Decomposition of ferrihydrite prepared from $Fe(NO_3)_3$ aqueous solutions under varying pH

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Abstract

Aqueous solutions of $Fe(NO_3)_3$ were subjected to precipitation at 20°C and pH in the range 2.9–8.14, at constant pH and temperature. The precipitates contained CO_3^{2-} and NO_3^- anions bound in the sample structure. It was found that the TG, DTA, DTG and evolved gas analysis (EGA) curves depend significantly on the pH of preparation of the ferrihydrite.

INTRODUCTION

Poorly crystalline precipitates formed by hydrolysis of ferric salts or natural minerals created during hydrolysis and oxidation of iron rich ground waters are called amorphous ferric oxide–hydroxide or ferrihydrite [1]. Ferrihydrite represents a natural source from which more crystalline minerals such as goethite, leipdocrocite and haematite are formed. Synthetic precipitates of ferrihydrite are used as the starting material for synthesis of catalysts, materials for magnetic recording, pigments etc. [1–4].

Synthetic ferrihydrite is formed during the neutralization of aqueous solutions of ferric salts [5–9]. In spite of the fact that ferrihydrite has sometimes been reported as an amorphous ferric gel, evidence of its poor crystallinity has been shown [9–15]. The characteristic powder diffraction pattern of this substance corresponds to a hexagonal cell with parameters $a = 5.08$ and $c = 9.4$ Å [2]. The composition is mentioned as varying; the water content fluctuates between 15% and 24%, and formulae reported are, e.g., $FeOOH \cdot H_2O$, $FeOOH \cdot 3H_2O$, $FeOOH \cdot 2.5H_2O$, $Fe_5O_{12}H_9$ etc. [2].

Dehydration of the above substance occurs during heating in dry air; haematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and the amorphous oxide Fe_2O_3 were found as products [2].

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The ageing of ferrihydride takes place in aqueous medium at elevated temperatures, resulting in the crystalline phases goethite (α-FeOOH) and haematite (α-Fe$_2$O$_3$). The ratio of the crystalline phases in the aged product depends significantly on the conditions of preparation of the starting ferrihydrite sample, namely on the type of the anion in the ferric salt and the pH of precipitation [6, 7].

As follows from these results, it was shown that pH influences the properties of precipitated ferrihydrite. This influence has, however, been inadequately described in the literature.

EXPERIMENTAL

Chemicals

Before each experiment a 3 M solution of NaOH was prepared from a 50% solution, filtered to remove the carbonates present and diluted to the required concentration before the beginning of precipitation.

A 1 M Fe(NO$_3$)$_3$ solution was prepared from Fe(NO$_3$)$_3 \cdot$ 12H$_2$O (analytical grade).

Apparatus and procedure

Samples of ferrihydrite were prepared by precipitation from aqueous solutions of Fe(NO$_3$)$_3$ by NaOH at constant pH in a glass apparatus. Additions of 0.002 ml of 1 M Fe(NO$_3$)$_3$ and 3 M NaOH solutions were made simultaneously to 500 ml of distilled water at the rate of 1 ml min^{-1}. The rate controlled introduction of the neutralization agent (1 M NaOH) made it possible to maintain the pH value during precipitation with accuracy better than 0.1 pH unit [6]. The precipitate was washed with water by decantation until reaction for NO$_3^-$ was negative and sucked dry on a Buchner funnel. The precipitation temperature was 60°C. The ferrihydrite samples were dried at room temperature in air to constant weight.

Characterization methods

Thermoanalytical measurements were carried out on a Netzsch STA 409 analyser connected by a capillary coupling system (Netzsch 403/4) to a Balzers QMG 420 mass spectrometer, using corundum crucibles (size 0.28 ml) and corundum as standard sample. The experiments were carried out in argon under a dynamic atmosphere (Ar of 99.997% purity) at flow rate 75 ml min^{-1} and heating rate 10°C min^{-1} in the range 0–1000°C; the thermocouples were Pt–PtRh, type S. The DTA measurement sensitivity was 35 μV mW^{-1}. Temperature and power calibration was carried out

using ICTA standards. The sample weights ranged between 170 and 180 mg. Results of the measurements were evaluated using Netzsch software with an on-line HP 310 C computer.

The X-ray powder structural analysis was performed with a DRON 2.0 apparatus using Co Kα line emission.

