

The thermal decomposition mechanism of iron(III) hydroxide carbonate to α -Fe₂O₃

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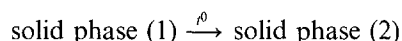
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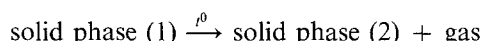
The thermal decomposition mechanism of iron(III) hydroxide carbonate prepared through hydrolysis and oxidation of FeCO₃ is studied under both static and dynamic conditions. It is established that the precursor is decomposed to α -Fe₂O₃ forming an intermediate phase, α -FeOOH. Up to 523 K the structural transformations proceed with limited cation diffusion which leads to the pseudomorphic formation of Fe₂O₃ with large specific area.

1. Introduction

The specific physicochemical properties of iron oxides predetermine their application to the synthesis of magnetic powders, catalysts, ferrites, etc. Apart from the structure and chemical purity of oxides, their properties also depend on the morphology, texture and crystal lattice defects. In some cases oxides prepared under the conditions of the so-called "gentle chemistry" according to the reactions



or



preserve some structural morphological peculiarities of the initial compounds [1]. This genetic predetermination is ascribed to solid transitions realized by collective rearrangement and limited diffusion of atoms [2, 3]. For this reason, both the type of precursor and its decomposition mechanism to oxides with controlled characteristics should be taken into consideration.

The processes of iron oxide preparation from hydroxide and oxide hydroxide phases have been studied in detail [4-6]. Very few data about the application of iron(III) hydroxide carbonate as an initial compound are available [7]. Recently, a pseudo-solid phase method for the synthesis of di- and trivalent metal carbonates from the corresponding double ammonium metal sulphates has been developed [8-10]. The method allows iron(III) hydroxide carbonate of high purity to be prepared and doped with isomorphous exchanged cations.

The present paper presents a detailed study of the iron(III) hydroxide carbonate to α -Fe₂O₃ decomposition mechanism.

2. Experimental procedure

The iron(III) hydroxide carbonate was synthesized according to the procedure described by Dobrev *et al.* [8]. Crystalline FeCO₃ was precipitated from a supersaturated solution of (NH₄)₂Fe(SO₄)₂ · 6H₂O (Mohr salt) and NH₄HCO₃. The crystal phase showed a structure corresponding to that of siderite. The precipitate was washed with distilled water until negative reaction for sulphate anions was achieved. By drying in air at room temperature the resulting wet FeCO₃ was oxidized and hydrolysed to iron(III) hydroxide carbonate.

The precursor was decomposed in a stream of dry air or CO₂ (2 ml sec⁻¹) under isothermal conditions for 4 h.

The chemical composition of the samples was determined by complexometric titration of Fe(III) and gravimetric analysis of CO₂ with natron asbestos. Differential thermal and thermogravimetric analyses were carried out in a steady state air medium at a heating rate of 5° min⁻¹. Mössbauer spectra were recorded on a spectrometer with a constant acceleration, symmetrical pulse velocity and computer registration. The radiation source was ⁵⁷Co in palladium. The isomer shifts were obtained relative to α -Fe absorber, and the non-linearity of the pulse velocity amounted to 0.2%. The spectra were treated by the digital filtering method and by a deconvolution procedure [11, 12]. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) observations were carried out on samples deposited on a carbon substrate (accelerating voltage 80 kV). The decomposition of the initial samples under the effect of electron irradiation was studied *in situ* in the microscope chamber. KBr tablets were used to record infrared spectra. X-ray diffraction analyses were performed with a powder diffractometer using CoK_α radiation.

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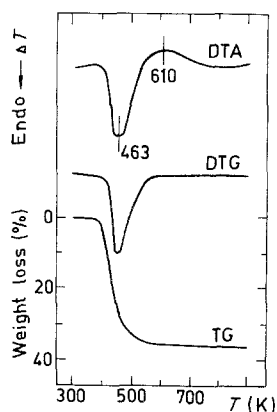


Figure 1 DTA, DTG and TG curves of iron(III) hydroxide carbonate.

3. Results and discussion

Iron(III) hydroxide carbonate is an amorphous substance with varying composition. The established maximum CO_2 content in the samples did not exceed 9 wt %. Further investigations were carried out with a sample of the formula $\text{Fe}_2(\text{OH})_{5.28}(\text{CO}_3)_{0.36}(\text{H}_2\text{O})_{1.26}$.

