

PREPARATION OF α -Fe₂O₃ (HEMATITE) BY OXIDATION PRECIPITATION OF AQUEOUS SOLUTIONS OF IRON(II) SULPHATE

Jan ŠUBRT, Alexandra ŠOLCOVÁ, František HANOUSEK, Antonín PETŘINA
and Vladimír ZAPLETAL

*Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Řež*

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The oxidation precipitation of aqueous solutions of iron(II) sulphate by oxygen gas was studied; the effect of pH, temperature, and presence of α -FeOOH and α -Fe₂O₃ crystal nuclei was examined and the conditions for the preparation of phase-pure α -Fe₂O₃ (hematite) were sought. The hematite prepared contained 3–5% structurally bonded water. The effect of the bonded water on the properties of the product is described and the way of the bonding in the structure is discussed.

Oxidation precipitation of aqueous solutions of iron(II) salts is a complex process involving nucleation of the reaction products and crystal growth of the solid phase. In dependence on the reaction conditions, a number of iron oxides and oxide-hydroxides with variable properties are formed, *e.g.*, $\alpha, \beta, \gamma, \delta$ -FeOOH, the so-called iron gel Fe₂O₃.n H₂O, or α -Fe₂O₃. Various pathways have been suggested to account for the relation between the reaction conditions and the phase composition of the products^{1,2}. At temperatures above 80°C, some oxide-hydroxides transform into α -FeOOH or α -Fe₂O₃ (refs^{3,4}). Based on the available thermodynamic data for the 2α -FeOOH \rightarrow α -Fe₂O₃ + H₂O transformation, Langmuir⁵ has been able to show that for spherical particles larger than 1 μ m in diameter, goethite (α -FeOOH) in aqueous suspension is the more stable up to 80°C, the transformation point shifting to lower temperatures as the particle size is lowered, *e.g.*, 40°C for 0.1 μ m or even –27°C for 0.04 μ m. In this manner it is possible to estimate the temperature region where hematite should be the product of the oxidation precipitation of iron(II) solutions if the process were controlled by thermodynamic effects solely.

The stability of the solid phase is also affected by the pH and the redox potential of the system (*E*). A plot of *E* vs pH based on the thermodynamic data was published by Pourbaix⁶; later this problem was studied by Detournay and coworkers⁷. The authors proceeded from the tabulated thermodynamic data at 20°C and considered goethite as the stable oxide phase of iron(III); at lower *E* and higher pH values, the region of its stability is bounded by the stability region of magnetite, at lower pH in the presence of sulphate, by the stability region of basic sulphates of jarosite type (*e.g.*, NH₄Fe₃(SO₄)₂(OH)₆).

In this work, the oxidation precipitation of iron(II) sulphate is studied at temperatures approaching the boundary of the temperature stability of hematite and goethite in aqueous systems. These substances in aqueous solutions of iron(II) sulphate have been found⁴ not to transform into one another at an appreciable rate at 70–100°C, and so both can be expected to appear under the reaction conditions used; the phase composition of the products then may be significantly affected by crystal nuclei of these phases in the system.

EXPERIMENTAL

Chemicals and Apparatus

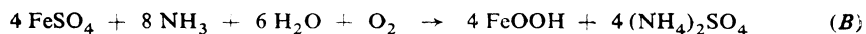
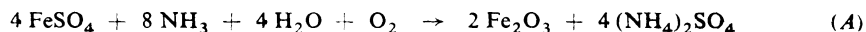
Iron(II) sulphate of reagent grade purity (Lachema, Brno) was used. The aqueous solution was made acidic with sulphuric acid of reagent grade purity to pH 1.5 and freed from trivalent iron by reduction with iron powder. Ammonia (a 25% solution) was of reagent grade purity (Lachema, Brno). Phase-pure α -Fe₂O₃, Transoxide Red type, was a commercial chemical of Hilton-Davis.

