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KINETICS AND MECHANISM OF THE DEHYDRATION OF γ-FeOOH

RUDOLF GIOVANOLI AND RUDOLF BRÜTSCH

Laboratory of Electron Microscopy, Institute of Inorganic Chemistry, University of Berne, 3 Freiestrasse, CH-3000 Berne 9 (Switzerland)

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ABSTRACT

The dehydration of γ-FeOOH to γ-Fe_2O_3 in vacuo has been investigated by thermoanalysis. Results have been checked by electron microscopy and diffraction and by x-ray diffraction. Authors find that formal kinetics are not conclusive. Electron micrographs, however, show directly that random nucleation occurs, producing perfectly oriented but disordered γ-Fe_2O_3 crystals of about 70 Å size. The results can be accomodated with an atomistic model of lattice collapse.

INTRODUCTION

We have set out in a short communication[1], that a comprehensive treatment of a reaction involving solids should not be restricted to formal kinetics but also include morphological, textural and structural investigations. To specify these terms, brief definitions are necessary:

(i) Structure: Lattice of the initial solid and the reaction products, as defined by a space group. Instrument: X-ray and electron diffraction.

(ii) Texture: Grain, aggregation and crystallite sizes; orientation of crystallites in the aggregations; specific surface; lattice defects and disorder. Instrument: X-ray and electron reflection profile analysis; BET surface determination; single crystal electron diffraction; electron microscopy in the dark field using selected reflections.

(iii) Morphology: Direct observation of nucleation and subsequent proceeding reaction; alterations of particle, aggregation and crystallite. Instrument: electron microscope; where suitable polarizing microscope.

It has been emphasized[2] that a thorough study of apparently trivial reactions involving solids is in fact fairly complex. As the specific surface may seem to be an additional disturbing factor, there is a distinct predelection to investigate single crystals, especially when also suitable for X-ray structural work. Diffusion paths, however, become important under these conditions and will as a rule dominate the time law and the mechanism. Suitably small single crystals, preferably of defined shape and size distribution, will thus be the proper substrate to investigate reactions of solids[2].

Authors are aware of only one reaction studied according to the viewpoint outlined above[3]. The present article deals with the results of another reaction. The

dehydration of γ-FeOOH and the occurring structural relations have been studied previously[4,5].

EXPERIMENTAL

1. Preparation of γ-FeOOH

A detailed description for well crystallized γ-FeOOH has been published earlier[1]. For comparison two more samples, from the department collection, of unknown history, have also been used. They were distinctly less crystalline.

2. X-ray procedures

A focusing Guinier–de Wolff camera mark I and FeK_α radiation were used. Crystallite size determination was performed with data from a Philips–Norelco goniometer using Mn filtered FeK_α radiation and α-SiO_2 as reference standard. Profiles were measured with a planimeter, and a $K\alpha_1\alpha_2$ doublet correction was applied. The evaluation followed standard procedures[6].

3. Electron microscopy

Samples prepared according to current techniques were investigated in a Siemens Elmiskop I, a Hitachi HU-11A, and a Hitachi HU-12A electron microscope. The lattice resolution of 3 Å of the last mentioned instrument proved to be crucial for the quality of the micrographs even when the magnification was below the upper limit. For that reason cooling and tilting stages with substantial loss in resolution were discarded. It could be shown that specimens were stable enough in the electron beam for some considerable time even when they had been quenched in halfway completed reaction. Each crystal investigated was repeatedly checked by selected area electron diffraction to make quite sure that it remained unaltered in the microscope.

4. Thermobalance

Unisothermal and isothermal runs were produced on a Mettler thermoanalyzer TA1 in vacuo (appr. 10^{-5} torr) using Pt–Rh (10%) crucibles of diameter up to 16 mm and sample thickness not exceeding a few tenths of mm.

5. BET measurements

The specific surface was determined on a Cahn electrobalance type RG using N_2 for adsorption.

RESULTS

1. Starting materials

The γ-FeOOH samples used are shown as powder patterns and as electron micrographs in Fig. 1. Figure 1f shows a representative electron diffraction of a single crystal of preparation 1.