Differential thermal analysis (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the precursor decomposition are shown in Fig. 1. One stage (endothermal decomposition) proceeds in the range 350 to 550 K. An exothermal process in the range 550 to 650 K, expressed by a diffusive maximum on the DTA curve, is observed.

The amorphous state of the precursor and products obtained hindered considerably the investigations of thermal changes up to about 450 K. By the combination of Mössbauer data (Fig. 2) and infrared (Fig. 3) spectra, more detailed information about decomposition was derived.

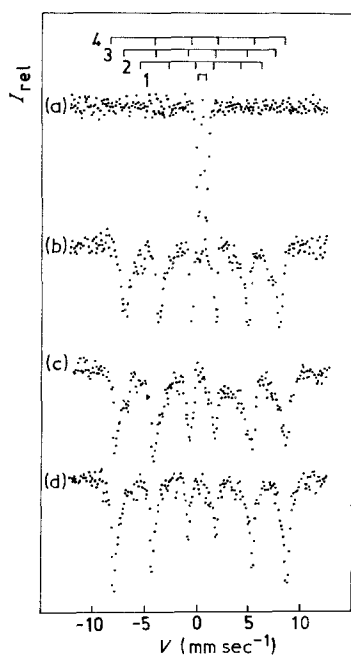


Figure 2 Mössbauer spectra (taken at 77 K) of (a) iron(III) hydroxide carbonate and of thermally treated products at (b) 403, (c) 453 and (d) 493 K in dry air: 1, 2, $\text{Fe}(\text{OH})_x(\text{CO}_3)_y(\text{H}_2\text{O})_z$; 3, $\alpha\text{-FeOOH}$; 4, $\alpha\text{-Fe}_2\text{O}_3$.

The Mössbauer spectrum of the initial phase (iron(III) hydroxide carbonate) recorded at liquid nitrogen temperature is a doublet with an isomeric shift $\delta = 0.45 \text{ mm sec}^{-1}$ and quadrupole splitting $E_0 = 0.8 \text{ mm sec}^{-1}$. The paramagnetic character of the sample cannot be assigned to superparamagnetism due to the particle size. The latter was determined by electron microscope measurements and was close to $1 \mu\text{m}$ (see Figs 4a and 7a). On the spectrum of the intermediate recorded at 403 K, two sextets can be distinguished with internal magnetic fields of $H_{\text{eff}} = 455$ and $H_{\text{eff}} = 368 \text{ kOe}$ (Fig. 2b). The first sextet corresponds to the goethite phase ($\alpha\text{-FeOOH}$), while the other should be ascribed to the presence of undecomposed precursor with magnetically arranged structure. The doublet to sextet transformation observed on heating iron hydroxide carbonate can be explained by a decrease of magnetic dilution resulting in the evolution of non-structural water. The high value of quadrupole splitting of this phase, $Q_s = 0.8 \text{ mm sec}^{-1}$, is an indication of a distortion of the Fe(III) surroundings, which is typical of compounds with layered structural fragments [13]. A further increase in the heating temperature to 453 K leads to the appearance of a third phase, $\alpha\text{-Fe}_2\text{O}_3$, with $H_{\text{eff}} = 508 \text{ kOe}$ (Fig. 2c). The weaker internal magnetic field, as compared to that of the standard, as well as the absence of a Morin's transition up to 77 K, indicate that a defect haematite structure is formed. These results are in connection with the low preparation temperature of $\alpha\text{-Fe}_2\text{O}_3$.

The established phase composition (from Mössbauer spectra) of the sample treated at 453 K was confirmed by X-ray diffraction analysis data. The XRD pattern indicates diffusive lines of $\alpha\text{-FeOOH}$ and two peaks of $\alpha\text{-Fe}_2\text{O}_3$ corresponding to the interplanar spacing of 0.369 and 0.259 nm. At the higher heating temperature of 493 K, the lines of the initial phase in the Mössbauer spectra disappear (Fig. 2d). A complete transition of $\alpha\text{-FeOOH}$ into $\alpha\text{-Fe}_2\text{O}_3$ was observed at 523 K.