Electron photomicrographs and electron diffraction patterns of the ferrihydrite samples were obtained by means of a Tesla BS-242 W electron microscope.

RESULTS AND DISCUSSION

Characterization of synthetic ferrihydrite samples

For the characterization of ferrihydrite samples, electron and X-ray diffraction patterns as well as electron microscopy have been used in previous papers [1, 8, 11, 12]. Two main types of ferrihydrite samples typified by two- or six-line diffraction patterns were reported in these papers, differing in the degree of ordering of primary particles ($\approx$4 nm) in aggregates. This ordering is more regular and wide ranging in the so called 6-line ferrihydrite [2]. The ferrihydrite samples described in the literature mentioned above were prepared by hydrolysis of ferric salts (chlorides, sulphates and nitrates).

In Table 1 the X-ray diffraction patterns of ferrihydrite samples prepared at various pH values, as obtained in this study, are compared with the literature data. It is obvious that the results of this study are in very good agreement with those of other authors, as follows from Table 1. The ferrihydrite samples prepared in an approximately neutral medium are less crystalline in comparison with the samples prepared in the acidic or alkaline region. The X-ray diffraction pattern of the ferrihydrite sample prepared at pH 5.57 consists of only one broad diffraction line at $d = 2.56$ Å.

Similar results were obtained from the analysis of the electron diffraction patterns. The samples prepared at pH 2.9, 3.9 and 8.14 exhibited electron diffraction patterns with distinct lines with lattice spacings corresponding to ferrihydrite. The samples prepared at pH 5.57 and 7.3 were almost amorphous according to the electron diffraction patterns. Only two diffuse diffraction rings with d values of $\approx$2.54 and 1.47 Å were observed in the electron diffractograms of these samples.

It can be concluded that pH appreciably influences the crystallinity of products of hydrolysis of ferric nitrate. The precipitates of ferrihydrite with the lowest crystallinity originated in the approximately neutral pH region.

TABLE 1

Evaluation of the X-ray diffraction patterns of synthetic ferrihydrite

hkl	Literature data		
	van der Giesen [11]	Towe and Bradley [11]	Chukhrov [1]
110	2.52 vs	2.54 s	2.50 ms
112	2.25 s	2.24 ms	2.21 w
113	1.97 s	1.98 ms	1.96 w
114	1.72 s	1.725 w	1.72 w
115		1.515 ms	1.51 w
116	1.48 s	1.47 s	1.48 s

hkl	Samples prepared at different pH values					
	2.90	3.90	4.21	5.57	7.30	8.14
110	2.54 ms	2.53 ms	2.53 ms	2.56 w	2.60 w	2.53 ms
112	2.23 w	2.23 ms	2.23 ms			2.22 w
113	1.96 vw					
114	1.72 vw					1.69 w
115	1.505 vw					
116	1.47 ms	1.47 ms	1.47 w		1.48 w	1.49 w

Thermal decomposition of synthetic ferrihydrite samples

The DTA, TG and evolved gas analysis (EGA) curves of ferrihydrite samples prepared at various pH values are given in Figs. 1–7. It is obvious from these figures that the character of each thermoanalytical curve differs significantly for samples prepared at various pH values. Total mass loss in the temperature range 20–1000°C varies between 12% and 20%, corresponding mainly to the loss of water. This value of mass loss corresponds to the stoichiometric composition ranging from FeOOH (10.14% of H_2O) to $FeOOH \cdot H_2O$ (25% of H_2O). The significantly highest values of weight loss were observed for the ferrihydrite samples prepared in the pH range 6–8.