The phase composition of the samples was examined by infrared and Mössbauer spectroscopy and powder X-ray diffraction analysis. DTA curves and transmission and scanning electron microscope photographs were also obtained, the surface area was determined⁸, and the colour characteristics were measured. The reflection spectra were obtained on an Acta M IV spectrometer (Beckman) using a tungsten lamp in conjunction with filters automatically controlled so that the spectral characteristics corresponded to conventional white light. A plate coated with barium sulphate served as the reference standard. The data handling has been described⁹. The samples were characterized by the dominant wavelength λ_d , spectral purity p_c , and x , y coordinates in the trichromatic system, treated by a standard procedure¹⁰.

Working Procedure

The oxidation precipitation was carried out in an apparatus⁸ consisting of a thermostated reaction vessel fitted with a dispersing stirrer, controlled air feed and a pH-stat.

One litre of FeSO₄ solution in a concentration of 1.6 mol l⁻¹ was placed in the reaction vessel and, if desired, crystal nuclei were added in an amount such that their iron content made up 10% of the total iron in the reaction vessel. The mixture was diluted to 1.5 l and the acidity was adjusted with H₂SO₄ or NH₃ to pH 2. The reaction mixture was heated under argon stream to the desired temperature of the oxidation precipitation. The pH was adjusted to a preselected value with ammonia and the argon stream was replaced with air stream (1.6 l min⁻¹) dispersed vigorously into the mixture with the stirrer. The reaction proceeded within the kinetic region, *i.e.*, its rate was not controlled by the diffusion of oxygen into the solution. Since H⁺ ions were generated by hydrolysis of the Fe³⁺ ions formed, ammonia had to be added repeatedly during the reaction for keeping the pH constant. The amount of ammonia used up was proportional to the amount of oxidized iron according to the equations



The consumption of ammonia was measured, whereby the reaction course was indirectly monitored (at the pH and reaction temperatures used, loss of ammonia by bubbling the suspension with air can be disregarded).

After the reaction the product was filtered out, washed with water to a negative reaction for sulphate, then washed repeatedly with methanol, and dried at temperatures below 50°C.

In some experiments the phase composition was modified by prior addition of hematite crystal nuclei, *i.e.*, suspension of finely dispersed hematite (0.01–0.05 μm particles), prepared by transformation of $\gamma\text{-FeOOH}$ (lepidocrocite) in water at 140–170°C under the corresponding water vapour pressure¹¹. Suspension of commercial micronized iron red, constituted by finely dispersed $\alpha\text{-Fe}_2\text{O}_3$ (0.01 μm), was also used. In other experiments, crystal nuclei of $\alpha\text{-FeOOH}$ (goethite) were also added. The suspension was obtained by transformation of $\gamma\text{-FeOOH}$ in aqueous solution of iron(II) sulphate⁴; the specific surface area of the crystal nuclei was about 70 $\text{m}^2 \cdot \text{g}^{-1}$.

RESULTS AND DISCUSSION

Reaction Course and Phase Composition of Reaction Products

A series of oxidations of FeSO_4 in aqueous solution was performed at temperatures of 80 and 95°C. At $\text{pH} < 2$, the major reaction product was a basic sulphate of jarosite type $(\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)$. At $\text{pH} 1.75\text{--}2$, $\alpha\text{-FeOOH}$ was also formed, and at $\text{pH} 2\text{--}4.5$ this substance was the sole product. At $\text{pH} > 4.5$, the product contained also Fe_3O_4 , which at $\text{pH} > 5$ became the single reaction product.

In experiments in which crystal nuclei of hematite in an amount of 10% Fe with respect to total iron had been added, the basic sulphate $\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ was again the product at $\text{pH} \leq 2$, and Fe_3O_4 was the product at $\text{pH} > 4.5$. In the $\text{pH} 2\text{--}4.5$ range, phase-pure $\alpha\text{-Fe}_2\text{O}_3$ was obtained.

In experiments where mixtures of hematite and goethite crystal nuclei were added to the reaction mixture in amounts such that the sum of their iron contents made up 10% with respect to total iron, the reaction product at $\text{pH} 2\text{--}4.5$ was a mixture of $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$, their fractions in the product being proportional to their fractions in the initial nucleation mixture. Thus both of them can grow on suitable nuclei of crystallization under the conditions used.

