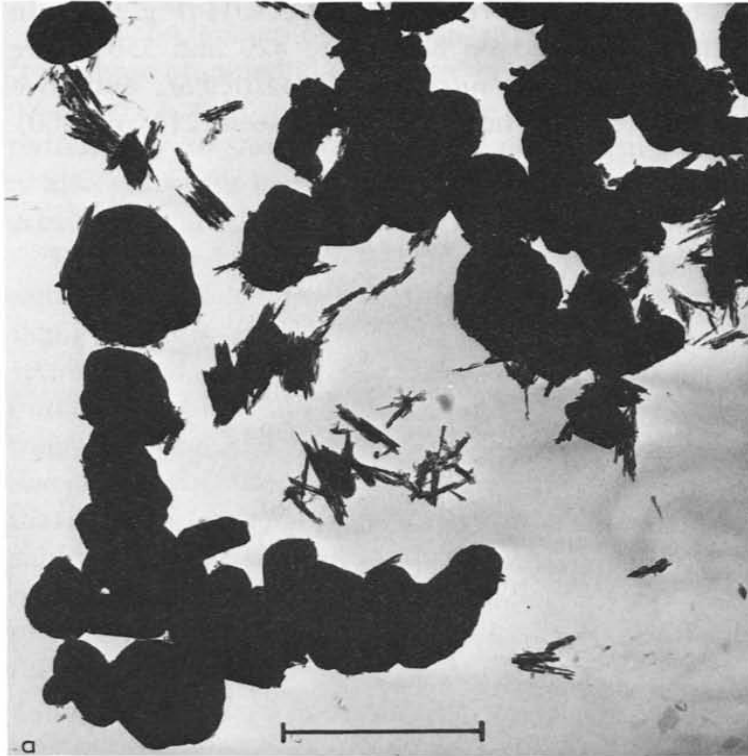Fig. 5. X-Ray diffraction patterns of β-FeOOH heated in (a) nitrogen and (b) oxygen.

Fig. 6. Electron micrographs of β-FeOOH heated to (a) 550°C in nitrogen and (b) 800°C in oxygen. Bar marker indicates 1 μm.

TABLE I

Variation of Fe/Cl molar ratio with temperature

Nitrogen atmosphere		Oxygen atmosphere	
Temperature (°C)	Fe/Cl ratio	Temperature (°C)	Fe/Cl ratio
Unheated	12.8	Unheated	12.8
400	17.8	400	15.1
520	134.0	520	39.6
735	>250.0	735	>250.0

The remainder of the poorly defined pattern may be derived from that of β-FeOOH. Only on heating to 800°C is the complete α-Fe$_2$O$_3$ pattern observed and, even then, significant line broadening occurs, indicating either structural disorder or very small crystallite size.

In addition to these phase changes occurring during heating, concomitant changes in morphology were also observed. In a nitrogen atmosphere, the lath-shaped crystals of β-FeOOH develop a striated and mottled appearance [7] on heating to 420°C and pseudohexagonal plates of α-Fe$_2$O$_3$ form upon heating to 550°C [Fig. 6(a)]. The morphologies of the products obtained at the same temperatures in an oxygen atmosphere are quite different from those obtained in nitrogen. The sample heated to 550°C retains the morphology of the starting material although the crystals have suffered considerable damage with pit-marks and holes evident. Even heating to 800°C, which, from the X-ray evidence, produces α-Fe$_2$O$_3$, does not destroy completely the lath-shaped crystals although a certain amount of sintering occurs and striations, indicative of considerable strain, can be seen in some particles [Fig. 6(b)].

The chloride content of the samples heated in an oxygen atmosphere are higher than those heated to the same temperature in nitrogen (Table I). In addition, qualitative analysis of the gases evolved on heating shows that, in a nitrogen atmosphere, a sudden evolution of hydrogen chloride occurs at the temperature of the exotherm on the DTA curve whereas chlorine is evolved over a much wider temperature range when the sample is heated in an oxygen atmosphere.

DISCUSSION

Mackay [10] has shown that the structure of β-FeOOH is very similar to that of hollandite with the iron(III) ions octahedrally co-ordinated to oxide and hydroxyl ions. These octahedra form double rows along the c axis and, by sharing corners with adjacent rows, the tetragonal unit cell is formed. Although it has been suggested

that the tunnels formed in the centre of the unit cell (Fig. 7) can contain a variety of ions and molecules, it seems likely that they contain only chloride ions and probably water molecules. The presence of chloride ions requires that some of the oxide ions in the structure be protonated to neutralise the charge caused by the anion excess, although the presence of HCl rather than chloride within the tunnels cannot entirely be excluded. Moreover, protonation will also occur at the surface of the particles in a manner similar to that observed for goethite [9] to neutralise the charge imbalance caused by the unsatisfied co-ordination of surface oxide ions. Thus, in addition to the bulk hydroxyl groups, excess surface hydroxyl will be present as well as the chloride ions located within the structural tunnels.