For ferrihydrite samples prepared at pH 5.57 and 7.30, characteristic exothermic effects in the range 330–380°C were observed. On the TG curves, small but reproducible mass loss effects (approximately 0.3%) correspond to these peaks. As is obvious from EGA, a sharp peak corresponding to the evolution of CO_2 is observed in the above temperature range. From the X-ray powder diffraction patterns it appears that sample crystallization takes place during this process. The sample is almost amorphous before this effect takes place, whereas after the process is accomplished hematite only is present in the sample. Sample crystal-
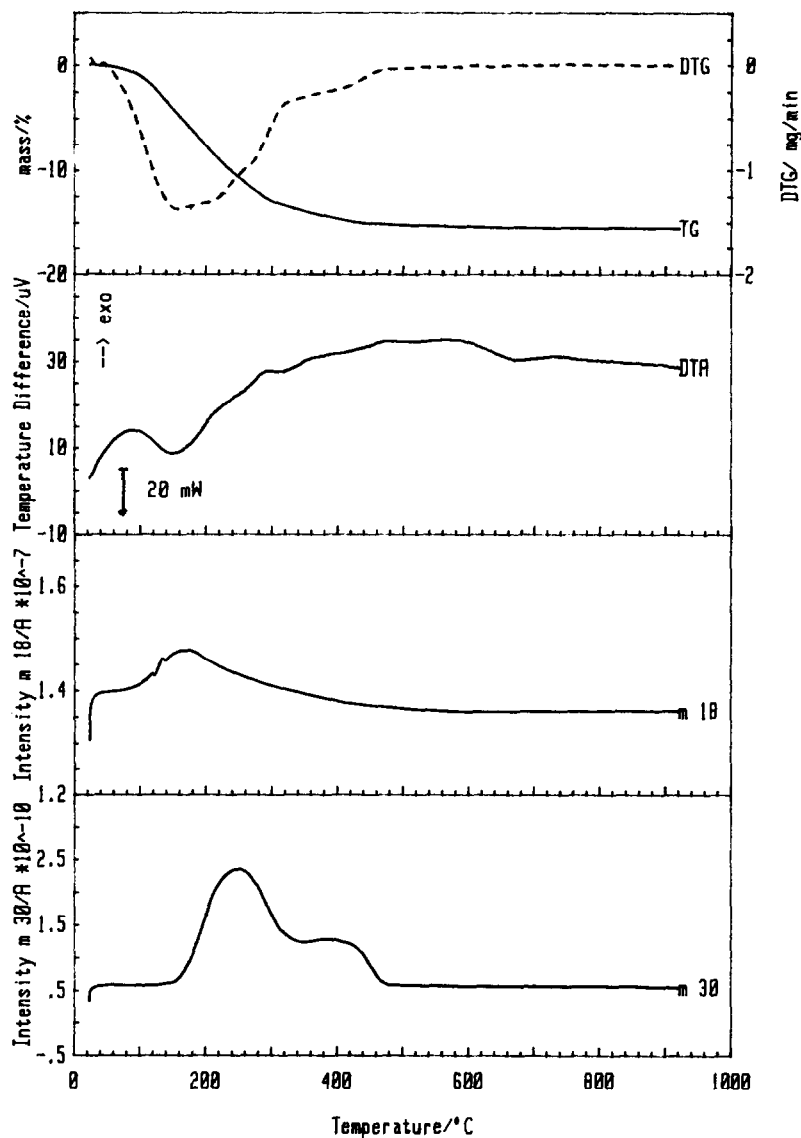
Fig. 1. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 2.90.

lization and hematite formation take place simultaneously during de-hydration in samples prepared in acidic or alkaline medium.

The position of peaks corresponding to sample dehydration is almost independent of the pH of preparation, and occurs at a temperature of 160–170°C.

