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# Dehydration of $\gamma$-FeOOH: Direct Observation of the Mechanism *

*Summary*

The dehydration of $\gamma$-FeOOH to $\gamma$-Fe$_2$O$_3$ has been investigated by thermoanalytical, electron microscopic and X-ray diffraction methods, using single crystals of suitably small size as a starting material, in order to maintain short diffusion paths. While kinetical data alone are not conclusive, the electron micrographs show unambiguously how the reaction proceeds in the crystals: Strings of perfectly oriented $\gamma$-Fe$_2$O$_3$ crystallites of about 70 Å diameter and disordered lithium site vacancies extend into the undecomposed matrix crystal which can be distinguished from decomposed parts by direct imaging of the (120) lattice planes of 3 Å spacing. An atomistic interpretation of this result is given.

## 1 Introduction

A comprehensive study of reactions involving solids should, in our opinion, include formal kinetics as well as morphological, textural and structural investigations. In order to exclude the influence of the surface, there is a tendency to use fairly large crystals. Under such conditions, however, diffusion paths are too long and will *eo ipso* influence the reaction mechanism. Such kinetic data, however good, will thus be of little help to decide between several possible mechanisms. FEITKNECHT[1] has pointed out that *small* single crystals will be the most suitable substrate to investigate solid state reactions. Only one reaction, however, has been studied along these lines, namely the oxidation of $Fe_3O_4$ to $\gamma$-$Fe_2O_3$[2,3].

We have studied a basically different reaction, i.e. the thermal decomposition $2\ \gamma$-$FeOOH \rightarrow \gamma$-$Fe_2O_3 + H_2O$. The relations between the two lattices involved are well known[4,5]. More recently GALLAGHER[6] has concluded from spectroscopic investigations that the $\gamma$-FeOOH lattice contains a considerable percentage of molecular water due to the peculiar arrangement of the OH...O bonds which yields, through a temperature dependent equilibrium, water molecules already at room temperature.

## 2 Experimental

$\gamma$-FeOOH was prepared by adding 0,15 L $FeCl_2$ 0,2 M to 0,1 L $H_2O$ and 0,1 L $NH_3/NH_4Cl$ buffer (pH 7,5), and introducing air at a rate of 0,5 L/min at 50 C in a waterbath. To maintain pH 6, $NH_3$ 0,1 M was added dropwise from a buret (about 0,66 L altogether) while the pH was observed continuously with a glass electrode. After about 2 h the suspension proved free of $Fe^{2+}$ (*o*-phenthroline test), i.e. the reaction was completed. The yellow-brown precipitate was isolated in a centrifuge, washed, and dried at 60 C. Its BET surface was about 14 m²/g.

For X-ray diffraction a de Wolff-Guinier camera and $FeK_\alpha$ radiation were used. Reflection profiles from a Philips-Norelco goniometer served to calculate crystallite size and lattice disorder. Direct observation of the crystals was undertaken using a Siemens Elmiskop I, a Hitachi HU-11 A, and a Hitachi HU-12 A electron microscope.
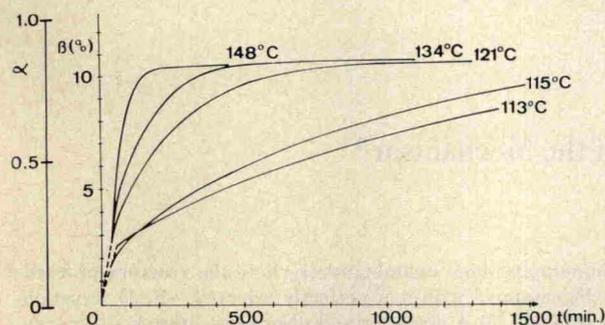
Fig. 1. Set of isothermal decomposition runs of $\gamma$-FeOOH. Abscissa: Time as measured, in minutes. Ordinates: $\beta$ = weight loss in percent, before correction for adsorbed water. $\alpha$ = Reaction rate going from 0 to 1 (or 0 to 100%) without corrections

Unisothermal and isothermal decomposition was produced on a Mettler Thermoanalyzer TA 1 *in vacuo* (about $10^{-5}$ torr). Pt–Rh (10%) crucibles of 3, 12 and 16 mm diameter were used, with sample thickness not exceeding a few tenths of a mm. Evacuation and, under unisothermal conditions, heating rates, were as small as possible.

## 3 Results

Fig. 1 represents a typical set of decomposition curves under isothermal conditions. The reaction always ended sluggishly, and some residual water cannot be removed at all unless $\alpha$-$Fe_2O_3$ nucleates.

When such results are plotted in a coordinate system with reduced time scale ($t/t_{1/2}$) on the abscissa and reaction rate 0 to 1 on the ordinate, fig. 2 results.
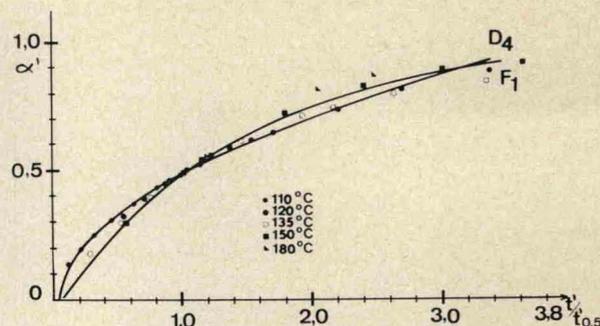
Fig. 2. Reduced time representation, after correction for adsorbed water, for isothermal decomposition of $\gamma$-FeOOH. The data used are a set different form that in fig. 1. Two calculated curves for different mechanism models from fig. 7 are also shown. $\alpha'$ = corrected reaction rate from 0 to 1 (or 0 to 100%)

The X-ray powder patterns of the samples undergoing decomposition (not shown here) are superpositions of the initial $\gamma$-FeOOH, with sharp reflections vanishing towards the end of the reaction, and of the $\gamma$-$Fe_2O_3$ pattern with extremely broad reflections. The profile analysis yields a crystallite size of the order of 70 Å and strong evidence for disorder, most probably in the vacant Lithium sites. It thus seems obvious that the tetragonal superlattice reflections of $\gamma$-$Fe_2O_3$ do not appear.

Electron micrographs of partly decomposed crystals show peculiar contrast phenomena which might be explained by strings of pores. As the crystals produce perfectly oriented electron diffraction textures (not shown here), these strings must be crystallites of $\gamma$-$Fe_2O_3$. Undecomposed crystals and, in partly decompo-

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