The data of the infrared spectra are in good agreement with the decomposition mechanism of hydroxide

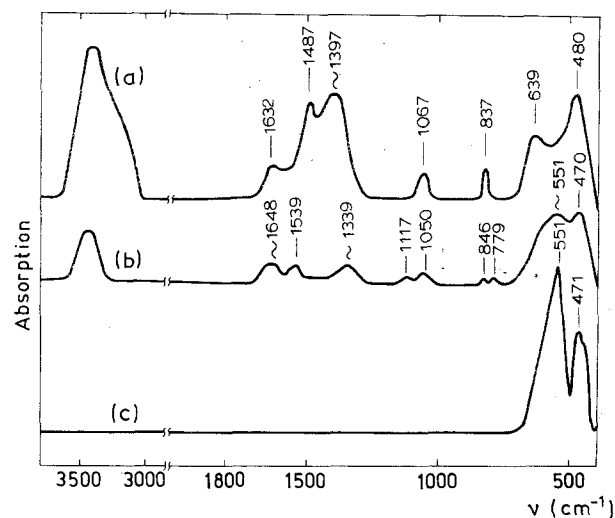


Figure 3 Infrared spectra of (a) iron(III) hydroxide carbonate and of thermally treated products at (b) 453 and (c) 673 K in dry air.

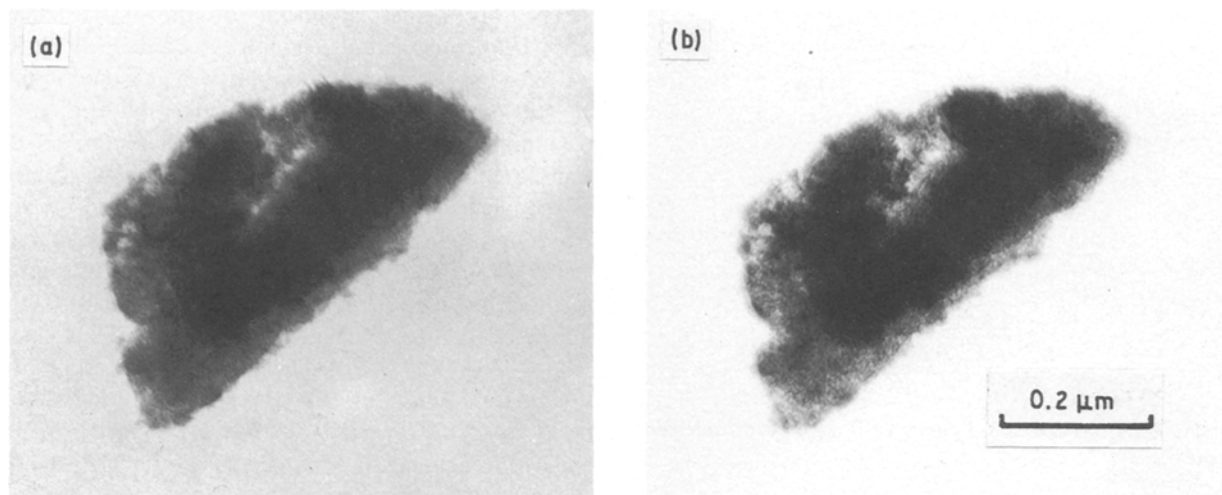


Figure 4 Transmission electron micrographs of iron(III) hydroxide carbonate: (a) initial particles; (b) decomposed particles under electron irradiation.

carbonate precursor derived from Mössbauer spectra data. In the infrared spectrum of the initial sample, the stretching modes of carbonate groups at 837 (ν_2), 1067 (ν_1), 1397 and 1487 (ν_3) were observed (Fig. 3a). The splitting of $\nu_3(\text{CO}_3)$ is an indication of a lower symmetry of carbonate groups than D_{3h} , which is characteristic of the free, relatively undistorted CO_3^{2-} ions. Hence, the Fe–O(CO_3) bond is either mono- or bidentate [14]. The bands at 480 and 639 cm^{-1} are assigned to stretching Fe–O modes in the Fe–O(OH) group. The first band is typical of iron(III) ions in an octahedral oxygen coordination [15]. With increasing heating temperature of the samples, the intensity of the $\nu(\text{CO}_3)$ bands mentioned, as well as of $\delta(\text{H}_2\text{O})$ and $\nu(\text{OH})$ at 1632 cm^{-1} and in the range 3200 to 3600 cm^{-1} is considerably reduced due to the evolution of H_2O and CO_2 . On heating the samples at 453 K, two new bands appear at 779 and at 1117 cm^{-1} . They are characteristic of the OH stretching modes in a goethite phase (Fig. 3b). The formation of a haematite phase at this temperature can be judged by the appearance of broad bands at 470 and 551 cm^{-1} of similar intensity. The intensities of these bands are comparable only in the presence of defects in the haematite lattice. Such intermediates are known as protohaematite phase [16, 17].