As is obvious from the results of chemical analysis and from IR spectra, samples of synthetic ferrihydrite contain a small amount of structurally bound NO_3^- and CO_3^{2-} anions beside Fe_2O_3 and H_2O. Therefore the gases
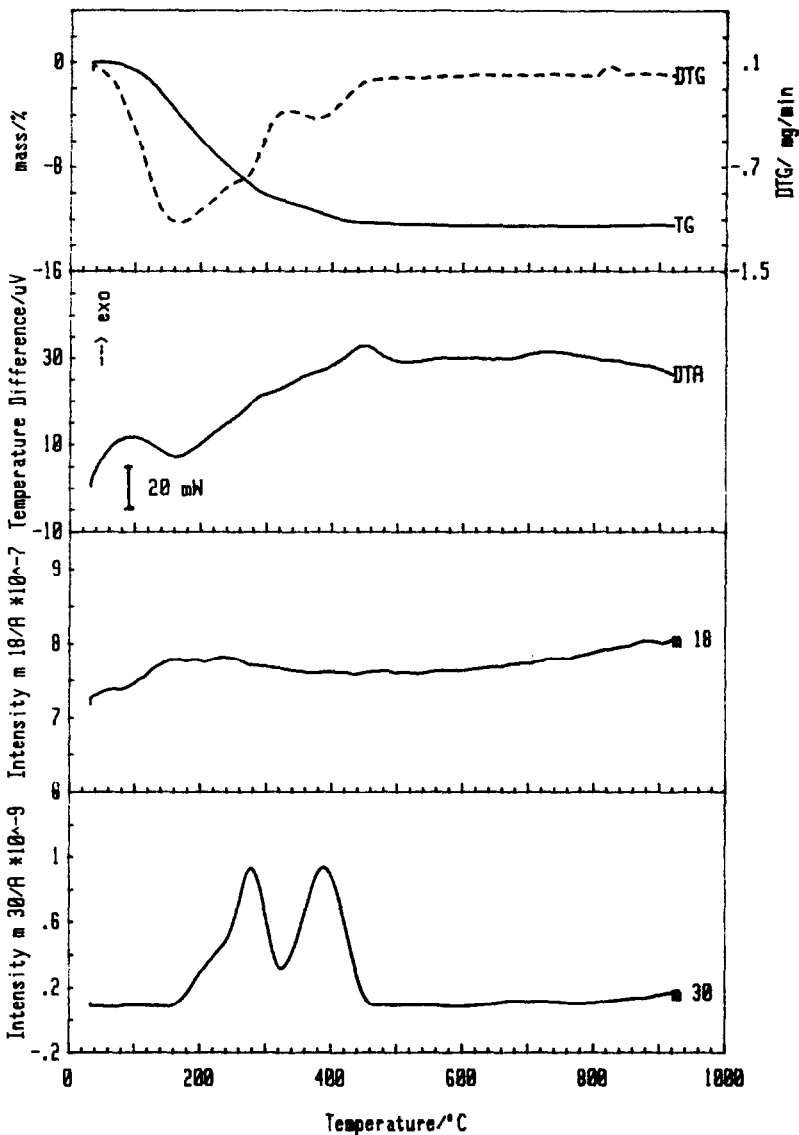
Fig. 2. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 3.90.

released during decomposition of ferrihydrite samples were analyzed in dynamic conditions by means of a QMG 420 analyser. NO, O_2, CO_2, NO_2 and H_2O were detected in the gases released during decomposition. The EGA results are given in Figs. 1–7.

It is obvious from the EGA curves of Figs. 1–7 that the thermal decomposition of ferrihydrite samples is a rather complicated process, and the decomposition of anions occurs at different temperatures depending on the conditions of sample preparation. To distinguish the decomposition
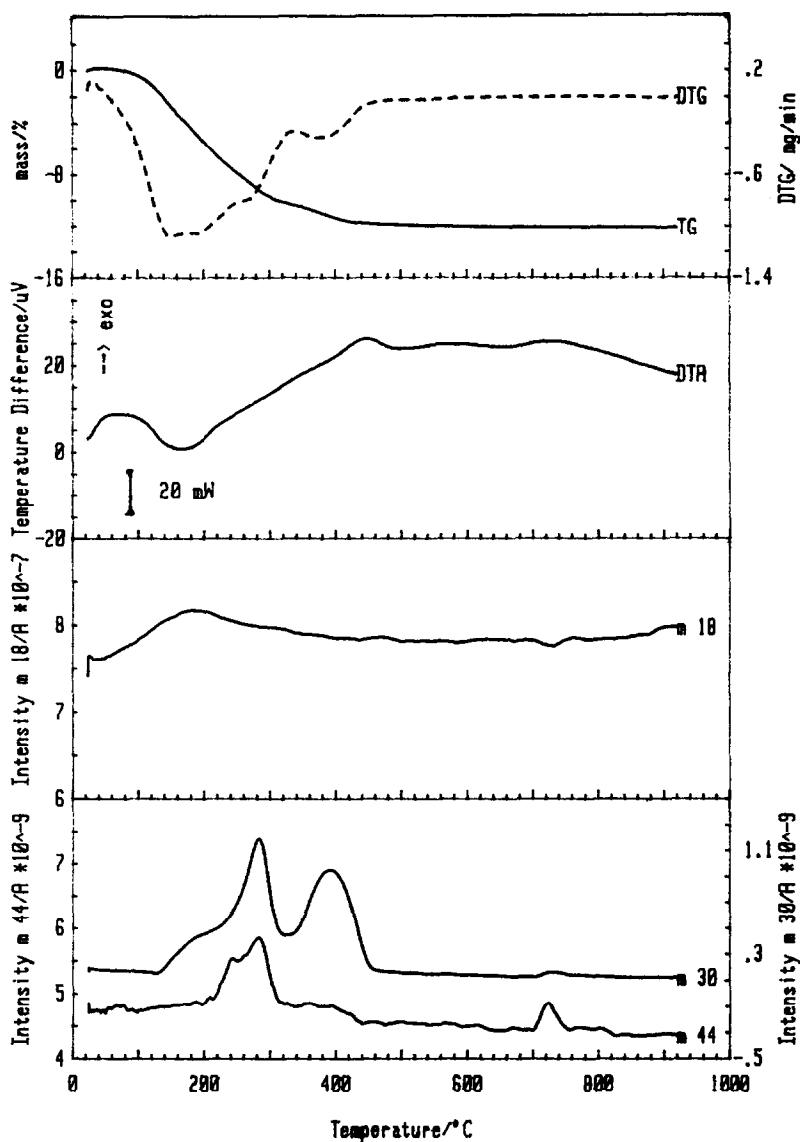
Fig. 3. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 4.21.

