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EVOLVED GAS DETECTION OF IRON OXYHYDROXIDES

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A procedure is described for recording evolved gas detection (thermal desorption spectra) of various FeOOH samples up to 400°. Characteristic curves of α-, β- and γ-FeOOH are discussed, based on the crystallographic structure which governs the sites for physisorbed H_2O as well as OH groups producing H_2O by dehydration. Examinations are also made of the variations of the desorption spectra with the progress of crystallization for α-FeOOH, and with the distortion of the crystal structure caused by the addition of Cu(II) to α-, β- and γ-FeOOH.

Three polymorphous crystalline ferric oxide hydroxides α-, β- and γ-FeOOH, are known as the major components of naturally-occurring oxidized products of iron, which, together with Fe_3O_4 and various amounts of amorphous hydrated oxides, constitute rust on steel surfaces [1, 2].

The properties of each component and the state of the composite formed from the minute crystal appear to govern the nature of a steel surface exposed to various environments, and whether the steel continues to corrode or is protected from further progression of the corroding reaction.

Although there would be numerous factors to be examined concerning the fundamental properties of those components, the clearly most important ones are the relationship between the structure of each FeOOH and physically bound water molecules on the crystal surfaces, and also the variation of the number and distribution of OH groups on the crystal surfaces with the degree of crystallization.

The present authors (K. I. et al.) have so far examined the crystallization accompanied by ageing at 30° of α-FeOOH [3], β-FeOOH [4] and γ-FeOOH [5], and given information on a particular effect of doped Cu(II), which in general retards crystal formation to give products approaching "amorphous" substances over a specific Cu content. In other words these studies indicated that one can prepare FeOOH samples with different degrees of crystallization, apart from the case of β-FeOOH, where almost no effect of Cu(II) on the morphological and crystallographic characteristics is observed.

When FeOOH crystals in different states of crystallization are subjected to definite heating rate, and the desorption of water molecules is examined, one

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could expect to learn in detail (1) the nature of water molecules adsorbed on FeOOH crystal surfaces, and (2) the mechanism of formation of water from OH groups on crystal surfaces or inside crystals.

Experimental

Samples

α-FeOOH

Crystalline α-FeOOH was prepared by the method employed by Feitknecht et al. [6]: 0.6 M $Fe_2(SO_4)_3$ solution was treated with 1 M KOH at pH 13.6 and 50° for 30 hr, the precipitate being washed with distilled water till free of SO_4^{2-}.

In order to obtain samples with different degrees of crystallization, the precipitate prepared at 25–30°, but otherwise under similar conditions as described above, was subjected to ageing at 30 ± 1° for 2, 6 and 10 days, meanwhile the pH being maintained at 13.6.

Cu(II) was doped into α-FeOOH crystals by mixing 0.6 M $Fe_2(SO_4)_3$ and 0.05–0.30 M $CuSO_4$ solutions in each desired Cu/Fe atomic ratio of 0 – ca. 6%, followed by hydrolysis at 25–30° and pH 13.6, and afterwards ageing at 30 ± 1° for 20 days in the solution [3].

β-FeOOH

Heating 1 litre 0.1 M $FeCl_3$ solution with addition of 100 g urea at 96–99° for 15 hr gave a β-FeOOH precipitate, which was washed with distilled water.

To dope Cu(II) into β-FeOOH at Cu/Fe atomic ratios of 0 – ca. 5%, mixtures of 0.2 M $FeCl_3$ and 0.2 M $CuCl_2$ solutions were made to hydrolyze at 96–99° for 5 hr and the precipitate was aged at 30 ± 1° for 20 days in the solution [4].

γ-FeOOH

γ-FeOOH was prepared by oxidation of a hydrochloric acid suspension (1 litre) of the product between $FeCl_2$ (40 g as $FeCl_2.4H_2O$) and hexamethylenetetramine (0.4 M) by use of $NaNO_2$ (27 ml 1 M solution) at 60° for 45 min [7]. The crystals isolated by filtering were washed with abundant distilled water.

The Cu-doped γ-FeOOH samples of different Cu/Fe ratios (0–15 atomic %) were prepared by the air-oxidation method initiated by Mayne [8]: $CuSO_4$ was added to an $FeSO_4$ solution (3.6 g $FeSO_4.7H_2O$ per 600 ml), through which air was blown at a rate of 9 l/min for 3 hr at 25° in the pH range 4.2–6.5, adjusted by 10% NH_4OH. The precipitate obtained was washed with distilled water.

