

# Investigation of the structure of protohematite — metastable phase of ferrum (III) oxide

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## Abstract

A new modification of Fe(III) oxide — protohematite — was produced by thermal decomposition of crystalline hydroxides and salts and by plasma chemical method. Protohematite is a metastable phase which transforms into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 1100°C, under pressure or mechanic chemical activation. IR and Raman spectroscopy, X-ray powder diffraction, and transmission electron microscopy were used to study the structure of protohematite. It was concluded that protohematite has unique structural characteristics. The hypothesis concerning the structure of protohematite was suggested. Specific chemical activity of the protohematite was assumed to originate from the presence of some ferric cations in quasi tetrahedral (distorted octahedral) coordination. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Hematite; Fe oxide; Phase transition; Structure

## 1. Introduction

At the study on thermal decomposition of  $\alpha$ -FeOOH, the unusual structure of Fe<sub>2</sub>O<sub>3</sub> was discovered [1,2]. The structure was found to differ from that of perfect  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite). The difference in IR spectra of the products of thermal decomposition obtained at different calcination temperatures was the reason to propose the special term protohematite in order to distinguish its structure from hematite [1]. On the other hand, the existence of protohematite phase was discussed and all the distinctions in IR-

spectra were explained by various morphologies of particles [3]. In our previous studies, the products of  $\alpha$ -FeOOH thermal decomposition were investigated and hypotheses about the structure of protohematite were proposed [4–7].

The purpose of the present study was to demonstrate the independence of some features of protohematite phase on the characteristics of their precursors and to investigate its chemical activity.

## 2. Experimental

Three methods of Fe-oxide specimen preparation were employed: (i) thermal decomposi-

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tion of  $\alpha$ -FeOOH at 400°C for 4 h followed by the calcination in the temperature range from 500°C to 1100°C for 1 h at every temperature step, (ii) thermal decomposition of sulfate, nitrate, and oxalate Fe(III) salts at the above temperatures, and (iii) plasma spraying of the water solution of  $\text{Fe}(\text{NO}_3)_3$ .

IR-spectra were obtained using Fourier spectrometers IFS-113v Bruker and BOMEM MB-102, the samples were prepared as suspension in nujol, by pressing in alkali metals halides or by dusting on the KBr and CsJ supports. Raman spectra were recorded with DFS-24 spectrometer; the excitation source was 647 nm line of a Kr laser.

X-ray diffraction (XRD) patterns were obtained with a HZG-4 diffractometer on Cu  $K_\beta$  radiation. The scan region was  $2\theta = 19$ – $120^\circ$ , and the profile step width was  $0.05^\circ$ . The computer program system Polycrystal was used to determine the structural parameters. A crystal structure refinement procedure using modified Rietveld method was also performed. All the specimens were examined in a JEM-100CX electron microscope (TEM). The resolution limit of the machine was about 4 Å, the accelerating potential 100 kV. Specimens were deposited onto a carbon film supported on a copper grid from ethanol slurry.

Mechanical activation was carried out in Ar atmosphere under 40 g acceleration in a planetary ball mill equipped with corundum drums and balls; ratio of the balls/oxide weights was 500:1. The time of activation was varied from 1 to 15 min.

Samples reactivity was characterized by the rate of carbon monoxide catalytic oxidation in the mixture of 1% CO + 1% O<sub>2</sub> in He determined in the range of 413–500 K using a micro reactor with the vibrofluidized bed of catalysts and pulse/flow kinetic installation. Before measurements, the samples were successively pre-treated at 500 and 673 K in the flow of purified oxygen. The rates were determined in essentially differing conditions (CO conversion < 10%) and expressed as a number of CO

molecules oxidized per square meter per second.

### 3. Results and discussion

Protohematite phase was produced by the thermolysis of crystalline hydroxides and crystalline salts in the temperature region from 400°C to 900°C. Thermal decomposition of amorphous precursors leads to the formation of hematite phase at these temperatures. Protohematite phase was prepared by plasma chemical method as well. This phase is metastable and transforms into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at temperature higher than 1000°C or under pressure and mechanic chemical activation. Protohematite spectra differ from that of hematite and allow one to distinguish the two modifications of Fe oxides. Typical IR and Raman spectra for hematite and protohematite are shown in Fig. 1.

