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THERMAL BEHAVIOUR IN AIR OF IRON OXYHYDROXIDES OBTAINED FROM THE METHOD OF HOMOGENEOUS PRECIPITATION. PART II. AKAGANEITE SAMPLE

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ABSTRACT

Differential scanning calorimetry (DSC), thermogravimetry (TG), infrared spectroscopy (IR) together with X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) have been employed to follow the structural and morphological changes happening in the thermal decomposition, in air, of a synthetic akaganeite sample (β-FeOOH). It has been stated that both the water molecules and chloride ions adsorbed within the structural tunnels have an important role in the stability of structure of akaganeite. At 300 °C, after the dehydroxylation, two broad reflections can be detected only in the X-ray diffraction pattern, which shows traces of both akaganeite and haematite. The sharp exothermic peak appearing in the DSC curve at 360 °C is related to both the loss of chloride ions as HCl and the formation of haematite. At this point there is a change in crystallite shape, and the porosity almost disappears indicating that a sintering process is occurring. From 430 to 700 °C the haematite crystallinity increases. At 700 °C two kinds of crystals, rhombic and hexagonal, can be observed.

INTRODUCTION

The thermal behaviour of synthetic akaganeite (β-FeOOH) and the structural and textural changes happening in this thermal process have been the subject of numerous studies. This is due to the interesting structure and morphology of the akaganeite crystals, which on heating can be decomposed in several ways, depending on both the atmospheric conditions surrounding the sample (in vacuum, air, N_2 or O_2), and factors concerning the precipitation process of the sample (temperature, pH, Cl/Fe ratio, nature of hydrolytic agent, hydrolysis rate, ageing time, etc.)

So, from the thermogravimetric data of akaganeite samples with different amounts of chloride, Weiser and Milligan [1] found that a sample containing

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appreciable adsorbed chloride (7.8%) starts to loose its hydrate water at a temperature 50 ° C higher than does a relatively pure sample. Therefore, they concluded that the adsorbed chloride stabilizes the crystal lattice of akaganeite. A similar conclusion was made by Dasgupta and Mackay [2].

The dehydroxylation reaction has been observed on the DSC or DTA curves as a single endothermic peak centered at about 250 ° C, depending on sample factors such as particle size, crystallinity, chloride content, etc.. After this, a sharp exothermic peak is always observed, at a temperature between 420 and 512 ° C, depending on the intermediate compound formed after dehydroxylation. The interpretations given by the authors of this exothermic effect have been contradictory.

Mackenzie [3] attributed it to recrystallization of α-Fe_2O_3, which is formed on dehydration. This was revised by Mackay [4] who first noticed that the exothermic effect was due to the transformation of an intermediate magnetic product such as the spinel γ-Fe_2O_3 to α-Fe_2O_3. The γ-Fe_2O_3 together with Fe_3O_4 were obtained by the author from heating single crystals of β-FeOOH in the beam of the electron microscope. The γ-Fe_2O_3 form was also detected by Galbraith et al. [5], after a short period of irradiation of β-FeOOH in the electron beam.

In agreement with ref. 5, Gonzalez-Calbet and co-workers [6,7] obtained a poorly crystallized ferromagnetic product like maghaemite from the heating in vacuo of β-FeOOH. The maghaemite transforms to haematite producing a very marked exothermic effect centred at 500 ° C.

According to ref. 4, Meroño et al. [8] pointed out that traces of magnetite Fe_3O_4 were obtained together with poorly crystallized maghaemite. The exothermic effect that appeared at about 440–510 ° C was interpreted as both the transformation γ-Fe_2O_3 to α-Fe_2O_3 and the increase of haematite crystallinity that occurs simultaneously with its formation.

On the contrary, Gallagher and co-workers [9,10] reported that the magnetic intermediate compound formed by heating akaganeite in vacuo was β-Fe_2O_3. This form shows anion vacancies created by the removal of water from the β-FeOOH structure. They proposed two kinds of co-ordination for the iron ions: all the internal Fe^{3+} was 5-co-ordinated whilst the surface Fe^{3+} ions were tetrahedrally co-ordinated.