Methods

The crystallographic identification of each sample was carried out with a Rigakudenki X-ray Diffractometer 2001 by use of FeKα at 30 kV and 10 mA.

The BET surface area was determined with a Shibata Surface-area Meter by means of nitrogen adsorption at liquid nitrogen temperature.

The copper contents of crystals were analysed by colorimetry in the presence of Cupferazone after dissolving the sample in HCL.

Evolved gas detection

Figure 1 is a schematic diagram of the apparatus for recording the evolved gas detection curve. The sample was kept in a $CaCl_2$ desiccator at room temperature (20–25° for at least 1 month prior to the measurement (denoted hereafter as dry sample)).

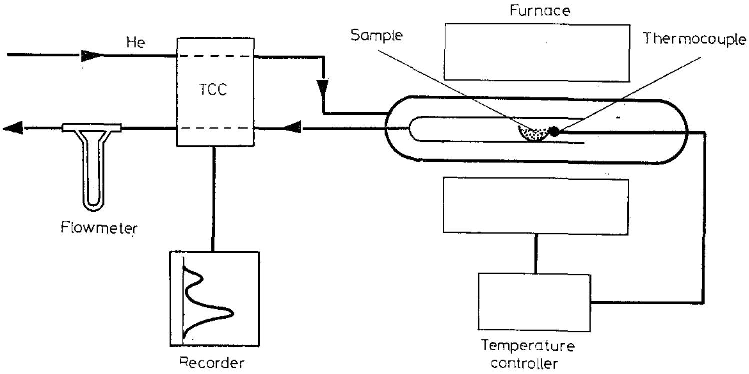

Fig. 1. Evolved gas detection apparatus

The sample (40 mg) was heated in an electric furnace at a heating rate of 20°/min by a programming controller. Heating rates of 5 and 10 °/min were also used to obtain the activation energy of water evolution (cf. Table 2). The amount of water evolved during the heating process was recorded by means of a thermal conductivity cell (Gow-Mac WX TCC) with reference to dry helium as the carrier gas at a rate of 75 ml/min. Calibration was performed by determination of H_2O in pure $BaCl_2.2H_2O$.

Results and discussion

Evolved gas detection of α-, β- *and* γ-FeOOH

The evolved gas detection curves for α-, β- and γ-FeOOH in Fig. 2 each show three marked peaks at approximately 70, 180 and 260°. These peaks correspond unquestionably to the evolution of H_2O, because they disappear when a cold trap is situated in front of the TCC. For β-FeOOH, however, an additional peak is observed at 370°, which remains unchanged even when a cold trap of –20° is inserted (see later).

Table 1

Amounts of water evolved at different peak temperatures

Sample	Amount of H_2O, wt. %						
	(1) 70°	(2) 180°		(3) 260°		Sum of (2) and (3) on FeOOH basis	Total wt. decrease on dry basis
	on dry basis	on dry basis	on FeOOH basis	on dry basis	on FeOOH basis		
α-FeOOH	1.6	2.0	2.0	7.6	7.7	9.8	11.2
β-FeOOH	1.8	4.4	4.5	7.5	7.6	12.1	13.7
γ-FeOOH	2.5	1.6	1.6	6.8	7.0	8.6	10.9

The amounts of H_2O evolved were determined by the measurement of peak areas and are given in Table 1 as weight percentage of the sample on dry and FeOOH bases. The FeOOH base value is the ratio of evolved water at 180–260° peak ranges to the weight of "dry sample" minus the water evolved at 70° peak range. In addition to other differences between the samples, it is noticeable that the amounts of H_2O evolved from γ-FeOOH at 70° and from β-FeOOH at 180° are larger than the corresponding values for the other samples. In contrast, the value for γ-FeOOH at 260° is comparatively small. The total H_2O evolved at 180 and 260° may be considered as fundamentally of structural origin, arising from dehydrating decomposition during the heating process, i.e. from the reaction $2FeOOH \rightarrow Fe_2O_3 + H_2O$. The water produced in this dehydration should amount to 10.1 wt.% of the FeOOH. The water desorbed below 100° consists of molecules adsorbed physically on crystal surfaces.

