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# Hydrothermal synthesis and characterization of some polycrystalline α-iron oxides

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## Abstract

Hematite powders with distinct particle morphology were obtained by hydrothermal synthesis, in the temperature range of 160–300°C. Goethite and ferric hydroxide precursors prepared by precipitation and oxidation under different reaction conditions were used. The hydrothermal reactions were developed in aqueous neutral or alkaline suspensions. In some cases additives were used as growth shape agents. By changing and controlling the reaction parameters, oxide powders with desired particle shapes (acicular, polyhedral, platelike, spherical, hexagonal) and dimensions (0.1–30 μm) were obtained. The characteristics of hematite powders, green bodies and sintered compacts were investigated by X-ray diffraction, electron microscopy, transmission and electron conversion Mössbauer spectroscopy. The correlation between the preparation conditions and the properties of the obtained iron oxides is discussed together with their potential applications. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* α-Iron oxides; Hydrothermal synthesis; Polycrystalline; BTEM/Mössbauer

## 1. Introduction

Besides its interesting magnetic properties, hematite, α-$Fe_2O_3$, has a wide field of technological applications (fabrication of ferrites, catalysers, inorganic pigments, raw material for magnetic recording media). The preparation method determines the final powder characteristics like shape, average particle size, specific surface, porosity, that are of considerable importance in the subsequent processing for specific applications.

In the last few decades the hydrothermal technique has been widely used for synthesis and growing of inorganic crystals because it is essentially less energy intensive, less polluting and leads to high homogeneity and well-crystallised products, with definite composition. A number of papers dealing with the hematite formation under hydrothermal conditions have been published [1–6].

It is the aim of this paper to report on the synthesis of hematite under various hydrothermal conditions, at moderate temperatures, as well as carry out the structural and morphological investigations by means of electron microscopy, X-ray diffraction and Mössbauer spectroscopy.

## 2. Experimental

A 21 stainless steel autoclave [5] (chrome–nickel–molybdenum) with stirrer or an 80 cc static silver lined autoclave were used for the hydrothermal treatments. The temperature control with an accuracy of ± 2°C was assured by a proportional controller with chromel alumel thermocouple. The precursors used in the hydrothermal transformation were prepared by usual chemical methods. By varying the nature of reactants (all of analytical grade) and the reaction parameters, the optimum conditions for the preparation of different hematite powders were established as follows:

- **A**. In the first step, ferric hydroxide was obtained by bubbling gaseous ammonia up to $pH = 8$ through a 0.2 M solution of ferric chloride hexahydrate. After filtration and washing with distilled water, the amorphous precipitate was suspended again in water and brought up to a volume equal with that of the starting solution.

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After adding some ml of 0.1 M sodium citrate solution, the pH was adjusted to ~12. The alkaline suspension was treated in autoclave under stirring with a heating rate of 4°C/min up to 160°C and kept at this temperature for 1 h.

- **B**. Another type of oxide was synthesised using the ferric hydroxide precipitated with 5 M sodium hydroxide from 1 M ferric sulphate nanohydrate solution. In the amorphous precipitate, sodium hydroxide was added in an excess concentration of 4 M. The strong alkaline reaction mixture was placed in a silver lined autoclave and treated at 180°C, for 2 h under static conditions.
- **C**. In other experiments, ferric hydroxide was precipitated with potassium hydroxide solution (2.5 M) from ferric nitrate solution (0.3 M) in the presence of oxalic acid, at pH≈9. The subsequent