The hydroxide carbonate decomposition was followed using transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) observations. The results are presented in Figs 4 and 5.

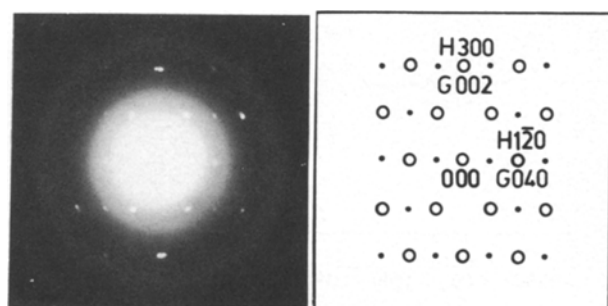


Figure 5 SAED pattern and schematic illustration of iron(III) hydroxide carbonate particle decomposed under electron irradiation.

The texture of the initial particles can be regarded as fibrous (Fig. 4a, see also Fig. 7a). The SAED pattern shows haloes typical of amorphous phases. The prolonged irradiation causes a partial decomposition of the hydroxide carbonate particles. The initial shape is preserved but the SAED pattern is transformed into a spot pattern (Figs 4b and 5a). One can distinguish two varieties of diffraction spots of different size. Two phases were indexed, goethite (G) and haematite (H). All reflections correspond to the [100] plane of the goethite lattice. Some of these spots also belong to the [001] haematite plane. In this case, spot overlapping leads to an increase in their size (Fig. 5b). The following orientation relationship is established: $[100]_G \parallel [001]_H$. The latter is one of the three observed topotactical goethite to haematite transformations [18]. The results show that the iron hydroxide carbonate decomposes preferably pseudomorphously and topotactically under these conditions.

Fig. 6 shows transmission electron micrographs of the hydroxide carbonate decomposition in dry air under varying temperatures. The shape and texture of initial particles are preserved up to about 523 K, at which temperature the sample is a protohaematite phase. Above this temperature the particles change their shape. Initially, spherical packings are formed in the bulk which grow to oval grains with the temperature increase (Fig. 6d). This is an indication that the recrystallization process “protohaematite \rightarrow haematite” runs according to a diffusion mechanism in contrast to previous decomposition stages which proceed at rather limited diffusion.

The specific area variation of iron(III) hydroxide carbonate treated in dry air and in CO_2 as a function of temperature is shown in Fig. 7. The curves follow a similar course; they pass through a maximum at about 500 K. In both gas media, the maximum corresponds to the goethite to haematite phase transition.

4. Conclusion

Two stages can be conditionally distinguished in the thermal decomposition mechanism of iron(III) hydroxide carbonate to $\alpha\text{-Fe}_2\text{O}_3$. The first stage includes the phase transitions iron(III) hydroxide carbonate \rightarrow