The time dependence of Fe^{3+} content at 95°C in the presence of $\alpha\text{-Fe}_2\text{O}_3$ crystal nuclei is shown in Fig. 1. The oxidation rate is appreciably affected by the pH used. The oxidation is unaffected by the air flow rate or the rotation speed of the stirrer; hence, the reaction rate is controlled by the oxidation itself rather than by the transport of oxygen.

The kinetics could be described by a 1st rate order equation with respect to oxidation of Fe^{2+} at a constant concentration of oxygen up to the degree of oxidation of approximately 70%, at higher degrees of oxidation the process accelerated considerably. The reaction rate was affected markedly by the amount and kind of crystal nuclei, which indicates that the oxidation is a complex process the kinetics of which is affected also by the reaction product formed.

The hematite particle size cubed is plotted against the amount of iron oxidized during the process in Fig. 2. The dependence can be fitted by a straight line, which indicates that during the process the particles grow in size but not in number. Based on the d^3 value read for the beginning of the process, the size of the crystal nuclei at the moment the oxidation precipitation sets in can be calculated. This value, 0.15 μm , is multiply higher than the value observed on the microphotographs of the hematite crystal nuclei (0.01–0.05 μm , Fig. 3*). From this it can be inferred that the centres of hematite growth in the initial stage of the oxidation precipitation are agglomerates containing tens or hundreds of the primary α -Fe₂O₃ crystal nuclei rather than the nuclei themselves.

Fig. 3* is a photograph of the hematite crystal nuclei prepared by hydrothermal transformation of γ -FeOOH, Fig. 4* is a photograph of the final product of the oxidation precipitation. The size and shape of the particles in the two photographs are apparently different. The morphology of the α -Fe₂O₃ particles prepared by the precipitation on crystal nuclei is characteristic of this type of hematite and is independent of the conditions of preparation. The specific surface area of such hematite, prepared by using 10% α -Fe₂O₃ crystal nuclei, was 2.5 m² g⁻¹; the calculated particle size, 0.49 μm , is in a good agreement with the size observed on the microphotographs.

Based on the experiments performed, the conditions requisite for obtaining phase-pure hematite can be formulated. Apart from the requirement of the appro-

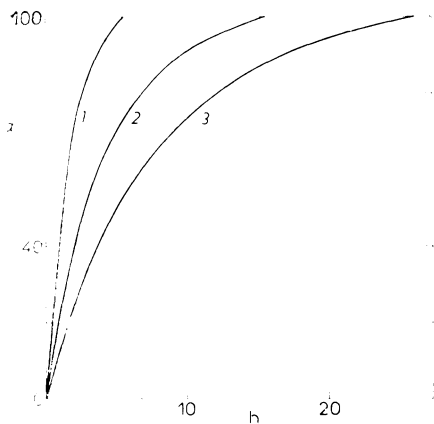


FIG. 1

Time dependence of the degree of oxidation of Fe²⁺ during the oxidation precipitation of aqueous solution of FeSO₄ at 95°C. 1 pH 4, 2 pH 3.5, 3 pH 3

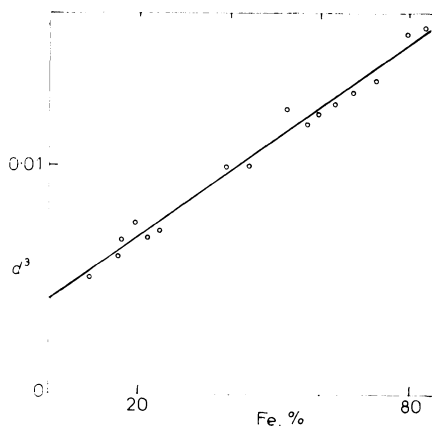


FIG. 2

Dependence of the α -Fe₂O₃ particle diameter cubed (μm^3) on the degree of oxidation during the oxidation precipitation of aqueous solution of FeSO₄ at pH 4, 95°C

* See insert on the p. 2484.

appropriate pH range, it is necessary that neither the initial FeSO_4 solution nor the hematite nucleation suspension contain goethite which would act as growth centres for this phase. Goethite crystal nuclei might form also by spontaneous nucleation particularly in the initial stage of the oxidation, where the oxidation rate is highest and the active surface area of the hematite crystal nuclei smallest. Neither of the two types of hematite crystal nuclei used contained goethite, and with the 10% Fe amount in the nuclei used, spontaneous nucleation at the beginning was not observed. Owing to this, the reaction products did not contain goethite in measurable quantities.

