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Behaviour of α-Fe_2O_3 (hematite), prepared by oxidation precipitation of ferrous sulphate, on heating

J. ŠUBRT, F. HANOUSEK, V. ZAPLETAL
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250, 68 Řež, Prague, Czechoslovakia

H. ŠTĚPÁNKOVÁ
Mathematico–Physical Faculty, Charles University, Ke Karlovu 5, 120 00 Prague 2, Czechoslovakia

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The effects of heating α-Fe_2O_3 (hematite) prepared by oxidation precipitation of ferrous sulphate, at temperatures up to 700° C were studied. It was found that, in the course of heating, losses of structurally-bound water occured, accompanied by the formation and removal of pores, the lattice constants changed and the optical properties were modified, an effect which is important from the standpoint of the use of hematite as ferric pigment. With increasing annealing temperature, the complementary wavelength was shifted to higher values and the spectral purity of the pigment colour was decreased.

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1. Introduction

By the oxidation of aqueous solutions of ferrous sulphate, under suitable reaction conditions, it is possible to prepare α-Fe_2O_3 (hematite) with characteristics making it possible to use it as a red ferric pigment. Thus prepared, α-Fe_2O_3 always contains rather higher amounts (2 to 3 wt%) of structurally-bound water. This content is sufficient for approximately ten per cent of the Fe^{3+} atoms in the crystal structure of hematite to have in their immediate neighbourhood one or more water molecules. Binding and structural changes in the vicinity of an iron atom resulting from the presence of water can of course also affect the properties of hematite prepared by the oxidation precipitation from aqueous solutions of ferrous salts.

In the present work the behaviour of hematite prepared by the oxidation precipitation of ferrous sulphate on heating up to 700° C is studied, and changes of certain properties are reported, occurring simultaneously with the losses of structurally-bound water.

2. Experimental procedure

2.1. Preparation of initial α-Fe_2O_3

The initial sample of hematite was prepared by the oxidation of 1.5 M aqueous solution of ferrous sulphate by atmospheric oxygen maintained at 95° C and at constant pH of 5 during the whole oxidation process. To prevent the production of α-FeOOH (goethite) in the course of the oxidation, and to ensure the production of phase-pure hematite as a product, nuclei of hematite were added into the solution before starting the oxidation process, prepared by the transformation of γ-FeOOH to finely-dispersed α-Fe_2O_3. The procedure for the preparation of initial γ-FeOOH, as well as its transformation to α-Fe_2O_3, has been described in [1]. The hematite nuclei were added into the system before starting with oxidation process in such an amount that the suspension contained 10% Fe in the form of hematite nuclei. The oxidation itself was performed under conditions of intense air-dispersion into the reaction mixture, using the Ultra-Turrax stirrer, in order that the oxidation reaction rate could not be

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affected by oxygen dissolution in the liquid. pH-value was kept constant using a continuous charging of 25% aqueous solution of ammonia into the system with the help of an automatic burette connected with a pH-stat (from Radiometer, Copenhagen). For a more detailed description of the effect of the oxidation conditions on the properties of the products see [1]. The surface area of the α-Fe_2O_3 sample obtained was 5.6 $m^2\ g^{-1}$ and the corresponding diameter, calculated for spherical particles, was 0.21 μm.

2.2. Dehydration of precipitated hematite

The thermal treatment of the sample of hematite was performed in a furnace in a stream of dried air. The temperature during the dehydration was measured using a calibrated Ni–NiCr thermocouple, placed just in the sample, and was kept constant during the dehydration to within ± 1%.

2.3. Analytical methods

Optical properties were calculated from emission spectra measured on the Beckman Acta M two-beam spectrometer fitted with an integrating sphere. A plate with deposited $BaSO_4$ served as a standard of the reflectance. In the whole interval of the measured emission spectrum (770 to 380 nm) a constant slit-width of 1 mm was used. A standard tungsten bulb was used as a source of polychromatic light, and its radiation passed through handled filters, so that the illumination of the sample corresponded to the white conventional light, *C*. For the calculation of trichromatic co-ordinates the products $S_\lambda \cdot \bar{x}_\lambda$, $S_\lambda \cdot \bar{y}_\lambda$, $S_\lambda \cdot \bar{z}_\lambda$ were used, and the trichromatic components were calculated from

