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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

CHARACTERISATION OF α-FeOOH GRINDING PRODUCTS USING SIMULTANEOUS DTA AND TG/DTG COUPLED WITH MS

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Abstract

Effects induced by grinding in synthetic goethite samples were studied. The products of α-FeOOH grinding were characterised by means of DTA, TG/DTG coupled with EGA (Mass spectrometry detection), powder X-ray diffraction analysis, and surface area determination.

Keywords: DTA, EGA, goethity hematite, grinding, mechanochemical decomposition, thermal behaviour

Introduction

It was stated by a number of authors [1–9] that prolonged grinding of α-FeOOH at room temperature leads to the formation of α-Fe_2O_3. Mixtures of α-FeOOH and α Fe_2O_3 were found as intermediate products of the mechanochemical decomposition. However, there exists only incomplete information about the thermal behaviour of α-FeOOH grinding products.

The aim of this paper is to present a more detailed description of the thermal behaviour of α-FeOOH grinding products differing in surface area, particle size and structure. The simultaneous DTA, TG/DTG coupled with MS were used in the characterisation of the thermal behaviour. Powder characteristics of the samples were obtained by XRD and surface area measurement.

Experimental

Materials studied

The sample of goethite (α-FeOOH) commercially available as yellow pigment type B-940 produced by Bayer AG (Germany) was studied. The initial

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product consists of a pure goethite of acicular particles of dimensions approximately 1×0.4 μm.

The grinding was carried out in a laboratory planetary mill type Pulverisette 5 (Fritsch, Germany) using two 25 ml agate jars filled with 7 agate bowls with diameter 12 mm. The initial amount of 15 g of goethite and a rate of 660 r.p.m. was used for grinding. The grinding was interrupted after 6, 15, 34, 46, 58, and 70 h in order to sample 0.3 g of the ground products for their characterisation. The bowls were hermetically closed during grinding, so that the water released during mechanical treatment from the samples was kept inside.

Methods used for the characterisation of samples

Thermal behaviour of the samples was characterised by Netzsch STA 409 analyser connected by a capillary coupling system (Netzsch 403/4) to a Balzers QMG 420 mass spectrometer. Corundum crucibles (size 0.28 ml) were used, the reference inert DTA material was sintered corundum powder. The experiments were carried out in the range 20–1000°C in argon (99.97% purity) under a dynamic atmosphere at flow rate of 75 ml min^{-1} and heating rate of 10°C min^{-1}; 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 mass was 0.15 g. 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 Philips PW 1060 apparatus using CuK$_\alpha$ radiation and graphite monochromator. The XRD diagrams obtained in order to monitor the conversion of goethite to hematite were recorded using a goniometer scanning rate of 2 deg min^{-1}. The dimensions of the coherently diffracting domains (crystallite size) of hematite were measured from the width of the half maximum of the (104) and (110) peaks by means of the Scherrer's method [10]. The scanning rate of the goniometer used for this purpose was 1/8 deg min^{-1}.

The surface area measurements were carried out using nitrogen adsorption at the liquid nitrogen temperature using the Rapid Surface Area Analyzer (Micromeritics, model 2200).

Results and discussion

We have observed that when synthetic goethite is ground at room temperature a decomposition takes place yielding products of hematite structure according to results published elsewhere [1–9]. First traces of hematite were detected by powder XRD after 6 h of grinding at the conditions used. The amount of the initial goethite decreased with the grinding time, no goethite was detected after 46 h of grinding.

We have observed that by grinding the mechanical destruction of acicular goethite particles is followed by their dehydration and formation of tinny hematite particles (~10 nm).

At the end of the mechanical decomposition the goethite phase fully disappears and the sample consists of small hematite particles only.

The samples ground for the periods from 6 to 46 h contained both the components of hematite and goethite structures. We have revealed by using the simultaneous thermal analysis techniques that the component of the hematite structure is composed of hematite and hydrohematite [11]. By prolonged milling (lasting 36–70 h) the growth of hematite particles takes place. The increase in particle size with the increasing grinding time was confirmed by XRD line broadening and surface area measurements. The detailed description of the morphology of the grinding products by various methods is published elsewhere [12]. In Table 1 we summarise the powder characteristics of goethite grinding products.

The characteristics of thermal behaviour of goethite grinding products were obtained using TG/DTG, DTA and EGA. The curves measured during heating of initial goethite sample and the samples ground for 14, 34 and 58 h are presented in Figs 1–4, respectively.

It follows from Figs 1–4 that the thermal behaviour of starting (non-ground) goethite differs from that of the ground samples. The EGA results monitored continuously the release of H_2O, SO_2 and CO_2 during heating of the samples.

