

Study of iron oxides obtained by decomposition of an organic precursor

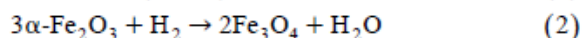
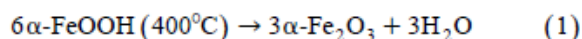
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Abstract

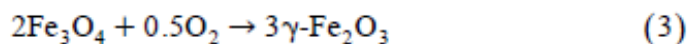
Iron oxide powders were obtained by the isothermal decomposition of ferric citrate in an oxygen atmosphere at different temperatures. Throughout the experiments, the product of decomposition was a mixture of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) with different relative proportions and particle size distributions. After TGA and DTA measurements, a decomposition temperature of 300°C was chosen, and a maximum specific saturation magnetization of about 40 emurg was obtained. Most of the product particles were less than $1\ \mu\text{m}$ in size, including a superparamagnetic fraction, as evidenced by Mössbauer spectroscopy.

Introduction

Nowadays, magnetic particles for recording of analogic and digital information is one of the most important applications of magnetic materials. The $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 and CrO_2 oxides comply with the required properties, but so far only $\gamma\text{-Fe}_2\text{O}_3$ and Co-doped modifications are the most widely used materials [1]. Several preparation methods have been used for synthesizing $\gamma\text{-Fe}_2\text{O}_3$ powders which aimed at producing uniform-sized particles for dispersed magnetic media [2]. To obtain elongated maghemite particles for magnetic recording, the traditional procedure is to start from $\alpha\text{-FeOOH}$ (ferric oxyhydroxide) in the form of small acicular crystals [1,3,4]. The process can be summarized by the equations:



Careful oxidation of the resulting acicular magnetite at about 2508C produces acicular particles of $\gamma\text{-Fe}_2\text{O}_3$ according to:



Maghemite has a defect inverse spinel structure being the completely oxidized form of magnetite. It contains Fe^{3+} ions in tetrahedral A sites (fully occupied) and in octahedral B positions, shared with vacancies '()', to compensate for the increase in the positive charge as a consequence of oxidation. Thus, in analogy to magnetite, the stoichiometric formula can be expressed as $(\text{Fe}^{3+})_1[\text{Fe}^{3+}_5/3\text{O}_{1/3}]_3\text{O}_4$, having a specific saturation magnetization of 74 emu/g due to the ferrimagnetic order of A and B sublattices. Since maghemite particles have a high degree of acicularity, shape anisotropy is a relevant contribution. However, incoherent mechanisms of magnetization reversal, as curling and fanning [1,5], can reduce noticeably the coercivity values. Different microstructures reported in previous studies are due to differences in the conditions of preparation [6,7]

Organic precursors are an interesting approach to achieve new morphologies and to explore potential applications. In this work, maghemite powders obtained from the isothermal decomposition of ferric citrate were characterized by X-ray diffraction, TGA-DTA, magnetization and Mössbauer measurements.

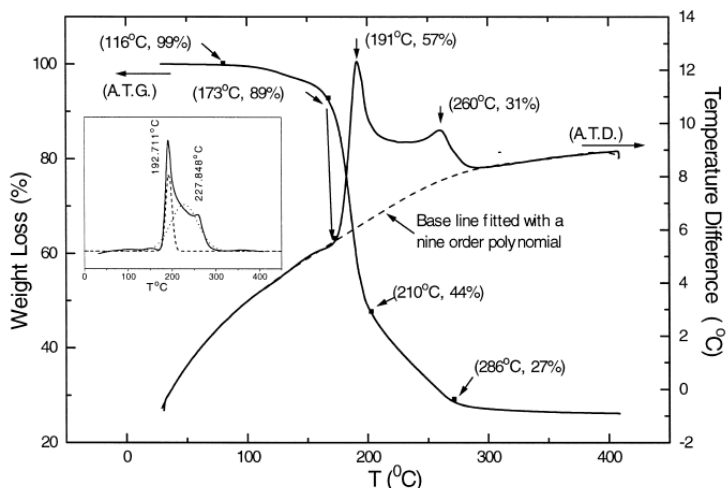


Fig. 1. Thermogram of ferric citrate in air flow. Heating rate: 2°C/min.

