

INVESTIGATION ON MECHANOCHEMICAL DEHYDRATION OF γ -FeOOH

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Received March 15th, 1985

The process of mechanochemical dehydration of γ -FeOOH has been investigated. It has been established that grinding of γ -FeOOH leads to its direct transformation into α -Fe₂O₃. The IR spectroscopy and X-ray phase analyses did not detect γ -Fe₂O₃ in the dehydration products. During dehydration, α -Fe₂O₃ with a defective magnetic structure is formed. The smallest size of the hematite particles obtained is 10 nm. The difference between mechanochemical and controlled thermal dehydration of γ -FeOOH is discussed.

The mechanochemical dehydration of metal hydroxides has been the subject of a series of investigations¹⁻⁴. The cases in which oxides with different phase compositions are obtained are especially interesting. This is the case of γ -FeOOH. It may be decomposed quantitatively to γ -Fe₂O₃ or α -Fe₂O₃, depending on the conditions of thermal treatment. Some preliminary results in this respect have already been published^{5,6}. The present paper contains data from a study of the behaviour of γ -FeOOH during the grinding process.

EXPERIMENTAL

The initial γ -FeOOH was obtained by oxidative precipitation from an FeSO₄ solution⁷. The mechanochemical treatment consisted in grinding the lepidocrocite in an automatic agate mortar. The IR spectra were obtained with Beckmann IR and Specord UR-20 spectrometers. The X-ray analysis was carried out on a DRON-1 apparatus using CuK_α radiation. The Moessbauer spectra were taken on an NTA-1024 instrument at room temperature. The specific surface areas were measured by a modified BET method. The products were reduced at a hydrogen pressure of 0.6 Pa in a gradientless regime⁸.

RESULTS AND DISCUSSION

Electron microscopy data showed that the morphology of the γ -FeOOH particles changed already at the beginning of the grinding process when dehydration was observed.

Fig. 1 shows a gradual disappearance of the lines of γ -FeOOH with increasing duration of the grinding process and appearance of lines of α -Fe₂O₃. No γ -Fe₂O₃ was detected in the solid reaction products either by X-ray phase analysis and the IR spectroscopy. The results from both analyses indicate complete dehydration of the initial γ -FeOOH to α -Fe₂O₃ after 80 h grinding (Fig. 1).

Moessbauer studies showed that as a result of mechanochemical dehydration of γ -FeOOH, α -Fe₂O₃ with a defective magnetic structure quite different from that of standard α -Fe₂O₃ was obtained. A strong decrease in the value of the internal magnetic field was observed ($H_{\text{eff}} = 462$ kOe for a sample ground for 57 h) as well as Non-Lorenzian shape of the Moessbauer spectra, and asymmetry of the central doublet.

The standard α -Fe₂O₃ has an internal magnetic field of 520 kOe. The deviations may be attributed to defects appearing during the sample grinding. This explanation is based on: 1) a small difference in the specific surface areas of the initial γ -FeOOH and the samples obtained (Table I); 2) the fact that the sample particles are not small enough to lead to superparamagnetism, which is evident from the strong X-ray lines in the diagram (Fig. 1). During grinding of iron oxides and ferrites a similar significant change in the Moessbauer spectra, e.g. a decrease in the value of the internal magnetic field and asymmetry have been observed⁹⁻¹². These changes could be attributed to defects appearing during the grinding process⁹⁻¹².

The α -Fe₂O₃ obtained after 80 h grinding has fewer defects in its magnetic structure. Its Moessbauer spectrum has six lines. The value of the internal magnetic field increases ($H_{\text{eff}} = 482$ kOe). This value is still considerably lower than those of the internal magnetic field of the standard α -Fe₂O₃ and the hematite obtained by controlled thermal decomposition. The ratio of the peak intensities of the oxide obtained after 80 h grinding is quite different from that for standard α -Fe₂O₃. There is also a significant difference between this ratio for hematite obtained by mechanochemical decomposition and that for hematite resulting from controlled thermal decomposition even when both compounds have close specific surface areas. These results show that the α -Fe₂O₃ obtained by grinding has more defects in its structure than the hematite prepared by conventional methods.