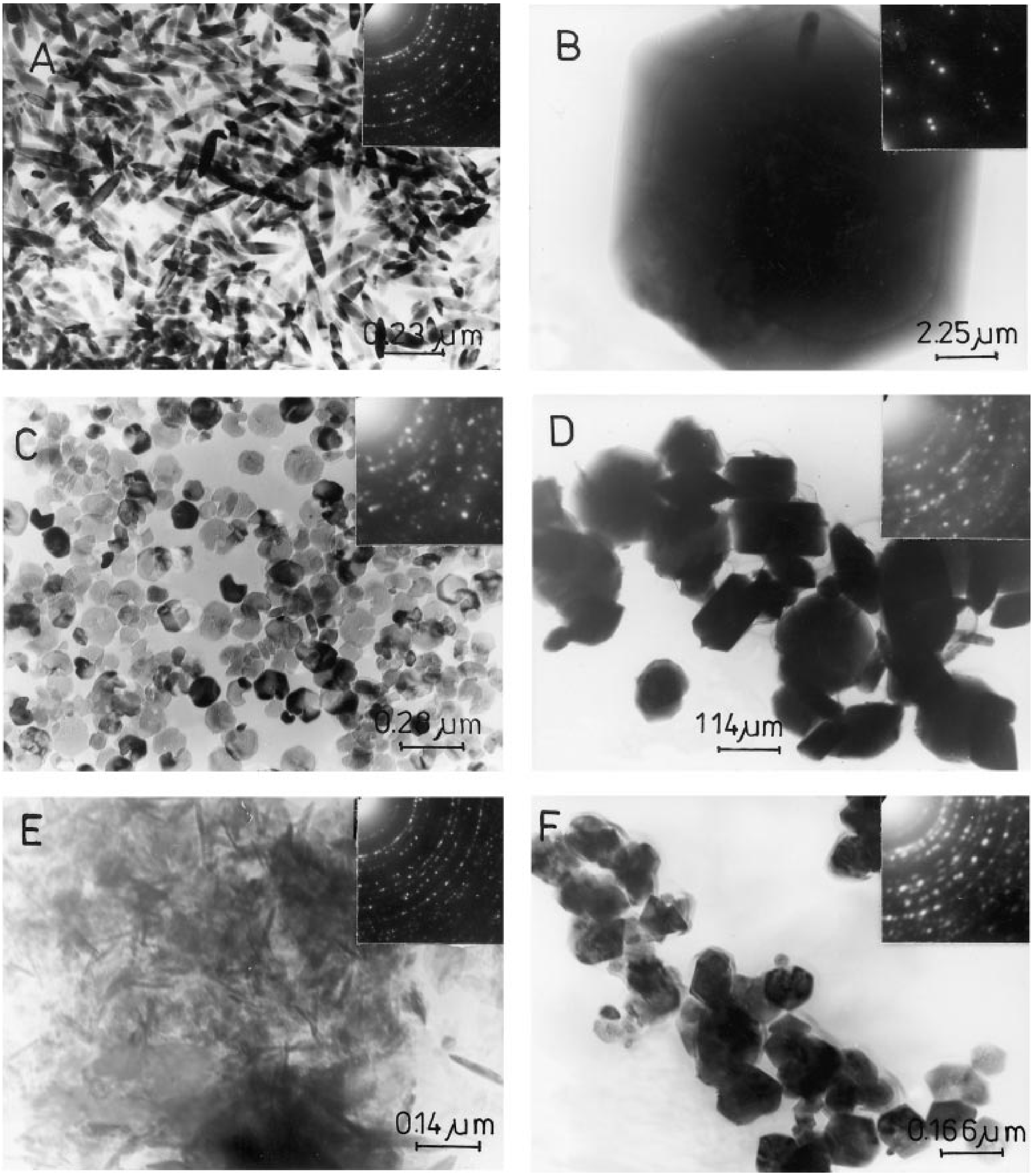

Fig. 1. A–F. BTEM images on hydrothermal hematite powders together with the electron diffraction patterns.

hydrothermal treatment was carried out at 120°C for 3.5 h, with stirring.

- **D**. Hematite powder was obtained also by the hydrothermal processing of a water–goethite suspension in the weight ratio of 2:1, at 200°C for 2 h. The goethite was prepared by air oxidation in suspension of the ferrous hydroxide precipitated with aqueous ammonia in ferrous sulphate solution [7,8].
- **E**. After the hydrothermal treatment (under the conditions mentioned above for the experiment D) oxide powder with a new morphology was obtained if ferrous hydroxide was first filtered and then oxidised by drying at 110°C in air.
- **F**. Another path in the hematite synthesis was the direct hydrothermal treatment of an homogeneous mixtures of ferric nitrate (1 M) and urea (1.5 M) solutions at 200°C for 4 h. At about 70°C urea decomposes into ammonia and carbon dioxide, acting as precipitation agent.

