Thermal behaviour of iron(III) oxide hydroxides

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Abstract: Two iron(III) oxide hydroxides, namely α-FeOOH (goethite) and γ-FeOOH (lepidocrocite), were studied by means of Differential Thermal Analysis (DTA), Thermogravimetry (TG) and Emanation Thermal Analysis (ETA) on heating in air. Surface area, Transmission Electron Microscopy (TEM) and X-ray diffraction patterns (XRD) were used for the characterization of the intermediate products of the thermal treatment. ETA enabled us to obtain a new sensitive insight into the aggregation processes of solid particles.

INTRODUCTION

Iron(III) oxide hydroxides, α-FeOOH (goethite) and γ-FeOOH (lepidocrocite) have been used as magnetic recording materials, catalysts, sorbents, etc (1-4). They are also present in nature, in aquifers, where they act as sorbents for radionuclides and other hazardous elements migrating into groundwaters (5-7). Their thermal behaviour has been widely studied by various methods. In this paper, we shall demonstrate how Emanation Thermal Analysis (ETA) can be used to characterize the intermediate and final products of the thermal treatment during heating "in situ" conditions. This method enabled us to reveal very fine changes in the porosity and morphology of the iron(III) oxide hydroxide particles. Thermal analysis (DTA and TG), surface area measurement and Transmission Electron Microscopy (TEM) were used to interpret the ETA results.

EXPERIMENTAL

Sample preparation methods

α-FeOOH samples were prepared by oxidation of 2 mol l^{-1} water solution of pure $FeSO_4$ at 80°C. Air oxygen was used as the oxidation agent, and aqueous ammonia was added during oxidation to neutralize the SO_4 ions and maintain the pH value constant from 2.5 to 3.5. In this range, the Fe(II) ions remain in solution and the Fe(III) ions formed in the oxidation process precipitate on the surface of the solid particles present in the reaction mixture. α-FeOOH seeds added to the $FeSO_4$ solution before starting the oxidation made it possible to obtain the goethite particles in the desired dimensions and shape, as well as the narrow particle size distribution, as requested by the magnetic recording materials technology (8,9).

γ-FeOOH was prepared by aeration of suspensions of $Fe(OH)_2$, $Fe(OH)_2$ being obtained by neutralization of 0.5 mol l^{-1} water solution of $FeSO_4$ with 13.5 wt. % aqueous ammonia. During oxidation, the pH value was kept constant from 6.0 to 8.5. The reaction time was 20-25 min for the reaction at each pH used and the temperatures did not exceed 25°C. The pure lepidocrocite phase (10,11) was obtained when the reaction was carried out at pH 7.0 and 7.5

Sample characterization methods

X-ray patterns were obtained with a Mikrometa X-ray diffractometer (Chirana Praha, Czech Republic) using CoK_α radiation.

The TEM micrographs were obtained with a Tesla BS-242E Transmission Electron Microscope (Tesla Brno, Czech Republic).

Surface area measurements were carried out according to the Nelsen-Eggertsen (12,13) method, using a N_2-H_2 gas mixture containing 14 % vol. of N_2.

Thermal analysis methods

The DTA and TG measurements were carried out simultaneously with a Mettler Thermoanalyser I (Mettler, Switzerland).

ETA (14) is based on the measurement of inert gas release from solids previously labelled with inert gases. The atoms of inert gases (e.g. radon) are used as trace indicators i.e. as a "microprobe" of the solids defect state and its changes. They do not react with the solid matrix and their release is primarily controlled by diffusion. The processes which influence the inert gas diffusion in the solid matrix and pores, or the surface area of the sample, can be investigated by this method. By means of ETA, fine effects in the solid can be revealed, which are not accompanied by changes of sample mass or enthalpy, i.e. which cannot be investigated by thermogravimetry and DTA respectively. The method can be used in the study of both crystalline and non-crystalline materials. The radioactive nuclides of inert gases have been advantageously used because of their easy and sensitive detection in trace conditions.

Sample preparation for ETA measurements: To prepare the samples for ETA measurements, trace amounts of ^{228}Th have been introduced into the sample by adsorption on the surface of the sample. ^{220}Rn is formed by spontaneous alpha decay according to the scheme

$$^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn}$$
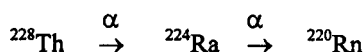
and can be introduced into the solid due to the recoil energy (100 keV/atom). This nuclear reaction gives rise to the radon nuclides and has also been used for incorporation of the inert gas into the solid sample. Radon atoms penetrate several tens of nanometers, depending on the composition of the target materials (for example, the penetration depth of ^{220}Rn in dense MgO is 41.7 nm, in dense SiO_2 is 65.4 nm).