Properties of Hematite Prepared

The products obtained in the presence of $\alpha\text{-Fe}_2\text{O}_3$ crystal nuclei can be characterized as hematite with a relatively high amount of water bonded within the structure. The powder X-ray diffraction patterns correspond to hematite free of crystalline impurities. The presence of other crystalline or amorphous iron(III) oxides or oxide-hydroxides is rejected also by infrared and Mössbauer spectra.

By chemical analysis, the products contained about 1% (m/m) sulphate and 3–5% (m/m) water. No Fe^{2+} was detected.

The ability of hematite to bind comparatively high amounts of water (3–5% (m/m); 10·14% H_2O corresponds to the formula FeOOH) has been reported^{12,13}. Part of this water is bonded rather strongly, temperatures as high as 1 000°C being necessary¹³ for its complete removal. Crystalline iron(III) oxides with a hematite structure and higher structurally bonded water content are sometimes referred to as hydrohematite^{12,13}. The water is assumed to be bonded in the form of OH^- groups replacing part of the O^{2-} in the $\alpha\text{-Fe}_2\text{O}_3$ structure. The charge deficit can be compensated either by a partial substitution of Fe^{3+} by Fe^{2+} or by partial occurrence of cationic vacancies in the Fe^{3+} sites. Since the chemical analysis revealed

TABLE I

Relative intensities of the X-ray diffraction lines of hematite and hydrohematite

<i>h k l</i>	<i>I</i> , % (113), for			
	anhydrous $\alpha\text{-Fe}_2\text{O}_3$	hydrohematite prepared at		
		pH 3	pH 3·5	pH 4
0 1 2	138	87	97	104
1 0 4	345	281	274	281
1 1 0	218	155	164	157
1 1 3	100	100	100	100
0 2 4	131	99	100	100

that our hydrohematite samples contained no Fe²⁺ even in trace quantities, the latter explanation seems to be more likely. This concept has also been confirmed¹³ by X-ray diffraction measurements: while the intensity of the diffraction on the (113) plane

TABLE II
Properties of α -Fe₂O₃ prepared by oxidation precipitation of aqueous solutions of FeSO₄

Parameter	Value for		
	hydrohematite ^a	hydrohematite ^b	hematite ^c
Space group			
Hexagonal parameters:			
R $\bar{3}$ c (No 167)			
<i>a</i> , nm	0.5038	0.5037	0.5035
<i>c</i> , nm	1.3767	1.3765	1.3749
Water content, % (m/m)	3.2	2.8	0
Density, g cm ⁻³	4.84	4.92	5.21
Complementary wavelength λ_d ,			
nm	603.5	613.2	629.0
Trichromatic coordinates ^b :			
<i>x</i>	0.5098	0.4570	0.4172
<i>y</i>	0.3411	0.3196	0.3101
<i>Y</i>	10.2275	6.4036	5.4495
Colour purity ^b , %:			
<i>p_e</i>	54.71	40.32	19.79
<i>p_c</i>	58.00	40.94	18.18

^a Prepared at pH 3; ^b prepared at pH 4; ^c prepared by dehydration of hydrohematite (pH 4) at 600°C; ^d ref.¹⁰.

