Phase Transition during Mechanical Dehydration of γ-FeOOH

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The mechanical dehydration of γ-FeOOH leads to α-Fe_2O_3; this has been confirmed by *X*-ray analysis and Mössbauer spectroscopy.

In a previous paper it was shown that the thermal dehydration of γ-FeOOH in air at 200—300 °C leads to the formation of γ-Fe_2O_3.[1] It was of interest to compare these results with the mechanical dehydration of this compound.

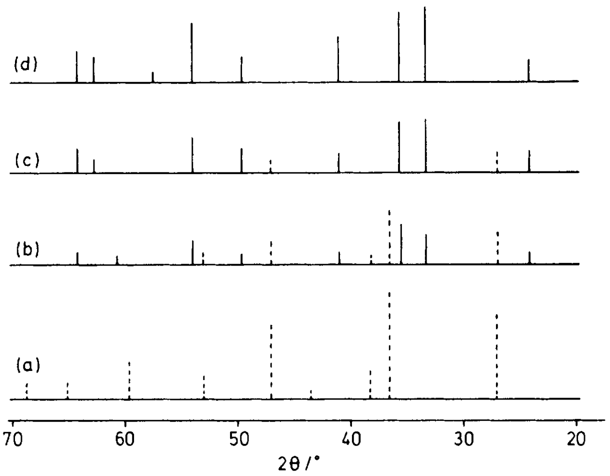

Figure 1. *X*-Ray analysis of (a) the initial sample of γ-FeOOH; (b) after 26 h grinding; (c) after 42 h grinding; (d) after 57 h grinding. ---- γ-FeOOH, ——— α-Fe$_2$O$_3$.

γ-FeOOH was obtained by the method of Sholtsova *et al.*[2] Both the *X*-ray phase analysis and the Mössbauer and i.r. spectra confirmed the high phase purity of the compound. Its specific surface area as measured and calculated by the Brunauer–Emmett–Teller method using low-temperature nitrogen adsorption[3] was 115 m^2/g. The mechanical dehydration was carried out by grinding specimens in a mechanically driven agate mortar for 60 h. At definite time intervals samples were taken and subjected to *X*-ray phase analysis using Co-K_α radiation and to Mössbauer spectroscopy. The results from the investigations by the two methods showed that after 25 h of grinding partial dehydration had taken place whereas after 60 h dehydration was practically complete.

The behaviour of γ-FeOOH during thermal dehydration is different from that in mechanical dehydration. It was established that mechanical dehydration led, at room temperature, to the direct transition of γ-FeOOH into α-Fe$_2$O$_3$. After grinding for 25 h the system consisted of two phases; α-Fe$_2$O$_3$ and the still undecomposed γ-FeOOH (Figure 1). After 57 h of grinding the transition to α-Fe$_2$O$_3$ was practically complete.

γ-Fe$_2$O$_3$ did not appear during mechanical dehydration. The Mössbauer spectra (Figure 2) show that grinding leads to α-Fe$_2$O$_3$ with a magnetically disordered structure which differs from the normal crystal state. This structure may be the reason for the non-Lorentzian spectral line shapes and for the appearance of a doublet. There is also a very small amount of undehydrated γ-FeOOH. The elucidation of the mechanism of the observed phase transition needs further investigation.

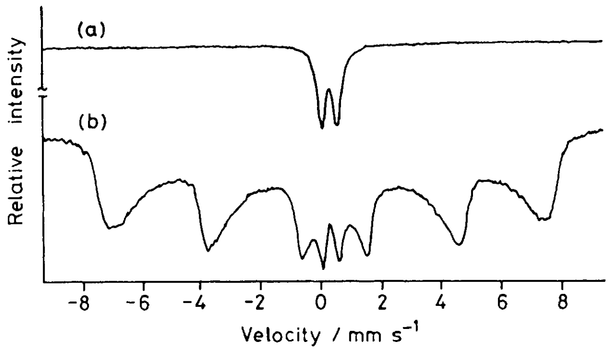

Figure 2. Mössbauer spectra of (a) the initial sample of γ-FeOOH; (b) a sample ground for 57 h.

The thermal dehydration of γ-FeOOH is pseudomorphic in character and takes place by a topotactic reaction.[4] The cubic structure of γ-Fe$_2$O$_3$ appears when γ-FeOOH is heated in air at temperatures below 300 °C.[1,2] It is probable that its formation needs a definite activation energy. Mechanical dehydration does not create the conditions for an activated process which is probably why the orthorhombic structure of γ-FeOOH converts into the close-packed hexagonal structure of α-Fe$_2$O$_3$.

In principle it can also be assumed that the conversion of γ-Fe$_2$O$_3$ into α-Fe$_2$O$_3$ during the grinding process[5] proceeds faster than its evolution. This seems, however, less probable. Obviously, the direct transition of γ-FeOOH into α-Fe$_2$O$_8$ upon mechanical dehydration is of interest from the viewpoint of non-equilibrium phase transition theory.

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