Naono et al. [11] pointed out that β-FeOOH transforms to α-Fe_2O_3 through an apparently amorphous state, which may be due to the porous character and ultrafine crystal structure of decomposed β-FeOOH.

When the thermal decomposition of akaganeite is carried out in air, N_2 or O_2 atmospheres, no γ-Fe_2O_3 is formed; on the contrary, α-Fe_2O_3 of varying crystallinity is obtained after dehydroxylation. In these cases, the exothermic effect is related to a recrystallization process of haematite [8, 12–14].

In contrast, Paterson et al. [15] indicated that after dehydroxylation, a different but poorly-crystallized phase occurs in each atmosphere. These phases change particle shape and increase crystallinity at higher temperatures, probably accounting for the exotherm, although the peak is also associated with the loss of chloride in a N_2 atmosphere.

Recent research by Chambaere and De Grave [16,17] showed that, under ambient atmospheric conditions, heating causes the crystal structure of β-FeOOH to degenerate gradually into a quasi-amorphous intermediate phase (QUAIPH), before the final phase transformation to α-Fe_2O_3.

In previous papers [18,19] we were concerned with the synthesis and characterization studies of β-FeOOH obtained by the method of homogeneous precipitation with urea, and the structural mechanism of the interconversion between β-FeOOH and α-Fe_2O_3 occurring as a result of heating akaganeite in the mother liquors at 100 °C. In Part I of this series [20] we studied the thermal behaviour in air of goethite samples of varying crystallinity. In this paper we describe a similar study of an akaganeite sample. This has been carried out by differential scanning calorimetry (DSC), thermogravimetry (TG), (DTG), X-ray powder diffraction (XRD), infrared spectroscopy (IR) and transmission electron microscopy (TEM).

EXPERIMENTAL

The synthetic akaganeite sample was obtained from a hydrochloric solution (pH 0.7) of 0.37 M Fe(III), which was hydrolized by freshly prepared 0.74 M urea solution. The solution was heated at 100 °C in a flask fitted with a reflux condenser. Forty-five minutes from the beginning of precipitation, the product was filtered off. This product was extensively washed with distilled water untill the wash liquid did not contain Cl^- or NH_4^+ impurities.

Chemical quantitative analysis for chloride and Fe(III) were carried out on unheated and heated samples at temperatures from 25 to 900 °C. The chloride content was determined by the Volhard method. Fe(III) analysis was by redox titration with dichromate. The gas released from the sample during decomposition was collected using 0.037 M NaOH solution. This was titred with 0.037 M HCl solution, at the end of the thermal process.

The thermal analysis of sample (TG, DTG and DSC) was carried out on a Mettler TA 3000 analysis system with a CTC10TA processor. Samples of about 20 mg were heated at a rate of 10 °C min^{-1} in an air stream using alumina crucibles.

Samples were obtained at different steps of the DSC curve (220, 300, 430 and 700 °C). These were selected for characterization studies.

X-ray diffraction patterns were recorded on a Siemens D500 diffractometer using Cu $K\alpha$, radiation and graphite monochromator K805. The IR study was carried out on a Perkin-Elmer 599B instrument. KBr pellets of 0.6% concentration of sample were used. Electron micrographs were performed on an AEI EM6 microscope. Samples were suspended in water, and a drop of suspension was deposited on a copper grid coated with a carbon film.

RESULTS AND DISCUSSION

Thermal analysis

The TG, DTG and DSC curves (Fig. 1) are different in shape from those reported previously [7,8,12].

As can be seen, from 25 to 350 ° C, total dehydration of akaganeite crystals takes place in three differentiated steps. Between 25 and 220 ° C, a large and broad endothermic effect with two maxima at 90 and 150 ° C appeared. We believe that these indicate the elimination of two different kinds of adsorbed water molecules from the surface of the crystals (2.9%) and structural tunnels (4.1%).