$$X = \sum S_\lambda \cdot \bar{x}_\lambda \cdot R_\lambda, \qquad (1)$$

$$Y = \sum S_\lambda \cdot \bar{y}_\lambda \cdot R_\lambda, \qquad (2)$$

and

$$Z = \sum S_\lambda \cdot \bar{z}_\lambda \cdot R_\lambda, \qquad (3)$$

where S_λ is a relative spectral composition of white light (*C*). $\bar{x}_\lambda$, $\bar{y}_\lambda$, $\bar{z}_\lambda$ are trichromatic coefficients and R_λ is the remission of the measured sample at a wavelength of λ. The values of trichromatic co-ordinates x and y were calculated from

$$x = \frac{X}{X+Y+Z} \qquad (4)$$

and

$$y = \frac{Y}{X+Y+Z}. \qquad (5)$$

For instructive expression of the colour value of the sample the value λ_d is presented [2] from values of the ratios

$$\frac{x - x_w}{y - y_w}, \qquad (6)$$

where x_w and y_w are trichromatic co-ordinates of the white conventional light (*C*).

For the differentiation of the purity of the colour tint, the values of the co-ordinate purity, p_e or spectral purity, p_c, were calculated from relationships

$$p_e = \frac{y - y_w}{y_s - y_w} \qquad (7)$$

and

$$p_c = \frac{y_s}{y} p_e, \qquad (8)$$

where y_s is the trichromatic co-ordinate corresponding to the point λ_d in the trichromatic diagram.

The specific surface of the samples was measured by a thermal-desorption method according to Nelsen and Eggertsen on a instrument with an adjustment according to Mangel [3]. The mixture of nitrogen and hydrogen containing 14 vol% N_2 was used.

The lattice constants of hematite were determined from X-ray records made using the Debye–Scherrer method. A cylindrical cell with a circumference of 360 mm, with asymmetrically inserted film, was used. A cobalt lamp served as a source of X-rays, with k_1 and k_2 radiation being used for the measurement. Powder samples were provided in hermetically sealed capillaries 0.3 mm in diameter, obtained from Lindeman glass. The exposure times were between 120 and 180 min. The lines shown in Table I were used for the calculation of lattice constants.

The infra-red spectra were measured at frequencies from 4000 to 250 cm^{-1} on the Beckman IR 20 A grating spectrometer in the form of tablets with TlBr. This medium was used because of its non-hygroscopic character and high refractive index.

3. Results

Fig. 1 shows the time dependence of the course of the weight loss of precipitated hematite at constant temperature. It is obvious that for each certain temperature, there is a weight loss with time, corresponding to a certain loss of structurally-bound water; however, after a particular time

TABLE I Diffraction lines used for calculating lattice constants of precipitated hematite (according to ASTM [4])

d (nm)	Relative intensity	hkl	Radiation used for the calculation
0.1102	14	2 2 6	$\bar{\lambda}$
0.1055	18	2 1 10	$\bar{\lambda}$
0.09890	10	2 3 2	λ_1
0.09890	10	3 1 8	λ_1
0.09601	18	3 2 4	λ_1
0.09512	12	1 4 0	λ_1
0.09512	12	0 2 13	λ_1
0.09080	25	1 3 10	λ_2

$\bar{\lambda} = 0.17902$ nm
$\lambda_1 = 0.17889$ nm
$\lambda_2 = 0.17928$ nm

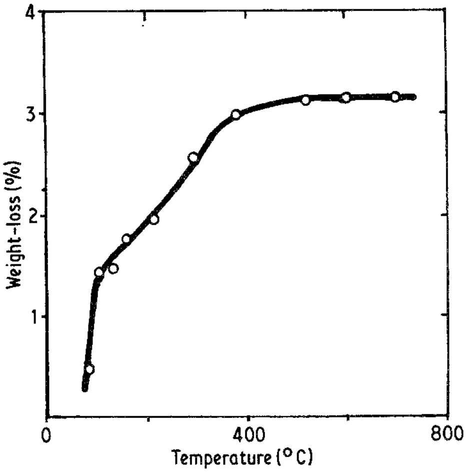

Figure 2 Dependence of the weight decrease (water-loss) on the annealing temperature.

there is no further weight loss seen and there is no further water loss.

Fig. 2 shows the temperature dependence of the final weight loss of precipitated hematite. It can be seen that in the temperature interval of 105 to 370° C the dependence is essentially linear. It is remarkably deflected from a straight line at temperatures below 100° C (probably resulting from the release of adsorbed water) and above 400° C when, however, the dehydration was already essentially completed.