In all cases after hydrothermal treatment, the powders were filtered, washed with distilled water, dried at 110°C in air and then investigated by different methods. Compacted disk-shaped samples were obtained by pressing the oxide powders at 0.5 tf/cm$^2$, in order to study the surface effects due to particle morphology by conversion electron Mössbauer spectroscopy (CEMS). The compacts sintered at 1050°C were used to study the degree of densification.

## 3. Results and discussion

The X-ray diffraction patterns (Seifert equipment, CuK$_\alpha$ radiation), electron diffraction measurements (JEM-200 CX electronic microscope) and Mössbauer transmission spectra (PROMEDA type spectrometer with $^{57}$Co/Rh source) indicated the formation of hematite structure in all cases. No other crystalline phases were identified. From the analysis of the bright transmission electron microscopy (BTEM) images (Fig. 1A–F) the morphological characteristics of the oxide powders were determined. They are given in Table 1 together with the specific surface measured by BET method, density of sintered samples and possible application fields.

One can observe the decrease of specific surface as the mean diameter of particles increases. The density of sintered oxides depends significantly on the particle size. The smaller the particle diameter, the higher becomes the density of the sintered bodies. The higher value (~5.1 g/cm$^3$) was found for the sample **E** being a little bit smaller than the X-ray density of 5.277 g/cm$^3$.

An excellent resistance to corrosion attack was found for the paint obtained with oxide **B**, when it was applied on iron metallic surfaces. This property could be due to the platelike form of particles that are arranged in parallel layers on the coated substrate as well as to the opacity to ultraviolet radiation. The oxide **D** was used for the preparation of soft ferrites (Mn–Zn ferrite) with good results. The catalyser obtained with **E** oxide

Table 1
Morphological characteristics of hydrothermally prepared α-iron oxides

| Oxide type | Precursor | Conditions of hydrothermal treatment | Particle shape | Average diameter (μm) | Specific surface (m$^2$/g) | Density of sintered oxides (g/cm$^3$) | Potential applications |
|---|---|---|---|---|---|---|---|
| **A** | $Fe(OH)_3$ obtained from $FeCl_3$ solution and gaseous $NH_3$ pH ~12 | 160°C<br>1 h<br>with stirring | Acicular | 0.20 | 20–25 | 4.61 | Starting material for magnetic recording media |
| **B** | $Fe(OH)_3$ obtained from $Fe_2(SO_4)_3$ and NaOH solutions (excess 4 M NaOH) | 180°C<br>2 h silver lined autoclave | Platelike | 7.45 | 1.1–1.3 | 3.06 | Pigment for anticorrosive protection |
| **C** | $Fe(OH)_3$ obtained from $Fe(NO_3)_3$ and KOH solutions in presence of $C_2H_2O_4$ pH ~9 | 120°C<br>3.5 h<br>with stirring | Spherical | 0.12 | 20–25 | 4.97 | Inorganic pigment |
| **D** | α-FeOOH obtained by air oxidation of $Fe(OH)_2$ suspension pH ~8 | 200°C<br>2 h<br>with stirring | Polyhedral | 1.40 | 2.3–3.4 | 3.55 | Oxide for the fabrication of soft ferrites |
| **E** | α-FeOOH obtained from $Fe(OH)_2$ oxidized by drying at 110°C in air | 200°C<br>2 h<br>with stirring | Acicular | 0.06 | 3–4 | 5.10 | Raw material for fabrication of catalysers |
| **F** | mixture of $Fe(NO_3)_3$ (1M) and urea (1.5M) | 200°C<br>4 h<br>with stirring | Platelike | 0.15 | 18–20 | 4.70 | Inorganic pigment |