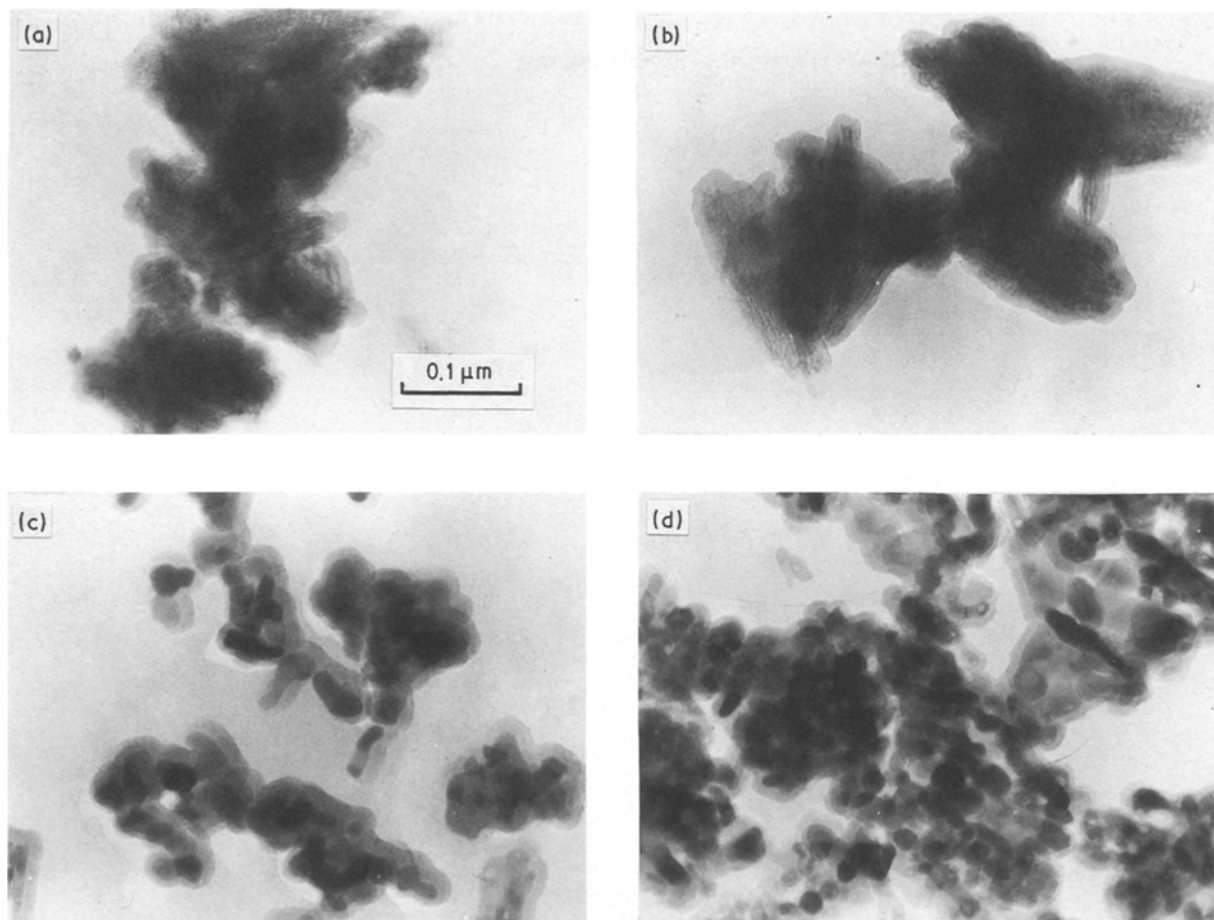


Figure 6 Transmission electron micrographs of iron(III) hydroxide carbonate treated thermally in dry air at (a) 298, (b) 423, (c) 573 and (d) 623 K.

goethite \rightarrow protohaematite, which proceed up to about 523 K. The preservation of the particle form as well as the presence of crystallographic relations between α -FeOOH and α -Fe₂O₃ subcrystallites is an indication that the structural transformations are realized through a limited diffusion. The collective rearrangement of structural units at phase transitions is facilitated by the similar type of oxygen coordination of iron(III) ions in hydroxide carbonate, goethite and haematite. In all three phases, iron cations have an octahedral coordination. The enhancement of specific area up to the protohaematite formation stage is probably due to pore formation.

The second stage comprises crystallization of the protohaematite intermediate to haematite. This pro-

cess proceeds by cation diffusion. As a result, the particle form is changed and some agglomeration is observed, leading to a decrease in the specific surface area of α -Fe₂O₃.

The interpretation of the experimental data allows selection of conditions for iron(III) hydroxide carbonate decomposition with a view to regulating the morphology and structural defects, and thus providing the desirable reactivity of the synthesized α -Fe₂O₃.

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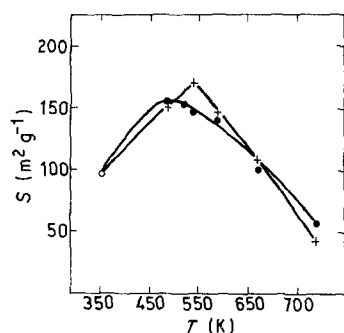


Figure 7 Specific surface area plotted against decomposition temperature dependence of iron(III) hydroxide carbonate in (●) dry air and (+) CO₂.

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