Fig. 3 shows the dependence of the surface area of samples of thermally-treated hematite on the temperature of annealing to constant weight. The course of the curve, with a remarkable maximum in the temperature interval where the structurally-bound water is lost, indicates that during hematite formation, dehydration pores are formed, which then vanish at higher temperatures. The formation of pores and their disappearance in hematite prepared by the thermal decomposition of goethite (α-FeOOH) was observed by other authors [5] at about the same temperature. From microscopic records of dehydration products of precipitated hematite it was ascertained that, in the course of the dehydration to 500 to 600° C, no observable changes in the shape or size of particles appear.

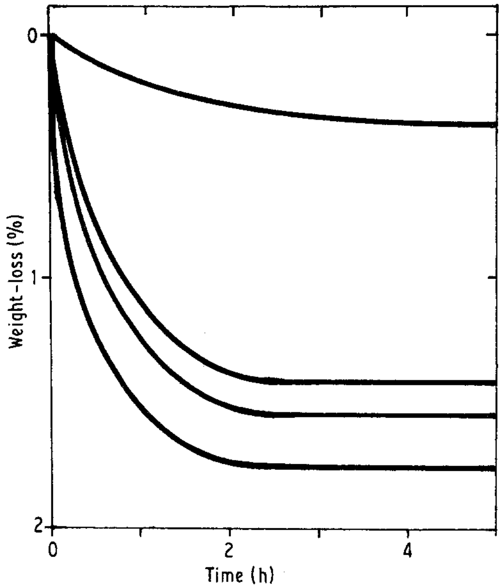

Figure 1 Course of the precipitated hematite dehydration.

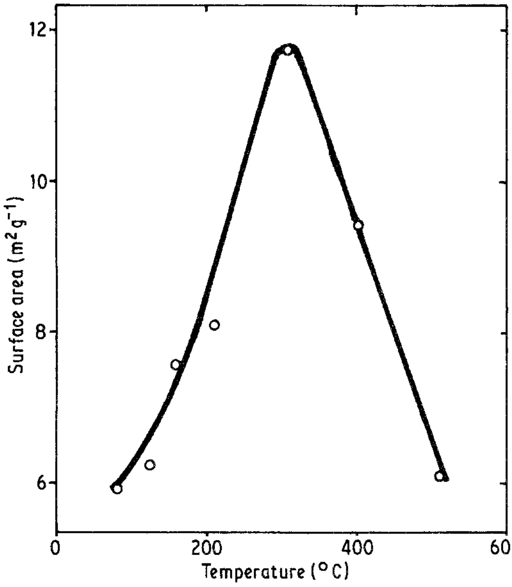

Figure 3 Dependence of the sample surface area of precipitated hematite on the annealing temperature.

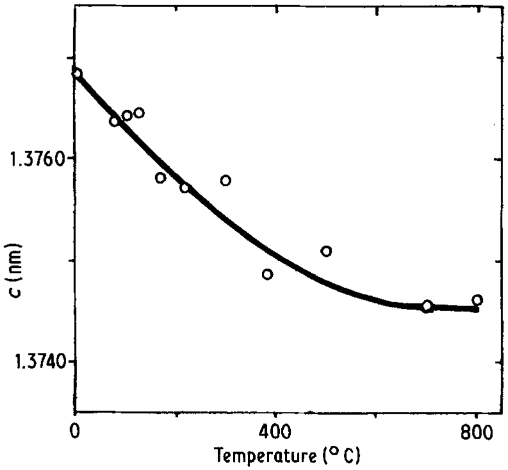

Figure 4 Dependence of the hematite hexagonal lattice parameter *c* on the annealing temperature.

Fig. 4 shows the dependence of the hexagonal lattice parameter *c* of precipitated hematite on the annealing temperauture. With increasing temperature the *c*-value distinctly decreases which, for samples heated to 500 to 700° C, approaches the value reported in the literature [4, 6, 7] for single-crystal hematite.

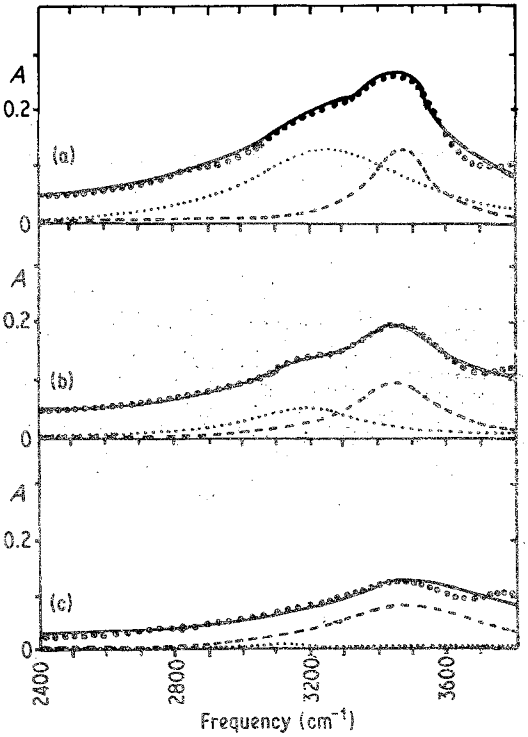

Figure 5 Infra-red spectra of precipitated hematite for a frequency inteval of 2400 to 3800 cm^{-1}: (a) initial sample; (b) sample annealed to 294° C; (c) sample annealed to 377° C.