Characteristics of the starting sample

It follows from the results of TG (Fig. 1) that water molecules bound on the non-ground sample surface are released in the temperature interval 200–450°C. This water loss takes place in two steps, being accompanied by a double endothermal DTA effect. The results of EGA (Fig. 1) demonstrated that the intensities of the water release corresponding to the double peak are similar.

The EGA curves corresponding to the starting goethite indicated the release of H_2O in the same temperature interval as DTA and TG/DTG results did. The release of SO_2 from the non-ground sample started at 350°C, i. e. practically after the dehydration of the sample. The onset of CO_2 release corresponds to the temperature of the sample dehydration, the maximum of the CO_2 release corresponds to the end of dehydration. Therefore, we suppose that the decomposition of remaining SO_4 ions corresponds with the formation of hematite after the decomposition of goethite. On the contrary, the release of CO_2 is accompanying the release of water from the sample. The EGA curve of CO_2 monitors its desorption from the sample, which contains goethite and its decomposition products.

It should be mentioned that the characteristic mass spectrometry results indicated the concentrations of SO_2 and CO_2 in the scale of the 10^{-9}. This ion current is by 2–3 orders lower than the scale of the EGA curves monitoring the water release.

Table 1 Characteristics of synthetic goethite samples produced by grinding

Sample/ grinding time	Geothite content/ %	Hematite like/ %	BET surface area/ $m^2\ g^{-1}$	BET particle size/ nm	XRD grain size/ nm	Mass loss/ %
Initial B-940	100	0	10.2	113.4	not determined	12.1
B-940/6 h	90	10	45.8	25.2	not determined	12.4
B-940/15 h	50	50	81.1	14.3	not determined	13.0
B-940/34 h	30	70	87.9	13.2	not determined	12.5
B-940/46 h	traces	100	85.6	13.5	20.55	8.2
B-940/58 h	traces	100	81.1	14.3	22.68	6.3

The particle size was estimated from BET assuming spherical synletry, according to the expression: $d=6/(\rho S)$, where d is the particle diameter in µm, ρ is the density of hematite in g cm^{-3} and S is the surface area by BET in $m^2\ g^{-1}$

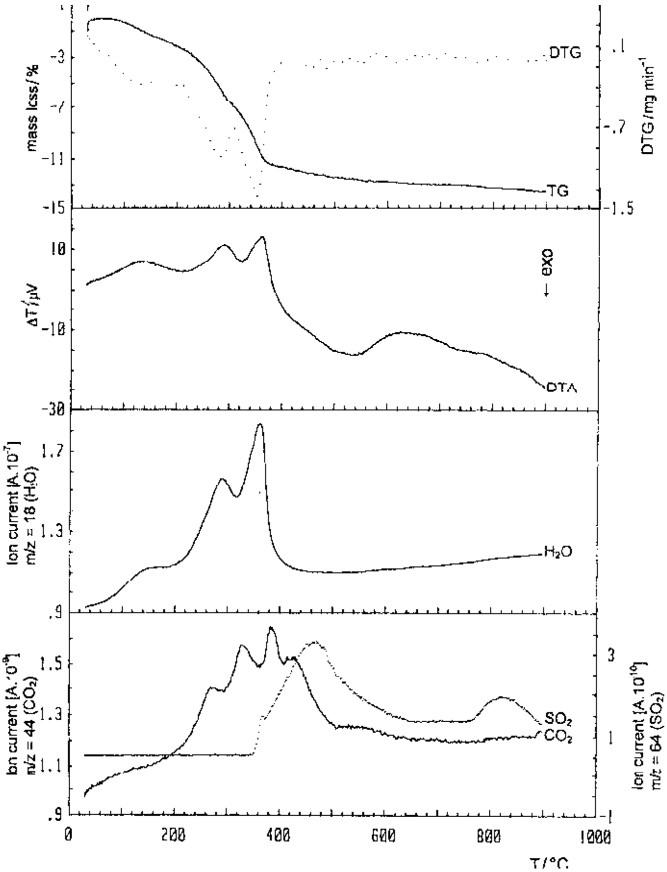

Fig. 1 Thermal analysis results characterising initial goethite sample

The fragments of m/z=64 corresponding to SO_2 and m/z=44 corresponding to CO_2 are released in much smaller amount than water molecules (m/z=18).

Characteristics of ground samples

It follows from the DTA, TG/DTG and EGA results in Figs 2–4 that the water release from the products of goethite ground for different time differs. For lower grinding times the water release is indicated as a double peak; the onset of the first peak is at 290°C, decreasing to 200°C for longer grinding times. Obviously, the mechanical treatment of goethite leads primarily to the destruction of goethite particles being accompanied by partial decomposition, which is reflected by a decrease of the temperature of water release and also by lowering intensity of the first effect. The XRD patterns of goethite sample ground for 15 h demonstrated that approx. 50% of goethite was transformed into the hematite-like structure sample. However, from the TG results it follows that nearly the same amount of water was released on heating this sample as compared to the mass loss of the starting goethite. We have therefore supposed that the considerable amount of water released during goethite decomposition was adsorbed on the surface of the sample. With the sample ground for more than 36 h the water release takes place in one step only at the temperature higher than 300°C. However, a distinct dehydration peak at ~300°C was observed even at the sample ground for 56 h where only component of the hematite like structure was detected by XRD.