#### 3.1. Hematite

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a structural type of corundum, the space group is  $D_{3d}^6$  with two formula units per unit cell. Fe atoms are on 4(c) sites and O on 6(e) sites. So at the Brillouin zone center, the vibrational modes are distributed as follows:  $2A_{1g} + 2A_{1u} + 3A_{2u} + 5E_g + 4E_u$ . The symmetrical modes are optically active in Raman

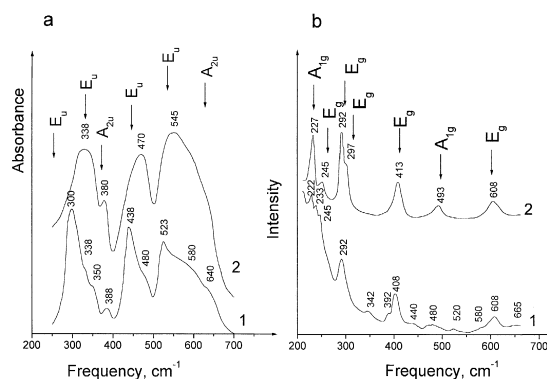


Fig.1. IR (a) and Raman (b) spectra of protohematite (1) and hematite (2).

scattering and the antisymmetrical ones, apart from  $A_{1u}$ , in infrared.

### 3.2. Protohematite

The presence of additional lines as compared to seven Raman and seven IR active vibrations in hematite spectra allows us to suppose that protohematite possesses symmetry lower than  $D_{3d}^6$ . On the other hand, XRD investigations revealed only  $\alpha\text{-Fe}_2\text{O}_3$  phase in all products of the thermal decomposition of Fe hydroxides and salts. This contradiction between XRD and spectral data may be explained with the hypothesis concerning  $C_{3v}^6$  space group of protohematite, indistinguishable from  $D_{3d}^6$  space group of hematite by XRD [5,7]. These space groups have the same rules of diffraction absence, but have different selection rules for IR and Raman active vibrations. Using the correlation between irreducible representation of  $D_{3d}$  and  $C_{3v}$  point groups, we obtained the distribution of vibrational modes for protohematite:  $4A_1 + 5A_2 + 9E$ , where the vibrations of  $A_1$  and E types are active both in IR and Raman.

Positions of peaks in XRD pattern of protohematite and hematite are practically the same, nevertheless, the Fe–O and O–O interatomic distances refined for protohematite somewhat differ from hematite distances (Table 1). In the

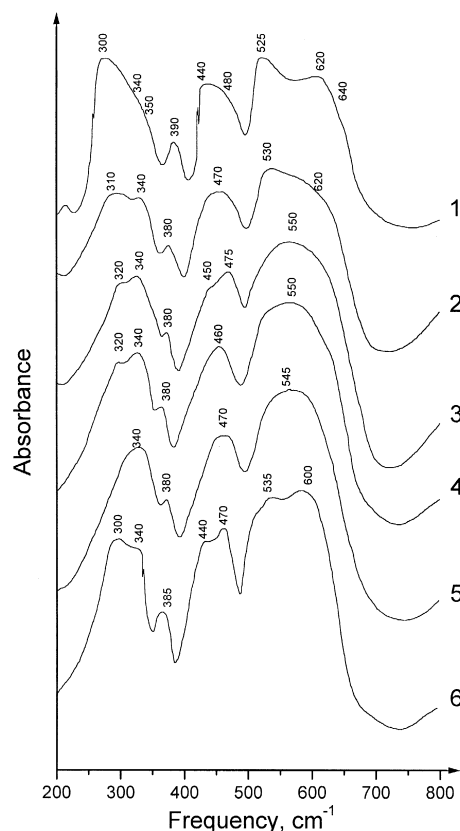


Fig. 2. IR spectra of industrial sample of Fe oxide (1) subjected to mechanical activation at 1 (2), 5 (3), 10 (4), 15 (5), and 15 min (6) with subsequent calcination at 400°C.

Table 1

Interatomic distances (Å) in  $\text{Fe}_2\text{O}_3$  specimens prepared from  $\alpha\text{-FeOOH}$  at different temperatures and industrial sample after mechanical activation

	400°	1100°	Industry sample	15 min	15min 400°C	$\alpha\text{-Fe}_2\text{O}_3$
Fe–O(3)	1.90	1.95	1.90	1.96	1.92	1.95
Fe–O(3)	2.18	2.10	2.18	2.10	2.14	2.10
O–O1(3)	2.95	3.05	2.96	3.08	2.98	3.05
O–O2(3)	2.86	2.89	2.86	2.90	2.87	2.89
O–O3(3)	2.83	2.76	2.81	2.76	2.80	2.76
O–O4(3)	2.82	2.64	2.81	2.60	2.76	2.64
Fe–Fe1	2.97	2.97	2.97	2.98	2.97	2.97
Fe–Fe2		2.91	2.91		2.87	2.89

table, refined interatomic distances for industrial reactant sample are presented as well. These distances are similar to protohematite distances and differ from that in perfect hematite structure, which practically coincide with 1110°C sample. IR spectrum of industrial sample is similar to protohematite spectrum too (Fig. 2, curve 1). Thus, the industrial sample has protohematite structure and namely, this sample was subjected to mechanical activation, and its catalytic activity was measured.