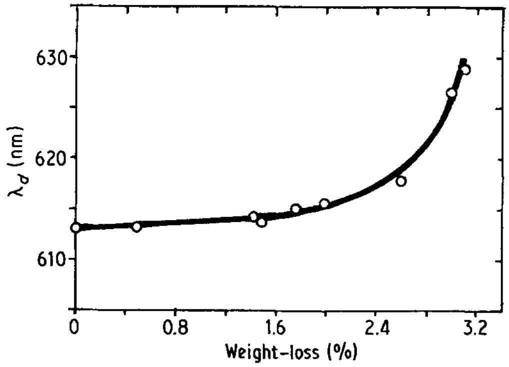

Figure 6 Dependence of the complementary wavelength, λ_d, on the weight-loss of water on annealing.

The study of infra-red spectra of the products of the precipitated hematite dehydration revealed that the weight lost on dehydration did not affect the location and shape of bands of Fe–O skeletal vibrations in the hematite lattice (bands at frequencies 320, 455 and 550 cm^{-1}). However, there is a different situation in the OH valence vibrations in a region 2800 to 3800 cm^{-1}. In the initial sample (shown in Fig. 5a) two bands, a band of structurally-bound H_2O at 3240 cm^{-1} and a band of surface-bound (adsorbed) H_2O at 3450 cm^{-1}, are present. At 294° C the intensity of the band at 3240 cm^{-1} decreases remarkably (Fig. 5b) and at 377° C (Fig. 5c) the band almost disappears. In comparison, the intensity of the band of surface-bound water at 3450 cm^{-1} decreases quite moderately (the infra-red spectra were measured in air and in the course of the measurement water from the air was adsorbed). So, the results of measuring infra-red spectra also demonstrated the presence of structurally-bound water in the precipitated hematite and its gradual loss on heating.

From the standpoint of the use of hematite as ferric pigment, changes of optical properties of the precipitated hematite with the dehydration temperature which may affect the thermal stability of the colour tint are important. Fig. 6 shows a change of the characteristic wavelength, λ_d, depending on the weight-loss of water in the course of the dehydration. It is obvious that the changes of this and further characteristics, important from the standpoint of the use of precipitated hematite as a ferric pigment, are not negligible. A shift occurs of the characteristic wavelength to a violet tint and the values of the colour-tint purity, p_e and p_c, decrease. These changes may not be explained by changes of the sizes of particles, which remained unaltered on microscopic photographs of hematite

TABLE II Changes of properties of precipitated hematite on heating

Temperature of heating (°C)	Weightloss (%)	d	x	y	Y (nm)	P_e (%)	P_c (%)
As-supplied		613.2	0.4570	0.3196	0.64036	40.32	40.94
80	0.46	613.0	0.4539	0.3198	0.65671	40.32	40.83
105	1.44	614.0	0.4508	0.3186	0.65098	37.57	38.01
120	1.46	613.8	0.4541	0.3190	0.63833	41.92	42.41
160	1.76	615.0	0.4437	0.3176	0.65971	36.06	36.31
207	1.97	615.6	0.4426	0.3170	0.64563	33.54	33.68
293	2.60	617.8	0.4384	0.3154	0.56911	25.92	25.71
377	3.00	627.1	0.4194	0.3107	0.54189	21.29	19.86
520	3.13	629.0	0.4172	0.3101	0.54495	19.79	18.18

before and after dehydration. Changes of certain optical values of the precipitated hematite on heating are summarized in Table II.

4. Conclusions

It follows from the results of studying the behaviour of precipitated hematite, in the course of heating up to 700° C, containing structurally-bound water, that structural changes occur simultaneously with water losses in samples which are accompanied by remarkable changes of optical properties. Besides the shift of the characteristic wavelength to a violet tint, there is also remarkable decrease in the purity of the colour tint. These changes do not result from changes in particle sizes, but they are obviously connected with changes of binding ratios in the vicinity of iron ions in the course of losses of structurally-bound water on heating.

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