Consequently, the water released from the sample in the temperature interval 20–200°C corresponds to the release of water molecules physically sorbed on the sample surface. The portion of the physically sorbed water molecules is in-

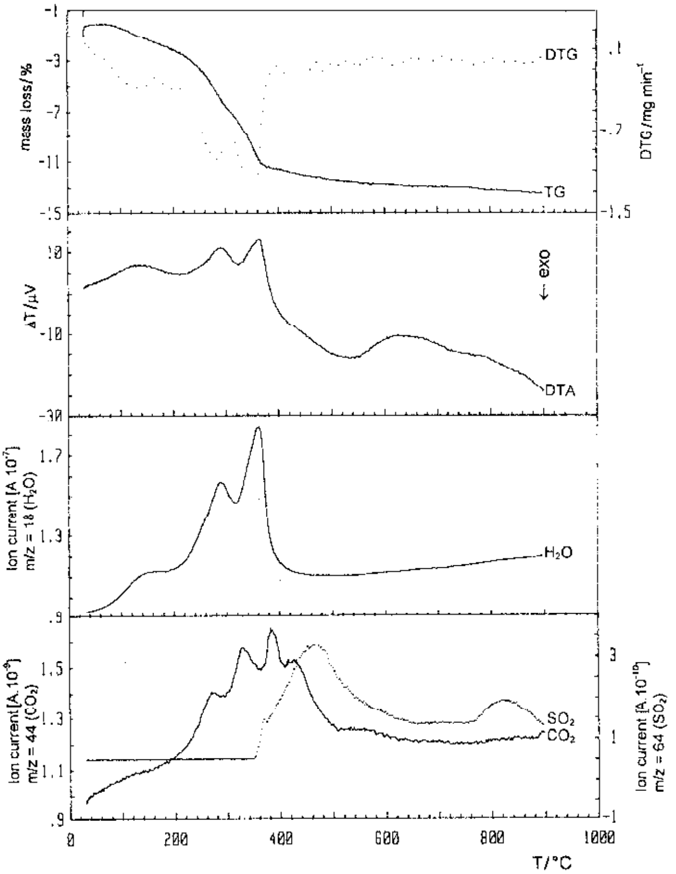

Fig. 2 Thermal analysis results characterising goethite sample ground for 14 h

creasing with the duration of milling. By this way, our hypothesis about the increase of sorption properties of ground goethite samples towards water is confirmed.

The effects observed in Fig. 4 on the EGA curve with the sample ground for 58 h in the temperature interval 350–420°C correspond to the release of hydroxyl groups from the sample containing practically only hematite-like structure component. This component looses the structure incorporated water at this rather high temperature. Such behaviour could be expected with the hydrohematite as described e.g. by Wolska [13, 14].

The SO_2 release from the sample ground for 14 h takes place in different temperature interval (EGA maximum at 710–850°C), that indicated for the initial goethite sample (600°C). By increasing the grinding time to 34 and 58 h the portion of SO_2 released in the interval 350–600°C strongly diminished. The 58 h-