A comparative study was carried out on the reactivities of α -Fe₂O₃(I) obtained by grinding of γ -FeOOH for 80 h and α -Fe₂O₃(II) prepared by controlled thermal decomposition of γ -FeOOH. Both oxides had very close specific surface areas: 115 m² g⁻¹ for α -Fe₂O₃(I) and 121 m² g⁻¹ for α -Fe₂O₃(II). It was established that α -Fe₂O₃(I) was reduced to Fe₃O₄ much more rapidly than α -Fe₂O₃(II) (Fig. 2). This indicates that α -Fe₂O₃(I) is more reactive on account of its defective structure.

The specific surface areas of the samples obtained during grinding showed a small change (Table I) due to reaching the limit size of 10 nm when the processes of particle aggregation are intense^{4,9,13,14}.

The above investigations showed that γ -FeOOH is dehydrated during its grinding, resulting in the formation of α -Fe₂O₃ and the appearance of significant defects in the structure of the solid reaction products.

TABLE I

Dependence of specific surface area ($\text{m}^2 \text{g}^{-1}$) changes on the duration (h) of mechanical treatment of γ -FeOOH^a

Time, h	25	33	49	57	80	100
Specific surface area	97	103	100	107	115	105

^a Specific surface area of initial γ -FeOOH = $115 \text{ m}^2 \text{g}^{-1}$.

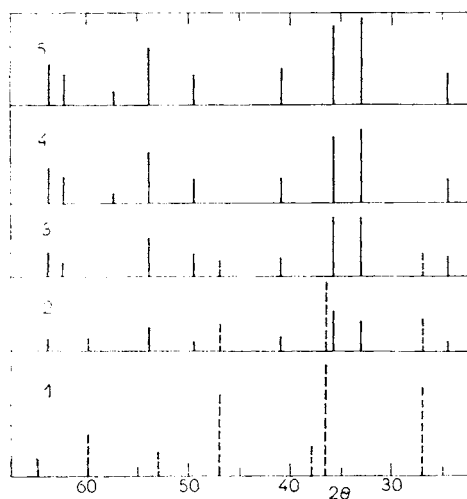


FIG. 1

X-ray phase diagram of γ -FeOOH 1 and products of its mechanochemical dehydration. Samples 2, 3, 4, 5 ground for 25, 49, 57, and 80 h. ----- γ -FeOOH, ——— α -Fe₂O₃

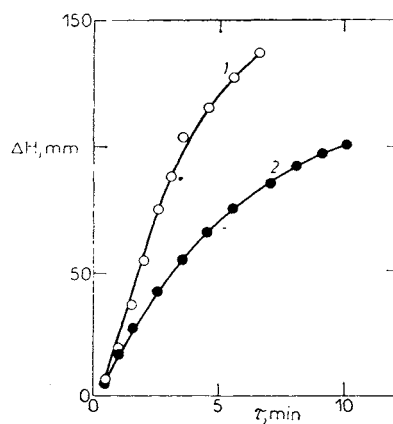


FIG. 2

Change of hydrogen pressure in the calibrated volume of a static-circulation apparatus (ΔP) during the reduction of α -Fe₂O₃ to Fe₃O₄. 1 Reduction of α -Fe₂O₃ (I) obtained by mechanochemical decomposition of γ -FeOOH, 2 reduction of α -Fe₂O₃ (II) obtained by controlled thermal decomposition of γ -FeOOH

During the mechanochemical dehydration of γ -FeOOH, no γ -Fe₂O₃, which is characteristic of controlled thermal decomposition of lepidocrocite, is observed. This may be ascribed to peculiarities of mechanochemical reactions, *e.g.* to a local sharp increase of temperature during a mechanical treatment^{12,15}, which favours the conversion of γ -FeOOH to α -Fe₂O₃. This process can also be accompanied by the liberation of the energy accumulated in the defects^{4,16}. We are of the opinion that the local sharp increase of temperature is prevailing. Thus, it may be expected that grinding in a heat-absorbing medium would lead to the formation of reaction products with a different composition.

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