In investigations dealing with very small particles of the type studied here, the influence of the surface ions becomes progressively greater as the particle size diminishes. For example, the three overlapping peaks at 147, 177 and 209°C are significantly larger and better resolved on the curve for sample 2 (Fig. 3) than those for sample 1 where only one broad endothermic effect is observed. From electron diffraction measurements, which show that the predominant surface plane is the 100, a knowledge of the structure, and the analogy provided by extensive investigations on the surface structure of goethite [9], it seems likely that the surface of synthetic β-FeOOH is composed of singly, doubly and triply co-ordinated hydroxyl groups. Recent work has shown that in a series of well-crystallised synthetic goethite samples of small particle size, each of the three species of surface hydroxyl decomposes at a specific temperature which is lower than that observed for bulk hydroxyl [8]. In the case of β-FeOOH, however, the peak temperatures for the surface dehydroxylations are considerably lower than those observed for synthetic goethite, indicating that the
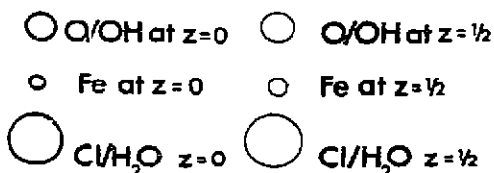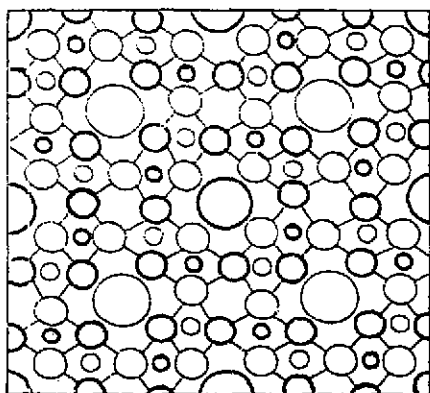

$\bigcirc$ O/OH at z=0 $\bigcirc$ O/OH at z=½

$\circ$ Fe at z=0 $\circ$ Fe at z=½

$\bigcirc$ Cl/H$_2$O z=0 $\bigcirc$ Cl/H$_2$O z=½

Fig. 7. Projection on (001) of β-FeOOH structure.

surface hydroxyl groups are less stable. Confirmation of the assignment of these peaks to surface reactions is provided by the influence of adsorbed phosphate on the DSC curves. At intermediate levels (500 μmole g^{-1}) of adsorbed phosphate, the three peaks coalesce to a very poorly resolved shoulder on the main dehydroxylation peak and at higher levels (1000 μmole g^{-1}) they are removed completely.

The theoretical weight loss for the reaction

$$2\ FeOOH \rightarrow Fe_2O_3 + H_2O$$
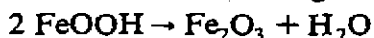
is 10.1% whereas the total weight losses for samples 1 and 2 are 19.3 and 21.3%, respectively. Although some of the excess weight loss is due to the presence of physically adsorbed water, the percentage weight losses after drying over phosphorus pentoxide are still considerably higher than the theoretical values at 14.4 and 18.8%, respectively, on an anhydrous basis. If, however, the theoretical weight losses are calculated allowing for the presence of occluded chloride and excess protons for charge compensation, then the calculated values become 12.8 and 14.1%, respectively, thus giving excess weight losses of 1.6 and 4.7%. For sample 1, the excess loss is of the same order as that observed for a series of synthetic goethite samples [8] and is probably due to additional hydroxyl in the structure arising from protonation of surface oxide ions.

Protonation of surface oxide ions cannot, however, wholly account for the discrepancy of 4.7% between the calculated and experimental weight losses for sample 2. An additional factor that must also be considered is the presence of a period of a rapid weight loss of about 3.5% at 420°C. Although the mass balance then becomes reasonably satisfactory for sample 2, the actual reaction responsible for this rapid weight loss is more difficult to identify, particularly in view of the inclusion of all normal paths of weight loss in the calculated figures. However, a number of observations including the evolution of a brown gas from which a red deposit condenses and the formation of HCl on heating β-FeOOH in a nitrogen atmosphere strongly suggest that chemical transport of iron is taking place. It is interesting to note that, whereas the classical transport in the system Fe_2O_3/HCl takes place in the temperature range 800–900°C [11], the process occurs over a narrow temperature range at about 420°C on heating β-FeOOH. This is undoubtedly due to the presence of chloride in the structural tunnels of β-FeOOH and the consequent close contact between the oxide structure and the nascent hydrogen chloride which will reduce the influence of the chlorination reaction in the chemical transport reaction sequence [11].