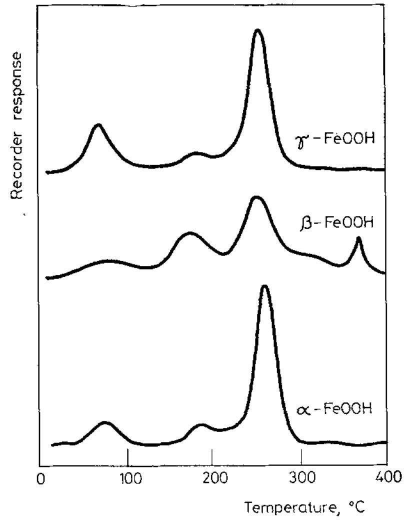

Fig. 2. Evolved gas detection curves of α-, β- and γ-FeOOH

The crystal structures of α-, β- and γ-FeOOH are illustrated in Fig. 3. These structures were obtained in crystallographic investigations by Ewing [9] for α-FeOOH, Mackay [10] for β-FeOOH and Ewing [11] for γ-FeOOH. There are two kinds of OH in each crystal type, though their situations in the crystal are specific to each structure. In its predominant *a*−*c* surface plane, α-FeOOH has two different OH groups at outer and somewhat inner positions; β-FeOOH has OH not only in the outer *a*−*c* and/or *b*−*c* planes, but also on the inside walls of small tunnels parallel with the *c*-axis; γ-FeOOH has a layer structure, in which lamellae in the *a*−*c* plane line up OH groups regularly. As discussed in a separate paper by Kaneko et al. [12] on the dielectric behavior of water molecules on these

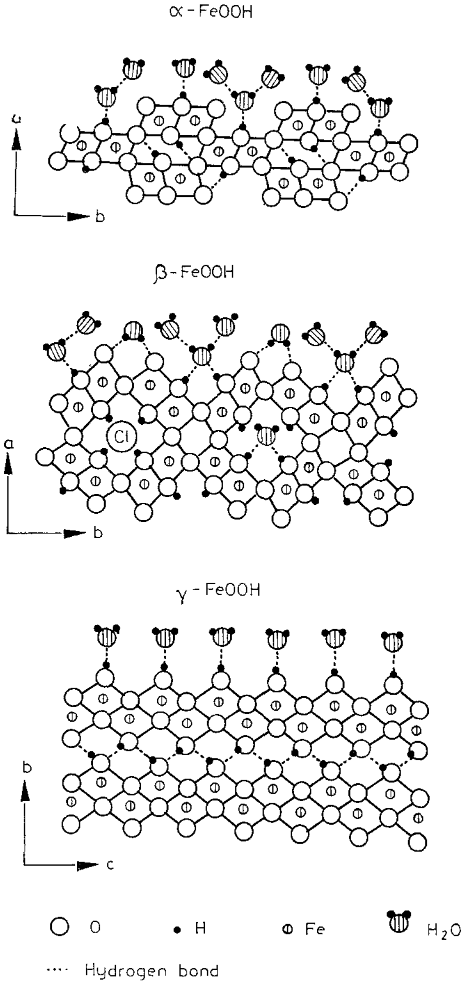

Fig. 3. Crystal structures of α-, β- and γ-FeOOH

crystals, H_2O molecules appear to bind with these OH groups with particular strengths for each site in each crystal, as illustrated in Fig. 3. When heated, physisorbed H_2O molecules depart from the surfaces in a low temperature range, i.e. at around 70°, as shown in Fig. 2. The larger amount of water evolved at 70° from γ-FeOOH stems from the complex nature of the surface of this compound, that is apt to dehydrate easily even on mild heating, as already suggested by a resultant increase in electrical conductivity due to the formation of oxygen vacancies [13]. This also results in a smaller amount of water evolved at 180 and 260°.

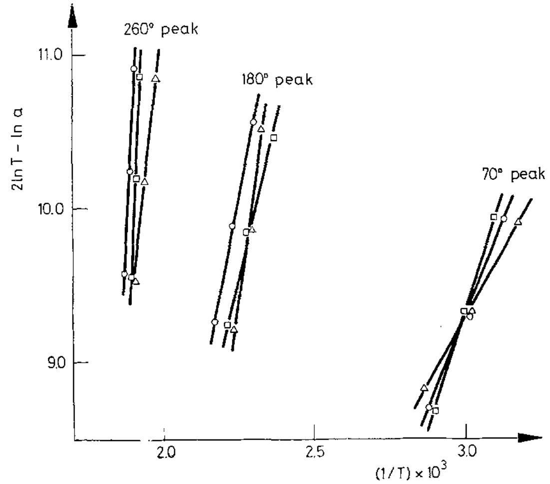

Fig. 4. Plots of $2 \ln T - \ln a$ vs. $1/T$. ○: α-FeOOH, △: β-FeOOH, □: γ-FeOOH

Water liberated at higher temperatures is produced by the transformation of FeOOH into Fe_2O_3, but it is natural to assume that the 180° peak is derived from "surface" dehydration, while the 260° peak is related to "bulk" dehydration; X-ray diffraction results show no change in reflexions below ca. 300°, where diffraction patterns of α-Fe_2O_3 start to appear. As for γ-FeOOH, however, the well-known transformation steps γ-FeOOH $\rightarrow$ γ-Fe_2O_3 $\rightarrow$ α-Fe_2O_3 are not reflected in the water evolution curve.