ETA measurements: 0.1-0.3 g samples were measured during heating in air (5 K/min) in a device constructed at the NRI Řež (15). The parameter measured was the rate of radon release from the sample. This value was normalized by the radioactivity of the parent nuclides introduced during labelling. The relative radon release rate E obtained in this way is expressed in relative units.

RESULTS AND DISCUSSION

α-FeOOH (goethite)

Results of DTA, TG and ETA measurements of goethite are summarized in Fig. 1. On the TG and DTA curves we have only observed effects corresponding to the loss of physically bound water (130°C) and the release of structurally bound water at 275°C. The significant increase in the radon release rate E, observed on the ETA curve in the temperature interval 70-310°C corresponds to the formation of micropores in the dehydrating particles. At temperatures above 350°C, the E values rapidly decrease, which indicates the disappearance of micropores and their accumulation in macropores. The decrease in porosity was directly observed on the TEM micrographs (Fig. 2). The surface area values (S) of the heat-treated intermediate samples given in Fig 1. indicate this process as the decrease of S. The decrease of E measured during heating in situ conditions from 375 to 500°C corresponds to changes in S as measured by gas adsorption at liquid nitrogen temperature.

At temperatures above 720 °C, the higher mobility of atoms in the crystal lattice leads to the E increase. This increased mobility causes the loss of hematite particle shape anisotropy and the interparticle sintering (as directly observed by TEM, see Fig. 2) and further decrease of the surface area observed in Fig. 1 in the region 720-850°C.

Fig. 2 shows that the intensive agglomeration and interparticle sintering in the sample occur at approximately 850°C, resulting in the formation of large α-Fe_2O_3 particles of an irregular shape (see Fig. 2) (diameter approx. 1.5 nm). This phenomenon was indicated on the ETA curve by a temporary decrease of E at temperatures about 850°C.

It is well known that hematite particles for magnetic recording materials should be as dense as possible, but not damaged by interparticle sintering and loss of shape anisotropy. The ETA method enabled us to determine exactly, under in situ conditions of the heat treatment, the optimum temperature of thermal densification of transition products (α-Fe_2O_3). On the other hand, a high porosity of iron(III) oxide hydroxides sorbents is required. In this case, the optimal temperature for preparation of sorbents from goethite or lepidocrocite can be determined from the ETA curves (it is that before the sharp decrease of E, i.e. about 300°C).
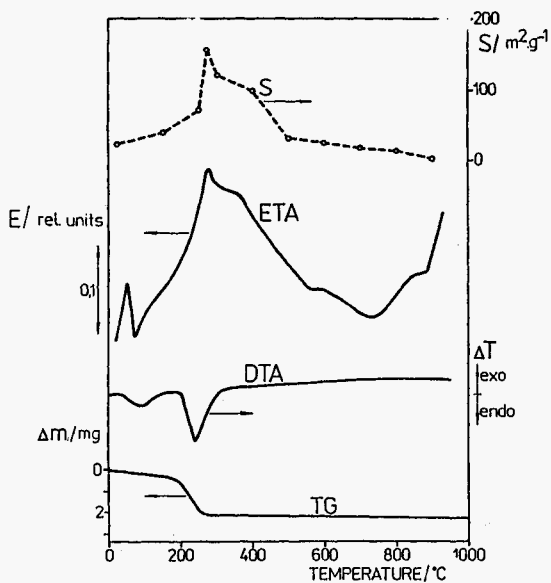
Fig. 1 Results of ETA, DTA, and TG measurements during heating of goethite. The surface area values (S) of heat-treated sample to selected temperature are denoted by (○)
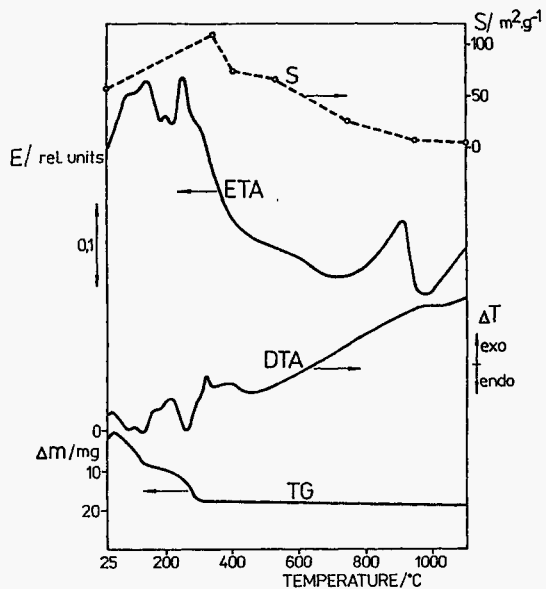