Between 220 and 300 ° C, a second endothermic peak appeared that is due to elimination of water from constitutional OH groups (11.5%).

At about 360 ° C a sharp exothermic peak on the DSC curve and an abrupt weight loss (3.2%) on the TG curve were detected. This last corresponds to elimination of chloride ions, as can be seen from the quantitative analysis of this ion from samples heated before and after the above mentioned abrupt weight loss. Also it can be calculated from the evolved gas analysis that the chloride ions are eliminated as HCl. On the other hand, the Fe^{3+} content of a sample heated up to 900 ° C is the same as that of the unheated akaganeite. Therefore, there is no loss of Fe^{3+} as sublimated $FeCl_3$.

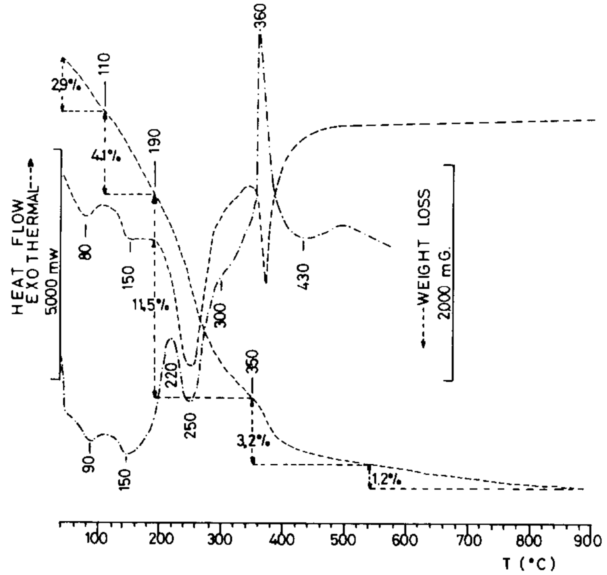

Fig. 1. TG, DTG and DSC curves of an akaganeite sample.

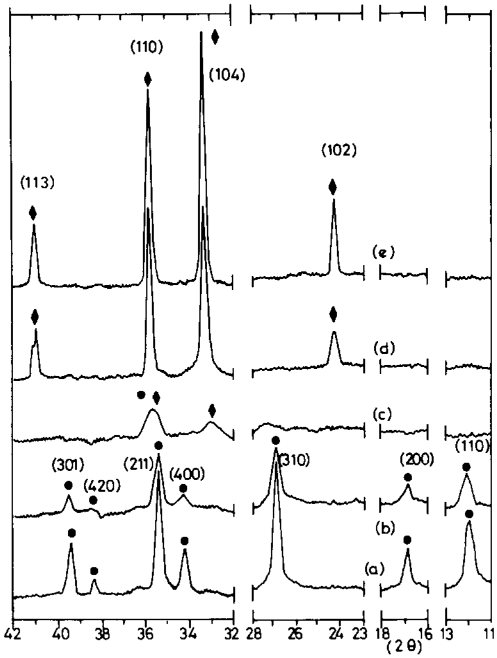

Fig. 2. X-ray diffraction patterns of akaganeite heated at different temperatures: (a) unheated, (b) 220 ° C, (c) 300 ° C, (d) 430 ° C, (e) 700 ° C. ●, akaganeite; ◆, haematite.

The XRD analysis of the sample heated at 430 ° C (after the exotherm), shows the haematite diffraction pattern (Fig. 2d). Therefore, the exotherm can be attributed to both the elimination of chloride ions and the formation of the haematite compound.

It is well known that the chloride ions, especially those adsorbed within the structural tunnels of akaganeite, have a decisive role in the stability of this material. So, the β-FeOOH to α-Fe_2O_3 thermal transition will be strongly related to both the amount of chloride and the way these ions are eliminated.

Ishikawa and Inouye [21] pointed out that the chloride ion was eliminated as HCl and $FeCl_3$ at about 375 ° C. In agreement with these authors, Naono et al. [11] reported that the total elimination of Cl was as HCl vapour at a temperature near 300 ° C, followed by sublimation of iron(III) chloride at higher temperatures. The haematite phase was detected by the authors after the total elimination of Cl at 500 ° C.