For β-FeOOH a broad peak at 180° (Fig. 2) and a larger amount of water evolved at this temperature (Table 1) mean that the H_2O originally accumulated in tunnels is desorbed in this temperature range. This accumulated water also results in a higher value of water evolution on dehydration of β-FeOOH (12.1% in Table 1) in comparison with other forms of FeOOH and with the theoretical 10.1%.

Amenomiya and Cvetanovic [14] proposed the following equation to describe the activation energy of desorption:

$$2 \ln T - \ln a = E/RT + \ln E/Rb \qquad (1)$$

where T is the desorption peak temperature, a is the rate of heating, E is the activation energy of desorption, R is the gas constant and b is a constant. By using data from experiments at different heating rates (5, 10 and 20 °/min), the relationships between $(2 \ln T - \ln a)$ and $1/T$ were found reasonably linear for each FeOOH (Fig. 4). E values obtained from the slopes of each linear relationship are tabulated in Table 2. The small value of the activation energy in the 70° range can be ascribed to the desorption of physisorbed molecules. Values in the 180° range are close to that for the dehydration of surface OH groups on TiO_2 (109 kJ/mole) [15] for example. The E value in the 260° range for β-FeOOH is markedly low, indicating easy dehydration accompanied by structural transformation. Although the reason why β-FeOOH decomposes easily on heating, to produce α-Fe_2O_3, is not fully understood, Gallagher [16] has suggested that no hydrogen-bonds exist in β-FeOOH.

Table 2

Activation energy of desorption

Sample	Activation energy, kJ/mol		
	70° range	180° range	260° range
α-FeOOH	42	92	290
β-FeOOH	29	120	160
γ-FeOOH	50	75	300

β-FeOOH exhibits another characteristic in its desorption spectrum (Fig. 2), in that a sharp peak is observed at 370°. The Cl constitutionally present in β-FeOOH (8 atomic Cl/Fe % in the present sample) is released as $FeCl_3$ and HCl in this temperature range, as found previously by the present authors [17]. Since the use of a cold trap at −20° did not alter the 370° peak, it appears to be due to HCl (b.p. −85°) formed during the heating process.

Crystallization of α-FeOOH *and water evolution*

In a preceding work [3], the authors studied the mechanism of crystal formation and growth of α-FeOOH during ageing at 30°: X-ray diffraction patterns gradually become distinguished from amorphous broad bands to yield very sharp reflections; the BET surface area decreases from 300 m^2/g for the initial amorphous product, up to ca. 80 m^2/g after 20 days of ageing; the crystal size estimated by electronmicrographs grow up to a final lenght of about 7000 Å within 10 days of ageing. Variations of the desorption spectrum with the degree of crystallization accompanying the ageing are shown in Fig. 5. It is clearly seen that the height of the 70° peak continues to diminish while that of the 260° peak increases with time. On the surface of an amorphous precipitate, abundant water is adsorbed physically around randomly distributed OH groups. The OH groups settle into lattice positions with the progress of crystallization, as indicated by the protruding of the 260° peak.

The changes in the amount of desorbed water in the three temperature ranges, shown in Fig. 6, demonstrate a continuous decrease of the water desorbed at lower temperatures and accordingly an increased water evolution at 260°. It also suggests that the crystal-forming process is rapid, being completed within several days.