of NaNO₃ impurities from that of structurally bound anions unwashed ferrihydrite decomposition was investigated. The decomposition of NaNO₃ impurities occurs at 600–700°C (Fig. 7), whereas the decomposition of structurally bound CO_3^{2-} and NO_3^- is complete below 400°C.

As is obvious from Figs. 1–6, release of the water bound in ferrihydrite samples takes place in the range 80–200°C. On the DTA curve, the dehydration is reflected by a simple endothermic effect with a minimum at 160–170°C, and the DTG curve of water release coincides with the main
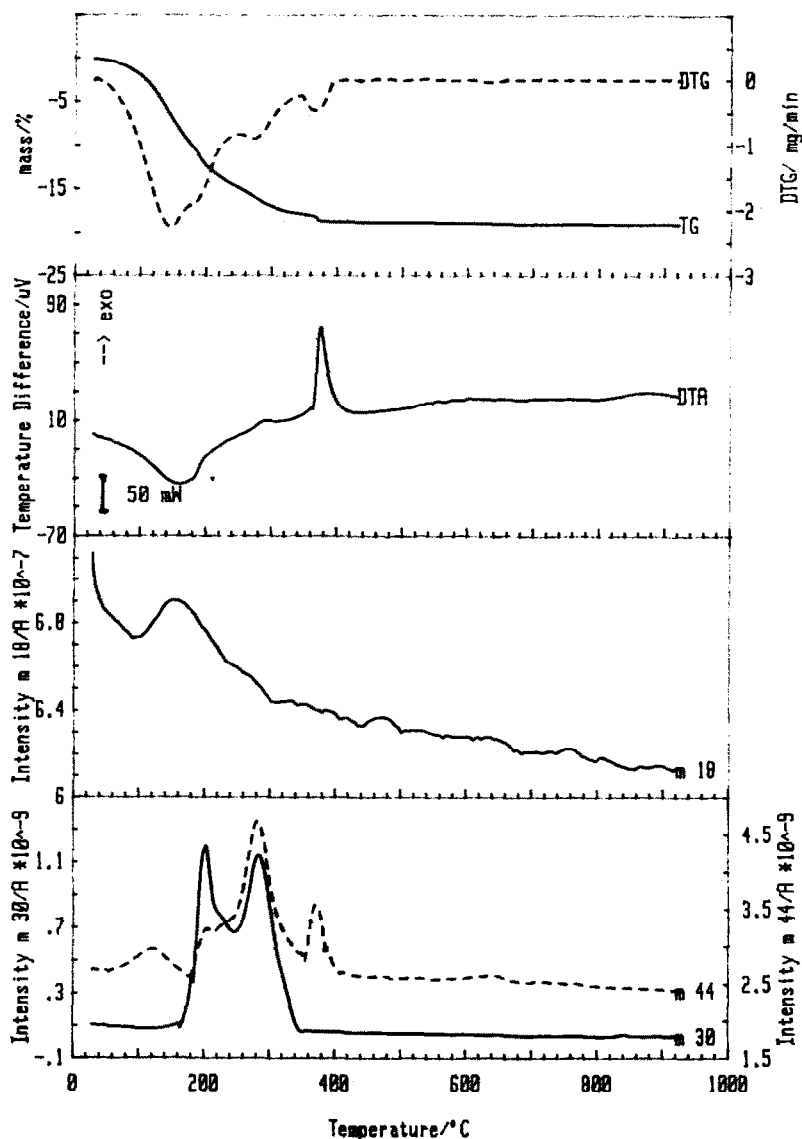
Fig. 4. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 5.57.