Gonzalez-Calbet et al. [6] attributed the small and narrow endothermic effect centred at 325 ° C to elimination of some of the chloride ions. These authors observed that the very marked exotherm centred at 500 ° C was always accompanied by a weight loss of the order of 3%. We believe that probably this last weight loss may be related to the elimination of the remaining chloride ions.

Chambaere and De Grave [17] studied the thermal evolution of the chloride content with neutron activation analysis on ^{37}Cl. They concluded that, far from being an easily removable contamination, a considerable amount of chloride remains in the structure at high temperatures and that massive loss of chloride is only observed when the final phase transformation to α-Fe_2O_3 occurs.

Thermal evolution of the crystal structure

X-ray diffraction analysis

Figure 2 shows the evolution of the XRD-patterns as a function of the heating temperature.

When the sample is heated to 220 ° C (after the first endothermic effect), the X-ray diffractogram is similar to that of the unheated akaganeite, but its reflections are less intense and broader (compare Fig. 2b and 2a). This suggested to us that the internal adsorbed water within the tunnels has an important role in the stability of akaganeite structure. This is in disagreement with ref. 6, which states that the elimination of adsorbed water from the structural tunnels does not alter the crystal structure of akaganeite.

According to Chambaere's study [16], the degeneration of the crystallinity of akaganeite is strongly related to the crystal water that the starting material contains. So, the more crystal water, the more clearly this effect is seen. The differences between our results and those of ref. 6 could be explained in this way.

After the second endothermic effect corresponding to elimination of constitutional OH groups, as might be expected the akaganeite diffraction pattern has disappeared: only two very broad bands can be observed (Fig. 2c). The more intense one can be attributed to the $d_{211} = 2.54$ Å of akaganeite, or the $d_{313} = 2.52$ Å of maghaemite, or the $d_{110} = 2.51$ Å of haematite. The second band can be attributed to the $d_{104} = 2.69$ Å of $I/I_0 = 100$ haematite.

The presence of maghaemite, γ-Fe_2O_3 in this sample was ruled out, since no maghaemite was detected from the Mössbauer spectroscopic analysis.

As will be shown below from the IR results, we concluded that the more intense reflection is due to both the $d_{211} = 2.54$ Å of akaganeite and the $d_{110} = 2.51$ Å of haematite. The second very broad reflection corresponds to $d_{104} = 2.69$ Å.

This quasi-amorphous intermediate phase has been considered by Chambaere and De Grave [16] as a new material (QUAIPH), which is not a well defined phase but rather a range of intermediate states between β-FeOOH proper and α-Fe_2O_3. In contrast, Babcan and Kristin [12], after dehydroxylation detected the haematite phase, but in a poorly crystallized form.

When the akaganeite sample is heated up to 430 ° C, after the exothermic effect, the X-ray diffractogram corresponds to the haematite diffraction

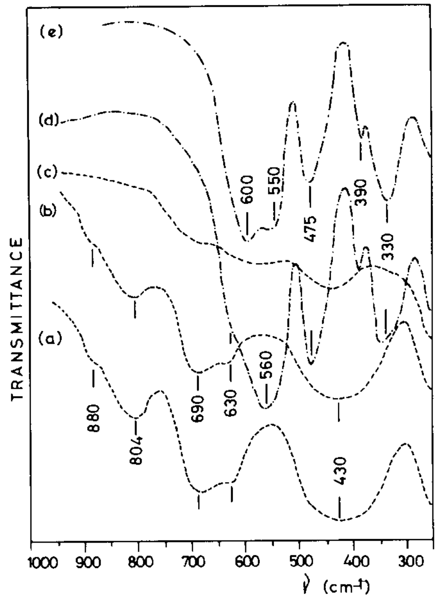

Fig. 3. IR spectra of akaganeite heated at different temperatures: (a) unheated, (b) 220 ° C, (c) 300 ° C, (d) 430 ° C, (e) 700 ° C.

pattern. The crystallinity of haematite increase with temperature up to 700 ° C (compare Fig. 2d and 2e). The crystallinity does not change at higher temperatures.