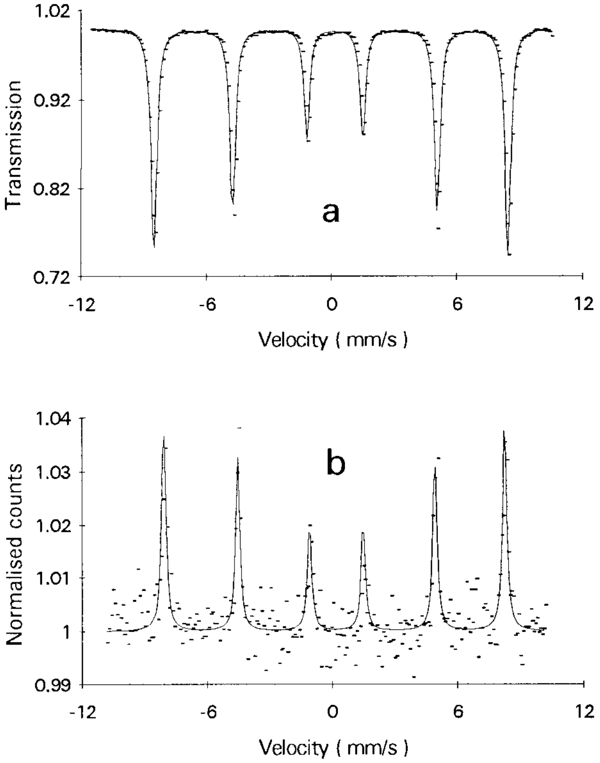

Fig. 2. (a) Mössbauer transmission and (b) CEMS spectra of sample **B**.

provided a high selectivity (~90%) in the dehydrogenation reaction of ethyl-benzene to styrene.

Mössbauer (M) transmission spectra of powder oxides exhibit characteristic six line pattern of $\alpha$-$Fe_2O_3$. The hyperfine M parameters given by the computer fit, quadrupolar splitting ($QS \approx -0.22$ mm $s^{-1}$) and the isomer shift ($IS \approx 0.18$ mm $s^{-1}$ with respect to $\alpha$-iron) are close to the standard values for hematite. The line intensities are satisfying the theoretical ratio $3{:}2x{:}x^2$ where $x$ varies between 0.99 and 1.15. A sensible increase (up to 527 kOe) from the standard value of 517 kOe was found for the hyperfine magnetic field ($H_{\mathrm{hf}}$) for all powder oxides except the oxide **A**.

$^{57}Fe$ conversion electron Mössbauer spectroscopy was used as a local probe for studying the surface of the oxide green bodies. Each sample was mounted inside a He-$CH_4$ flow electron detector [9] designed to record CEMS electrons of all energies emitted from a depth sampling range of 0 to 300 nm. The CEMS spectra of the investigated green bodies exhibit six line spectra with narrow line widths and generally smaller hyperfine magnetic fields (502–515 kOe) as a result of surface effects [10]. The $x$ values in the $3{:}2x{:}x^2$ relation given by the computer fit are in the range 0.82–1.22; the maximum value was found for the oxide **B**. One of the noticeable effects of this thin layer measurement is the enhanced intensity of the second and fifth lines of the spectra, in the case of oxides. This behaviour can be explained by the preferential orientation of the platelike particles, parallel to the surface of the sample. Consequently, the mentioned enhancement of the M lines can be a measure of the orientation of the particles at the surface of the green body. To illustrate, Fig. 2 shows (a) the transmission and (b) CEMS spectrum of the platelike oxide **B**, recorded at room temperature, together with the computer fit (continuous lines). The parallel orientation to the surface of the sample, in the case of platelike particles, was confirmed also by scanning electron microscopy images.

## 4. Conclusions

The possibility to obtain polycrystalline hematite powders with desired particle morphologies by hydrothermal route, at moderate temperatures, has been presented. The structural and morphological properties of the $\alpha$-$Fe_2O_3$ powders (investigated by BTEM, X-ray diffraction, Mössbauer spectroscopy and BET measurements) along with their potential technological applications have been evidenced. Thus the hydrothermal route can be successfully used for the synthesis of various-iron oxides taking the advantage of an environmentally friendly and of a less energy consuming procedure.

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