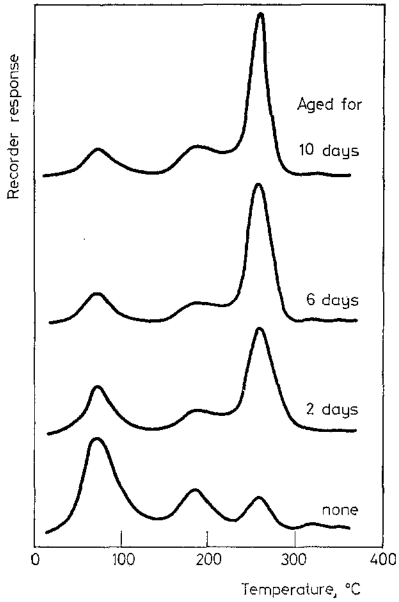

Fig. 5. Variations of water evolution curves of α-FeOOH with ageing

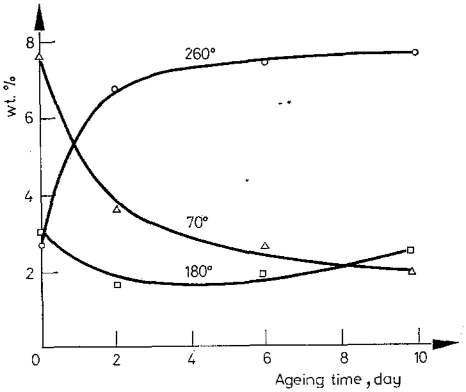

Fig. 6. Variations of amount of evolved water with ageing of α-FeOOH expressed in wt. % at 70° on dry basis, and at 180 and 260° on FeOOH basis

As the water from the 70° peak appears to arise from the crystal surfaces, recalculation of the amounts of evolved water in mg/m^2 was performed by using the BET specific surface area to show that the physically bound water per unit surface area is almost constant at 0.30 mg/m^2, irrespective of the degree of crystallization. The cross-sectional area of the H_2O molecule obtained from this value is approximately 10 Å^2, which is close to the value of the effective area of the adsorbed water molecule (10.5 Å^2) calculated by the Emmett–Brunauer method [18].

This fact appears to indicate that physical adsorption on dry α-FeOOH at all times involves a monolayer of water.

Water evolution and imperfection

As regards the crystallographic structures of α-FeOOH and γ-FeOOH, doping of Cu(II) into the crystals gives rise to lattice distortions possibly owing to the Jahn–Teller effect [19], producing more or less imperfect crystals. Over a certain limit of the Cu/Fe ratio, these two polymorphs tend to change into an amorphous state [3, 5]. In the case of β-FeOOH, however, distinctively no effects of Cu are observed on the structural and morphological situations [4].

Figures 7, 8 and 9 give the desorption spectra for α-, β- and γ-FeOOH, respectively, with various Cu contents. It is evident that the variation of the peak height with the Cu/Fe ratio reveals a certain resemblance between α-FeOOH (Fig. 7) and γ-FeOOH (Fig. 9): the 70° peak continues to develop with the Cu

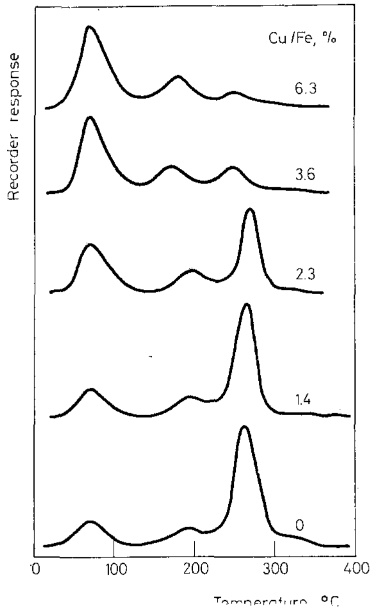

Fig. 7. Variation of water evolution curves of α-FeOOH with the Cu(II) content

content, whereas the 260° peak in particular declines; the 180° peak remains virtually unchanged. It is noteworthy that the desorption curves of β-FeOOH are the same for all the samples with different Cu contents, except that a shallow peak at 370°, showing the release of Cl, diminishes with the Cu addition. It has been suggested previously [4] that Cu and Cl are bound in the crystal. All these results