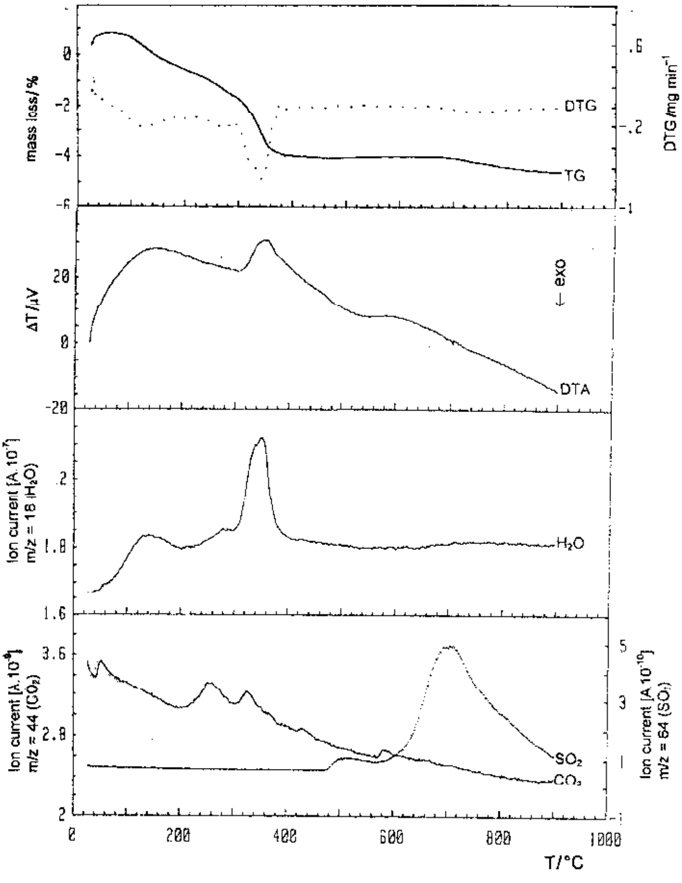

Fig. 3 Thermal analysis results characterising goethite sample ground for 34 h

ground sample is characterised by the effect with the maximum at 710°C only. These results of EGA demonstrate that by grinding of goethite the transport of SO_4 ions from the surface layers of goethite inside the structure of hematite formed by mechanical decomposition takes place.

From the EGA effects corresponding to CO_2 release (Figs 2–4) it follows that mechanically ground goethite is able to adsorb significant amount of CO_2 gas released during heating in the temperature interval 200–450°C. Most probably, the active centres on the goethite surface are controlling this adsorption (the EGA curves is characterised by 2 peaks at 388 and 430°C). From the multipeaked release of CO_2 from the samples ground for 4 and 14 h we can suppose that the active centres formed on the grinding products (hematite and hydrohematite) are responsible for the CO_2 adsorption. At the same time we can suppose that with samples ground for longer time (above 34 h) the CO_2 adsorption is controlled by

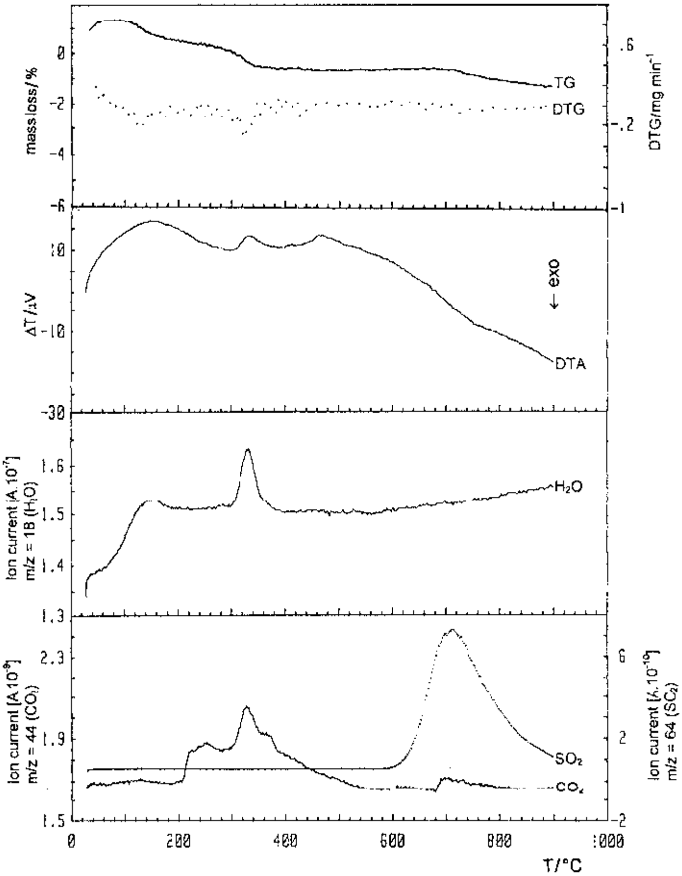

Fig. 4 Thermal analysis results characterising goethite sample ground for 58 h

the active centres corresponding to hematite only. The temperature of the onset of CO_2 released from the samples ground for 34 and 58 h, decreased to 250°C.

Conclusions

We have demonstrated by thermal analysis results that the mechanical treatment of goethite leads primarily to the destruction of goethite particles being accompanied by partial decomposition. The results of TG/DTG and EGA simultaneously measured during heating of the samples in air indicate that thermal decomposition of mechanically treated goethite differs from that of initial synthetic goethite. The changes in the mechanisms of dehydration and in the decomposition of remaining sulphate ions were revealed by the EGA results. A decrease of the temperature of water release and lowering intensity of the corresponding TG effect was observed. The transport of SO_4 ions from the surface layers of goethite inside the structure of hematite formed by mechanical decomposition takes place by grinding of goethite. Mechanically ground goethite is able to adsorb significant amount of CO_2 gas which is released during heating in the temperature interval 200–450°C. Most probably, the active centres on the goethite surface are controlling this adsorption.

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