The good agreement between the calculated and experimental values for sample 1 implies that water, if present in the structural tunnels, is removed by evacuation over phosphorus pentoxide. The weight loss which occurs during this drying procedure is 6.3%, a value three times the calculated monolayer capacity for adsorbed water on particles of the same size as those of sample 1. Such a large amount of adsorbed water seems improbable for a sample equilibrated at 56% relative humidity and may include a contribution from water removed from the structural tunnels, although the mechanism by which water molecules can pass the tight-fitting chloride ions within the tunnels is not readily apparent.

Much of the discussion on the thermal decomposition of β-FeOOH and, indeed, of poorly ordered hydrous oxides of iron, has, in general, been concerned with the reaction responsible for the exothermic peak between 400 and 500°C. Mackenzie and Berggren [1] suggested that this is due to the crystallisation of hematite and the present results are consistent with this interpretation. For the samples heated in an atmosphere of nitrogen, poorly crystallised α-Fe$_2$O$_3$ is present before the sharp exotherm but it has the same morphology as the reactant, β-FeOOH, whereas after the exothermic peak, the X-ray pattern shows only α-Fe$_2$O$_3$ and the electron micrographs demonstrate clearly the formation of pseudo-hexagonal plates of α-Fe$_2$O$_3$ (Fig. 6).

The change in the position and shape of the exotherm in an oxygen atmosphere has not been reported previously and it is interesting to note that the phase first noted by Chandy [12] on heating β-FeOOH is stable over a fairly wide temperature range and it seems reasonable to conclude that it is the dehydroxylate of β-FeOOH, namely β-Fe$_2$O$_3$ [3]. The exothermic peak which occurs at higher temperatures in oxygen can then be interpreted as the phase change β-Fe$_2$O$_3 \rightarrow \alpha$-Fe$_2$O$_3$.

The explanation for this unusual behaviour lies in the products obtained in the two different atmospheres. In nitrogen, the chloride ions contained within the structural tunnels are lost relatively easily (Table 1) and the evolved gas is HCl, formed presumably by reaction between the water molecules produced by dehydroxylation and the chloride ions

$$2\,H_2O + 4\,Cl^- = 4\,HCl + O_2 + 4\,e^-$$
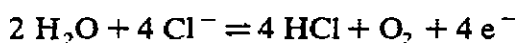
The presence of oxygen, however, will affect this reaction considerably by delaying the release of chloride ions until chlorine formation occurs. In this way, the dehydroxylate in an oxygen atmosphere will retain chloride ions in the structural tunnels maintaining the main structural features of β-FeOOH and stabilising the dehydroxylate. A similar mechanism may explain the stability of β-Fe$_2$O$_3$ under dynamic high vacuum conditions reported by Braun and Gallagher [13]. Thus, in addition to playing an important role in the formation of β-FeOOH [11], chloride ions also play an important part in its decomposition.

CONCLUSIONS

The general features of the thermal decomposition of β-FeOOH are similar to those of the other polymorphs of FeOOH with a dehydroxylation reaction at about 300°C, but there are a number of significant differences. The first is the instability of the surface hydroxyls compared with those on goethite, although both oxides exhibit a similar stabilisation of the surface on adsorption of phosphate. The second difference is in the atmosphere dependence of the phase changes which occur after dehydroxylation. In a nitrogen atmosphere, the product immediately after dehydroxylation is poorly crystallised hematite pseudomorphous with the original β-FeOOH but after the sharp exothermic peak on the DTA curve, the crystallinity of the

hematite increases and the characteristic plate-shaped morphology of α-Fe_2O_3 develops. In an oxygen atmosphere, however, a poorly crystallised phase, probably β-Fe_2O_3, is formed and is stable over a wide temperature range. This phase then undergoes a transformation to α-Fe_2O_3 at temperatures of 600–750°C depending upon the chloride content of the initial β-FeOOH.

Finally, the suggestion that chemical transport occurs with in situ chlorination of the transported phase during the thermal decomposition of β-FeOOH clearly merits further investigation.

ACKNOWLEDGEMENTS

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