DTA endothermic effect. The shape of the DTA peaks corresponding to water release is almost independent of the pH at which the samples were prepared; the water content fluctuates and reaches a maximum at a pH of preparation between 6 and 7.5.

The thermal decomposition of small amounts of NO_3^- anions present in the ferrihydrite samples is reflected by the presence of NO in the analysed gases. The maxima of NO concentration on the EGA curves are at temperatures of ≈ 240, 280 and 300°C. Moreover, a small amount of CO_2
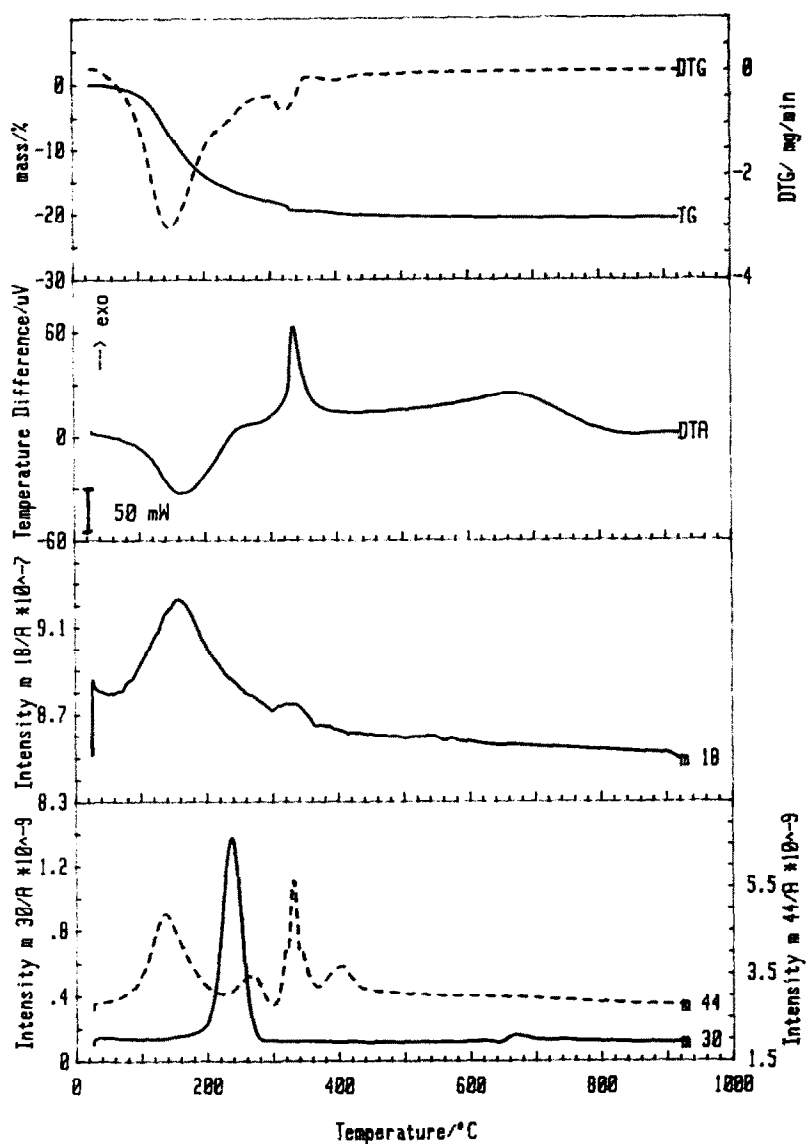
Fig. 5. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 7.30.

was found in the decomposition products of the samples of ferrihydrite prepared at pH 4.21 and higher, as may be seen from the EGA curves (Figs. 1–7).