According to TEM data, particles of the industrial sample are of platelet morphology with rounded or hexagonal contours; typical size was about  $400 \times 400 \times 100$  Å. After activation, microstrains and intergrain boundaries disappear,

while partial separation of thin (80–100 Å) platelets from more bulky ones occurs. The latter results explain well some increases on the specific surface value, from 14 to 20 m<sup>2</sup>/g after 2 min of activation. From XRD data, it follows that in industrial protohematite sample, a pronounced distortion of the oxygen octahedron in the structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> takes place. For activated sample, some inter-atomic distances approached those for the regular  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structure (Table 1).

In the IR spectra some noticeable variation appear even after the first minute of activation (Fig. 2, curve 2). As activation proceeds further up to 15 min (Fig. 2, curves 3–5), the position of bands became nearly the same as in high temperature sample, i.e. practically coincided with the position in perfect hematite structure (Fig. 1). Note that calcination of the 15 min activated sample at 400°C leads to the appearance in the IR spectrum of 300, 440 and 535 cm<sup>-1</sup> bands, characteristic for protohematite phase, and corresponding changes in inter-atomic distances (Fig. 2, curve 6; Table 1).

For all pretreatments and conditions of activity measurements, critical regime of mechanical activation of the protohematite leads to a decrease in its catalytic activity [6], thus protohematite is about 10 times more active than hematite. When getting relationship between the activity of Fe oxides and their spectra and inter-atomic distances, an interesting hypothesis arises. Absorption bands at about 600–650 cm<sup>-1</sup> are characteristic for tetrahedral coordination of Fe atoms in Fe oxides structures. It seems likely that distortion of Fe–O octahedron in protohematite structure as compared to that of hematite is due to the quasi-tetrahedral coordination of a few Fe atoms in protohematite. We suggest that specific protohematite activity originates from the distortion of octahedral coordination of Fe cations.

Protohematite structure was detected when Fe oxide catalyst was formed from the nitrate and sulphate salts on the SiO<sub>2</sub> support as well [8]. Spectra of catalyst together with the differ-

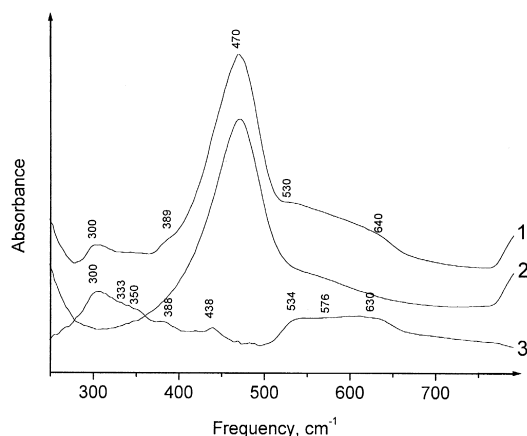


Fig. 3. IR spectra of Fe containing catalyst (1), SiO<sub>2</sub> support (2), and differential catalyst minus support spectrum (3).

ence spectra (catalyst minus support) are presented in Fig. 3.

#### 4. Conclusion

Protohematite phase was synthesized by three different methods, its characteristics were independent on the precursors. This phase is metastable and transforms into hematite at high temperature (above 1000°C) or under mechanic activation. Protohematite has the unique structural characteristics. IR spectroscopy is a reliable tool which tells the difference between the structures of hematite and protohematite. Catalytic activity of protohematite was assumed to originate from the peculiarity of its structure, namely of the presence of some ferric cations in distorted octahedral coordination.

#### References

- [1] S. Yariv, E. Mendelovoci, *Appl. Spectrosc.* 33 (1979) 410.
- [2] E. Wolska, U. Schwertmann, *Z. Kristallogr.* 189 (1989) 223.
- [3] C.J. Serna, J.E. Iglesias, *J. Mater. Sci. Lett.* 5 (1986) 901.
- [4] G.N. Kryukova, S.V. Tsubulya, L.P. Solovijeva, V.A. Sadykov, G.S. Litvak, M.P. Andrianova, *Mater. Sci. Eng., A* 149 (1991) 121.
- [5] G.N. Kustova, E.B. Burgina, V.A. Sadykov, S.G. Poryvaev, *Phys. Chem. Miner.* 18 (1992) 379.
- [6] V.A. Sadykov, L.A. Isupova, S.V. Tsubulya, E.B. Burgina,

- G.N. Kustova, V.N. Kolomiichuk, V.P. Ivanov, E.A. Paukshtis, A.V. Golovin, E.G. Avvakumov, *J. Solid State Chem.* 123 (1996) 191.
- [7] E.B. Burgina, G.N. Kustova, S.V. Tsybulya, G.N. Kryukova, G.S. Litvak, L.A. Isupova, V.A. Sadykov, *Zh. Strukt. Khim.* (2000) in press (In Russian).
- [8] G.A. Bukhtiyarova, N.S. Sakaeva, V.A. Varnek, E.B. Burgina, L.M. Plyasova, V.I. Bukhtiyarov, V.V. Kaichev, B.P. Zolotovskii, *Khimiya v Interesah Ustoichivogo Razvitiya* 7 (1999) 359.