IR spectroscopic analysis

As can be seen in Fig. 3 the IR results confirm the above mentioned XRD conclusions. The akaganeite absorption bands are broadened with increasing temperature. At 300 ° C, the absorption bands corresponding to δ(OH) vibrations at 804 and 690–630 cm^{-1} had disappeared. However, the lattice vibration Fe–O–Fe at 430 cm^{-1} could still be observed. The haematite absorption appeared at 560 cm^{-1}. From the IR results together with those from the XRD analysis, we concluded that the sample can be considered as a mixture of quasi-amorphous akaganeite and haematite.

In agreement with ref. 22 we believe that the band appearing at 804 cm^{-1} corresponds to the δ(OH) vibration of constitutional OH groups of akaganeite, and not to interactions of the H_2O molecules with the structural tunnels of akaganeite, as ref. 6 pointed out. This is supported by the comparison between the IR spectrum at 220 and 300 ° C (compare Fig. 3b and 3c).

At 220 ° C (all the adsorbed water had been eliminated), the absorption at 804 cm^{-1} still remained; however, at 300 ° C (after the dehydroxylation reaction) this band had disappeared.

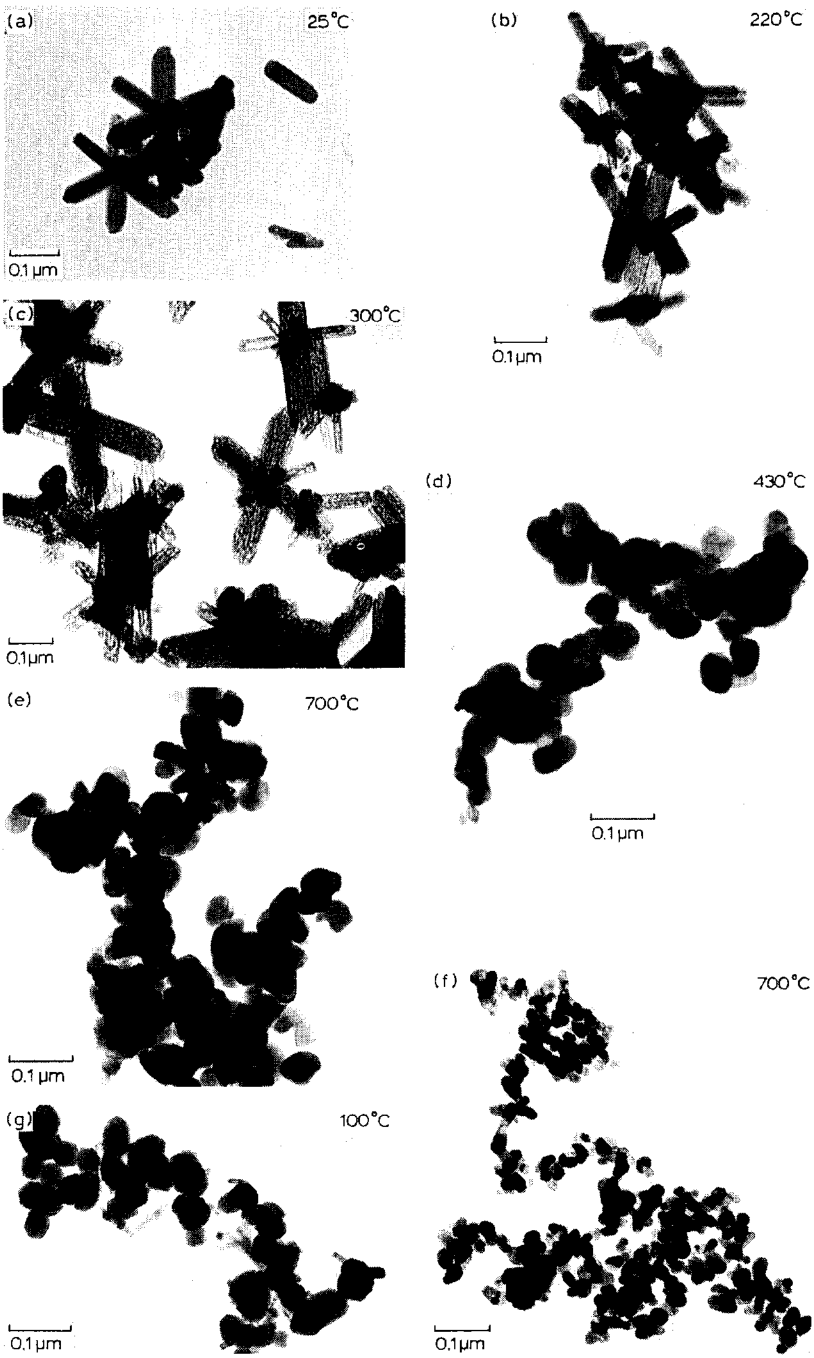

Fig. 4. Transmission electron micrographs: (a) unheated akaganeite, (b) 220 ° C, (c) 300 ° C, (d) 430 ° C, (e) 700 ° C, (f) haematite sample obtained from heating goethite at 700 ° C, (g) haematite sample obtained from akaganeite, via solution, at 100 ° C.

At 430 °C, after the exothermic effect, the haematite absorption bands can be clearly detected at 560, 475, 390 and 330 cm^{-1}. The shoulder appearing at about 630 cm^{-1}, according to Rendon's study [23] can be assigned to an A_{2u} surface mode vibration of haematite. This band almost disappeared in the IR spectrum of haematite formed at higher temperatures due to sintering.

Because the haematite sample at 430 °C contains water molecules (1.2%) from the akaganeite decomposition (see the TG curve in Fig. 1), the shoulder also could be assigned to the $\delta(OH)$ vibration at 630 cm^{-1} of akaganeite.