TABLE III
Wavenumbers ν (cm⁻¹) and relative intensities *B* of Fe—O vibrations of anhydrous α -Fe₂O₃ and of hydrohematite obtained by oxidation precipitation of aqueous solution of FeSO₄

Sample	ν_1	B_1/B_3	ν_2	B_2/B_3	ν_3	ν_4	B_4/B_3
Anhydrous α -Fe ₂ O ₃	345	0.809	469	0.605	553	597	1.066
Hydrohematite ^a	325	1.606	462	1.061	542	579	1.980
Hydrohematite ^b	327	1.593	461	1.018	539	574	1.956

^a Prepared at pH 3; ^b prepared at pH 4.

was independent of the water content, the intensities of diffraction on the (012), (104), (110), and (024) planes in hydrohematite were lower than in the pure α -FeO₃, which can be well accounted for in terms of the vacancies. Our X-ray diffraction patterns exhibited the same trend although our samples were somewhat different from those used in ref.¹³ (Table I).

Some properties of hydrohematite and anhydrous α -Fe₂O₃ prepared by annealing hydrohematite at 600°C are compared in Table II. (At 600°C hydrohematite releases virtually all the structurally bonded water while particle sintering that might alter the optical properties does not yet set in.) The lattice parameters a and c are higher for the water-containing samples; the differences, which are well-reproducible, can be understood in terms of the defects in the hydrohematite structure brought about by the substitution of O²⁻ by OH⁻ groups and the occurrence of cationic vacancies. The infrared spectra, exhibiting four absorption bands in the 250–650 cm⁻¹ range, resemble each other, still some differences are observed in the relative intensities as well as in the band positions; the differences depend only slightly on the pH used during the preparation (Table III). In the region of OH stretching vibrations, the spectra of hydrohematite display two broad bands with maxima at 3 250 and 3 400 cm⁻¹, which can be attributed to the structurally bonded water and to water adsorbed on the sample surface, respectively. These bands are absent from the spectra of anhydrous α -Fe₂O₃, while similar bands are present in the spectra of other iron(III) oxide-hydroxides.

From the practical point of view, the changes in the optical properties of hydrohematite associated with the presence of structurally bonded water are of great importance. The loss of this water is associated with changes in all optical characteristics (Table II), although up to now such changes were only related to the particle size.

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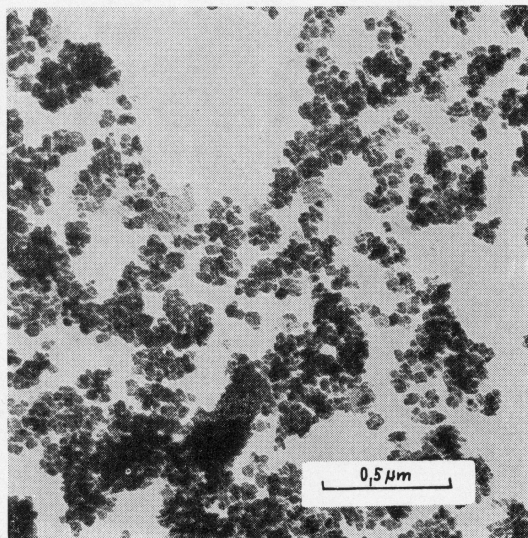


FIG. 3
Microphotograph of the α -Fe₂O₃ crystal nuclei used

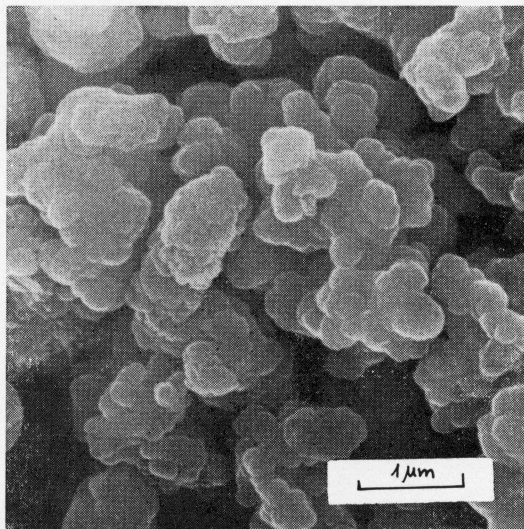


FIG. 4
Microphotograph of α -Fe₂O₃ obtained by oxidation precipitation of aqueous solution of FeSO₄