Fig. 3 Results of ETA, DTA, and TG measurements during heating of lepidocrocite. The surface area values (S) of heat-treated sample to selected temperature are denoted by (○)
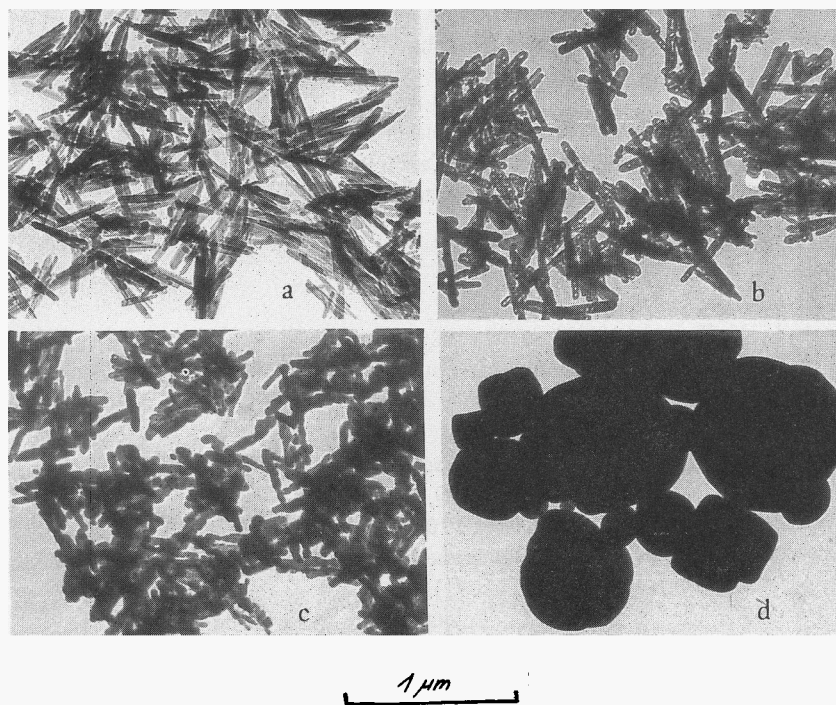

Fig. 2 TEM micrographs of goethite annealed at various temperatures
a - the starting sample   b - annealing temperature 520°C
c - annealing temperature 680°C   d - annealing temperature 850°C

γ-FeOOH (lepidocrocite)

Thermal decomposition of γ-FeOOH (lepidocrocite) is characterized in Fig. 3 based on the results of DTA, TG, ETA and surface area measurements. As for goethite, two endothermic effects were observed on the DTA curve: The endotermic peaks at 120°C correspond to the loss of physically bound water, the second one corresponds to the loss of structurally bound water, as well as to the topotactic and pseudomorphic dehydration of γ-FeOOH to cubic γ-Fe$_2$O$_3$. On further heating, the γ-Fe$_2$O$_3$ is transformed to hexagonal α-Fe$_2$O$_3$ (at 380 - 420°C). Further information was obtained by ETA. Fig. 3 shows that changes of E in the range 25-300°C indicate the formation of porous and highly defective structure, as was proved by the XRD pattern. The sudden decrease in E at 380 - 420°C corresponds to the change of the γ-Fe$_2$O$_3$ to the more ordered α-Fe$_2$O$_3$, and to the disappearance of micropores. The minimum of E at ~700°C corresponds to the formation of dense α-Fe$_2$O$_3$ particles. The interparticle sintering and loss of shape anisotropy take place during heating to higher temperatures. The sudden decrease of E at 850-900°C corresponds to the aggregation of particles and formation of large irregular particles of α-Fe$_2$O$_3$ (as proved by TEM).

On comparing the ETA curves on Figs. 1 and 3, we can see that the thermal behaviours of α-FeOOH and γ-FeOOH differ. The decrease of E, corresponding to the aggregation of particles, is more pronounced with the γ-FeOOH sample than with α-FeOOH. This is in agreement with the observation made by TEM (see Fig. 2) and may be caused by the fact that the size of the initial γ-FeOOH particles before heat treatment is much smaller than that of the α-FeOOH.

CONCLUSIONS

Thermal behaviour of α-FeOOH (goethite) and γ-FeOOH (lepidocrocite) was described by means of DTA, TG, ETA, surface area measurements, XRD patterns and TEM. The temperature intervals were determined where the dehydration of iron(III) oxide hydroxides takes place. The phase transformations and changes in particle morphology caused by changes of microporosity and by the disappearance of particle shape anisotropy were characterized by ETA and TEM. The use of ETA enabled us to reveal the fine changes in the morphology of samples taking place during heating and made it possible to determine the optimal temperature for thermal treatment with regard to their final properties (dense acicular pure γ-Fe$_2$O$_3$ phase particles). For the iron(III) oxide hydroxides prepared as sorbents, the temperature limits of their thermal stability were determined from the ETA curves.

ACKNOWLEDGMENT

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