At 700 °C (Fig. 3e), the band centred at 560 cm^{-1} appeared with two maxima at 600 and 550 cm^{-1}. This difference in haematite spectra can be interpreted in terms of the different size and shape of the particles [23], as is shown below, from the electron microscopic results at this temperature.

Electron microscopic analysis

The morphological evolution of akaganeite crystals with temperature is shown in Fig. 4. As can be seen, there are no changes up to 430 °C (after the elimination of chloride ions). The microporosity observed in the somatoids of the unheated crystals (Fig. 4a) is due to the partial dehydration caused by the damage during the electron beam exposure [5,24].

At 220 °C (Fig. 4b), an increase of microporosity is detected, which is correlated with the elimination of water from the structural tunnels of akaganeite [6]. The micropores widen to elongated-shaped mesopores and near cylindrical macropores at 300 °C (Fig. 4c). This is due to the elimination of water from constitutional OH groups, as previously reported [6,11].

A marked change in particle shape takes place at 430 °C (Fig. 4d). These, homogeneous enough, show a rounded shape typical of synthetic haematite crystals. The porosity has almost disappeared, though several near spherical pores can be observed. In contrast Chambaere and De Grave [16] after the phase transition (the compound is single-phase haematite), observed two different morphological varieties: for some crystallites the recrystallization did not alter the original spindle shape; others are hexagonal.

Morales et al. [14] found that the haematite particles obtained at 300 °C have an elongated shape. When the sample was heated to 525 °C (after the exothermic effect), the authors obtained haematite crystals with a morphology similar to the crystals obtained by us.

At 700 °C (Fig. 4e) the haematite particles have a different size and shape. Some of them present a rhombic shape and others a hexagonal one. The porosity has still not disappeared.

Finally, note (Fig. 4f) the marked decrease of particle size of synthetic haematite obtained from heating goethite at 700 °C. When the haematite is obtained from akaganeite, via solution, at 100 °C, the size of particles increases, and they are very much better formed (Fig. 4g).

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