The ferrihydrite samples prepared at pH 5.57 and 7.30 yield both CO_2 and NO in their gaseous decomposition products. In addition to CO_2 and NO peaks at 200–300°C, additional peaks of CO_2 at 120–140°C and 340–380°C occurred on the EGA curves. The CO_2 peaks on the EGA curves observed at 340–380°C (Figs. 4 and 5) are accompanied by intense
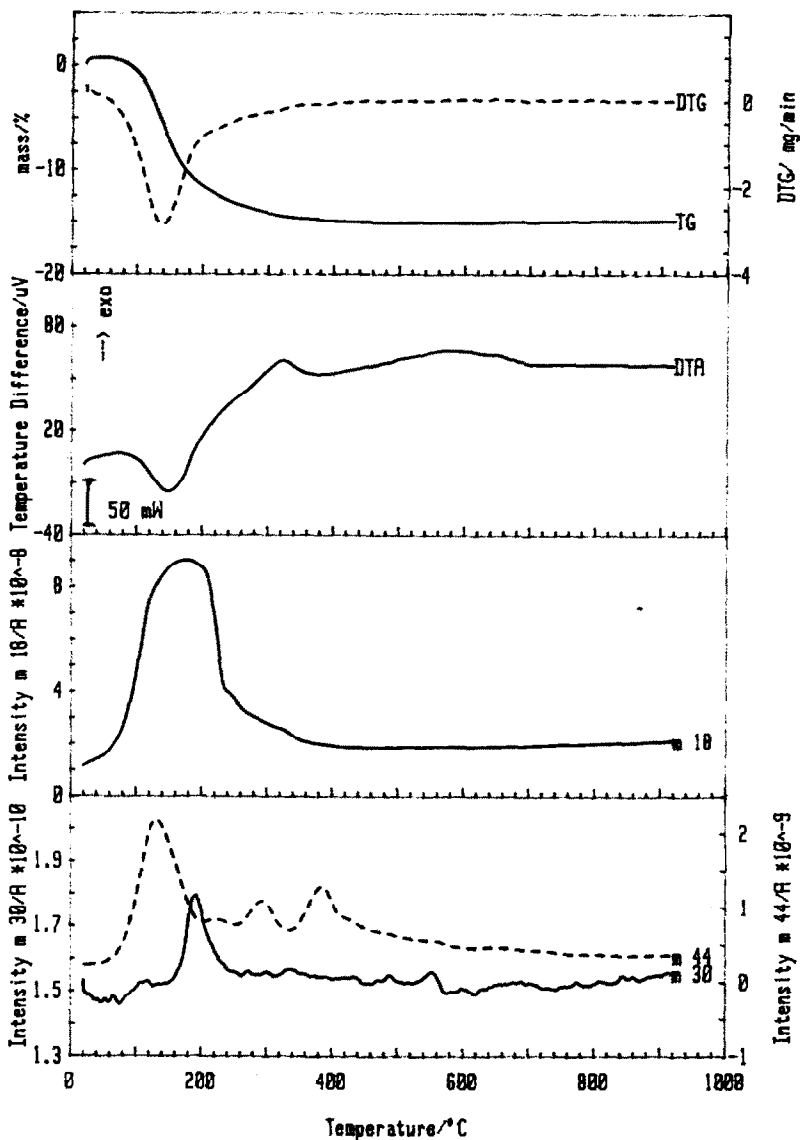
Fig. 6. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 8.14.

exothermic effects on the DTA curve, which enabled us to conclude that the crystallization of amorphous anhydrous iron(III) oxide as α-Fe$_2$O$_3$ (haematite) takes place. This assumption was confirmed by phase analysis of the products before and after this effect took place.