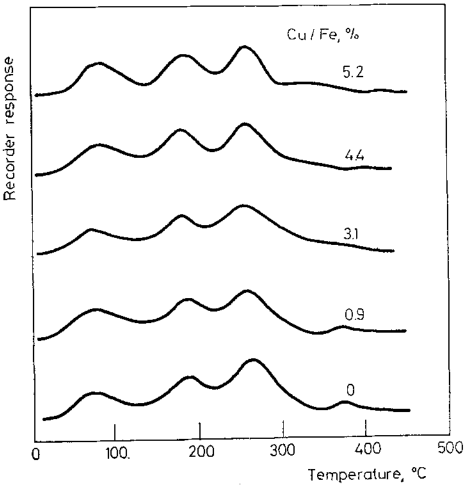

Fig. 8. Water evolution curves of β-FeOOH with different Cu(II) contents

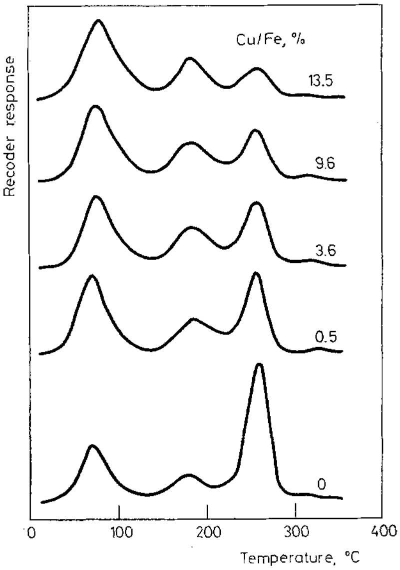

Fig. 9. Variations of water evolution curves of γ-FeOOH with the Cu(II) content

are envisaged to be coincident with the view of changes in each FeOOH caused by the addition of Cu(II).

Evaluating the amount of desorbed water from each peak area and dividing by the BET surface area, one can estimate the amount of water evolved per unit surface. It is interesting that the water desorbed per unit area at 70° is 0.30 ± 0.03 mg/m^2, which depends on neither the type of FeOOH (α or γ) nor the imperfection caused by Cu. For both α- and γ-FeOOH the 180° peak area appears to increase with the Fe/Cu ratio, whereas the 260° peak area decreases with the Cu/Fe ratio but they are still approximately constant for β-FeOOH. It appears that the activation energy of desorption calculated via eq. 1 shows similar tendencies as described above for each FeOOH: decreasing with the Cu/Fe ratio for α- and γ-FeOOH and being invariable for β-FeOOH.

Reviewing all the experimental results described above, one of the interesting facts is that the desorption temperature does not shift considerably, notwithstanding the crystal type or its structural changes; only the height and peak area vary with the structure. This fact suggests that the formation of H_2O from OH groups is governed not only by the number of OH groups but also by the mutual geometrical positions of adjacent OH groups. There is, however, one exception in that α-FeOOH containing more than 3% Cu/Fe exhibits of the desorption peaks normally at 180 and 260° to somewhat lower temperatures of 170 and 245° respectively (Fig. 7). It has been found [3] that these samples are X-ray amorphous, with entirely disordered structures, and cannot be transformed into oxide by calcination as high as 500°.

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Résumé — Description d'une technique d'enregistrement des courbes de détection des gaz émis (spectres de désorption thermique), jusqu'à 400°, de divers échantillons de FeOOH. Les courbes de désorption caractéristiques des variétés α, β et γ-FeOOH sont discutées en considérant la structure cristallographique qui gouverne les sites de H_2O physisorbée ainsi que des groupes OH donnant H_2O par déshydratation. Les variations des spectres de désorption sont également examinées pendant l'avancement de la cristallisation de FeOOH-α et en fonction de la distortion du réseau provoquée par l'addition de Cu(II) à FeOOH-α, -β et -γ.

Zusammenfassung — Es wird ein Verfahren zum Registrieren thermischer Desorptionsspektren verschiedener FeOOH-Proben zu 400° beschrieben. Die charakteristischen Desorptionskurven von α-, β- und γ-FeOOH werden an Hand der kristallographischen Strukturen erörtert, welche die Lage des physikalisch gebundenen H_2O sowie der, H_2O durch Dehydratisierung produzierenden, OH-Gruppen bestimmen. Die Änderungen der Desorptionsspektra von α-FeOOH mit fortschreitender Kristallisation und mit der durch Zugabe von Cu(II) zu α-, β- und γ-FeOOH hervorgerufenen Verzerrung der Kristallstruktur wurden ebenfalls untersucht.

Резюме — Описан метод для регистрации кривых выделенного газа (спектры термической десорбции) различных образцов FeOOH до температуры 400°. Характеристичные кривые десорбции α-, β- и γ-FeOOH обсуждены на основе кристаллографической структуры, которая определяет стороны для физически сорбированной воды, а также и для OH групп, дающих воду при дегидратации. Исследованы изменения спектров десорбции α-FeOOH в процессе кристаллизации, а также в связи с нарушением кристаллической структуры, вызванной прибавлением Cu(II) к α-, β- и γ-FeOOH.