With the sample prepared at pH 8.14, which contained a large amount ($\geqslant$10%) of NaNO$_3$ as impurity, no significant release of NO at temperatures below 400°C was observed (Fig. 6). However, NO (as the decomposition product of NaNO$_3$ admixtures) is present in the gases formed at
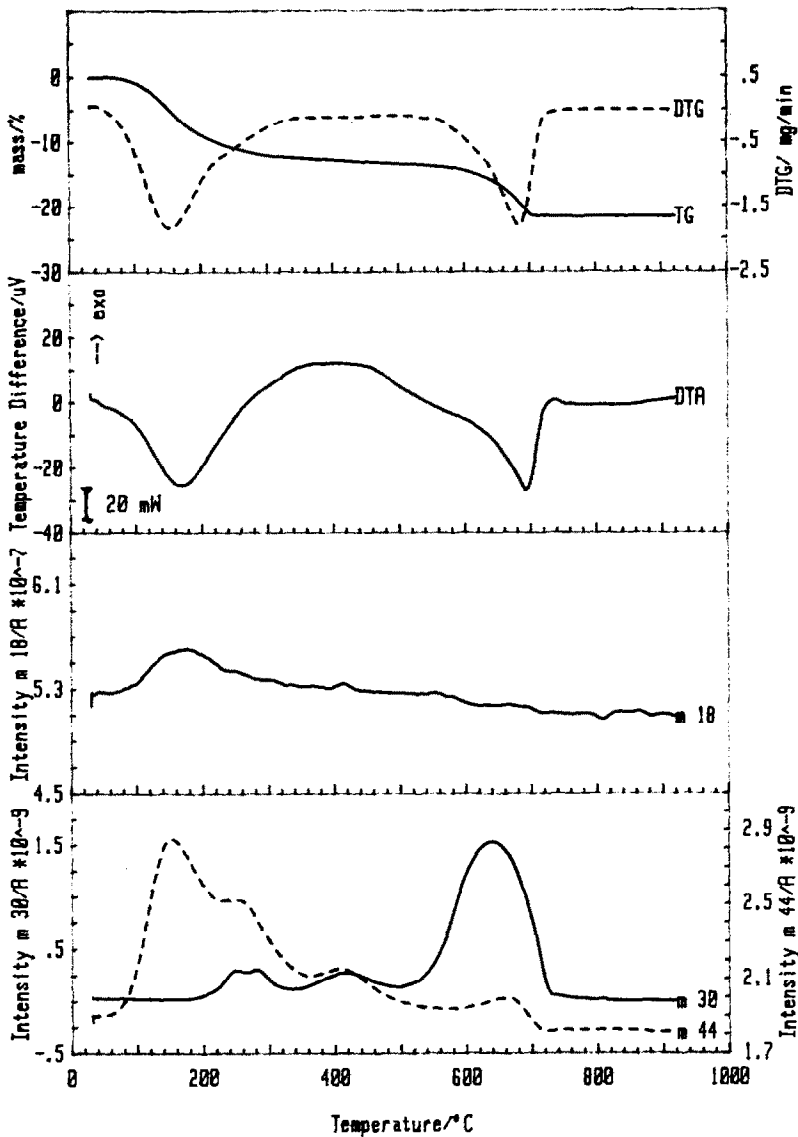
Fig. 7. Thermoanalytical curves of sample of synthetic ferrihydrite prepared at pH 8.14. Soluble precipitation products were not removed.

600–700°C. If $NaNO_3$ is removed from the sample, the EGA peaks are similar to that of a sample containing $NaNO_3$ except for the effect above 500°C (Fig. 7).

From the comparison of EGA curves (corresponding to NO and CO_2) and TG curves it follows that the release caused by the decomposition of NO_3^- and CO_3^{2-} anions bound in the structure of ferrihydrite is not accompanied by changes of mass on the TG curve (because of the low

content of these anions in the ferrihydrite). In conjunction with the main effect on the DTG curves (release of bound water), shoulders can be found corresponding to the decomposition of NO_3^- and CO_3^{2-}. The most significant feature in comparison of DTA, TG, DTG and EGA curves is the coincidence of the EGA effect (release of CO_2) and the exothermic DTA effect, accompanied by significant effects on the TG curve as well as on the EGA curve of H_2O (Figs. 4 and 5). These effects, which are observed only for samples prepared in neutral and weakly alkaline solutions, are related to the crystallization of amorphous iron oxide to crystalline haematite in the region 340–380°C. It can be supposed that processes relying on H_2O release and effects depending on CO_2 and NO release during ferrihydrite decomposition are mutually independent. Consequently one can assume that CO_3^{2-} and NO_3^- anions are bound on the surface of the ferrihydrite particles.

CONCLUSIONS

It was found that the crystallinity and the thermal decomposition of ferrihydrite depend significantly on the conditions of preparation, namely the pH of precipitation. This is in a good agreement with the findings of other authors, who demonstrated the dependence of crystallinity and the course of ageing in water on the preparation conditions of ferrihydrite. Samples of ferrihydrite were prepared which were both X-ray amorphous and crystalline.

It was found that the release of structurally bound water is almost independent of the pH of the solution used for sample precipitation. The decomposition of NO_3^- and CO_3^{2-} anions present in the sample takes place independently of the release of structurally bound water, therefore we can infer the existence of surface bonding of these anions.

It was observed that the exothermic effect at 330–370°C corresponding to the crystallization of haematite is accompanied by a significant effect of CO_2 release on the EGA curve. Consequently it can be concluded that CO_3^{2-} anions bound on the surface prevent the crystallization of amorphous Fe_2O_3 formed during the dehydration of ferrihydrite.

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