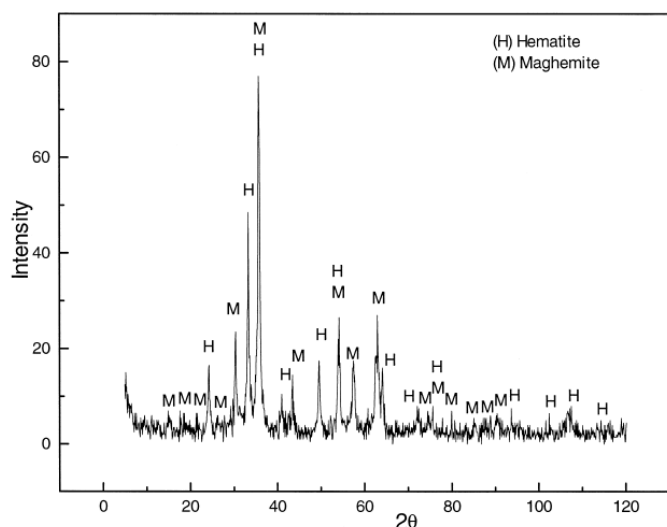


Fig. 2. X-ray diffraction pattern of ferric citrate annealed during 8 h at 300°C.

Experimental

High purity n-hydrated ferric citrate (16% Fe minimum) from J.T. Baker was milled during 8 h in a vibratory micro-mill. The thermal decomposition of the obtained powders was followed by TGA-DTA measurements in a 2960 TA-Instruments analyzer, heated at a constant rate of 2°C/min from room temperature up to 400°C. Based on these results, the citrate powder was heat-treated during 1, 4 and 8 h at 300°C in a oxygen USP grade Praxair. flow in a programmable tube furnace, in order to obtain a

high conversion of the ferric citrate particles into iron oxides, as well as the formation of various grain size distributions and relative proportions of the products. Any possible rest of ferric citrate was eliminated by filtration using a Whatman polycarbonate membrane filter with a pore size of 1 μm and tridestilled water, followed by drying at 40°C.

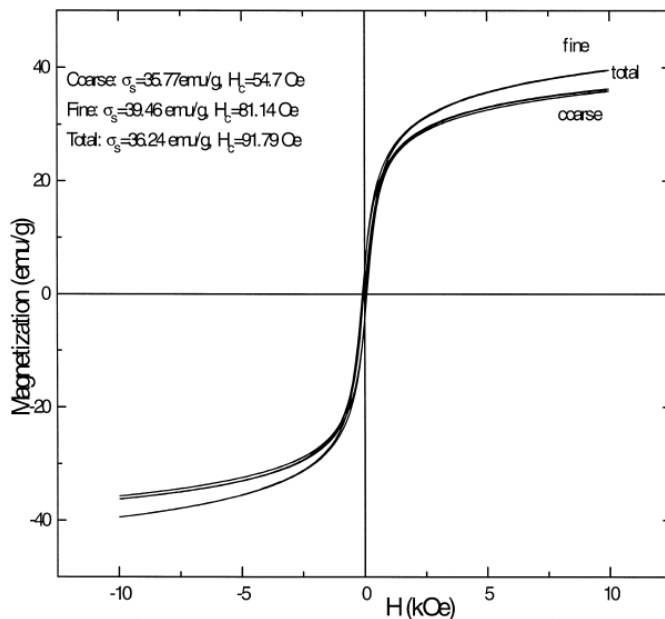


Fig. 3. Hysteresis loops of total ferric citrate decomposed during 8 h at 300°C (total), and its fractions greater than 1 μm (coarse) and smaller than 1 μm (fine).

Magnetic properties were measured in a vibrating sample LDJ Electronics 9600 magnetometer, with a maximum applied field of 1.6 T. Transmission Mössbauer spectra were collected at liquid nitrogen and room temperatures in an ASA spectrometer in constant acceleration mode. Phase analysis of the products was performed by X-ray diffraction in a Siemens D5000 powder diffractometer at room temperature, using Cu-K α radiation.

Results and discussion

Fig. 1 shows the TGA-DTA curves for the decomposition of ferric citrate. The thermogravimetric analysis reflects a water weight loss of about 10% in the 90–150°C interval, followed by a rapid decrease, which matches with the emergence of two overlapped exothermic peaks; no further changes beyond 300°C were observed. After deconvolution, by fitting two gaussian curves, the maxima of the DTA peaks were determined to be at 191 and 260°C, respectively, as shown in the insert of Fig. 1, reflecting two stages of the decomposition process.

Fig. 2 shows the X-ray diffraction pattern corresponding to the isothermal decomposition of ferric citrate during 8 h at 300°C. The phase identification reveals a mixture of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$).

The ferric citrate decomposed during 8 h at 300°C was separated by filtration with a polycarbonate membrane into a fine fraction ($< \mu\text{m}$) and a coarse fraction ($> 1 \mu\text{m}$); the former represents about 95 wt.% of the product. Fig. 3 shows the hysteresis loops for both fractions and for the original sample, before separation. The values of the specific saturation magnetization were 39.46 (fine), 35.77 (coarse) and 36.24 (sample) emu/g, respectively.

Fig. 4 shows the evolution of the specific saturation magnetization with the decomposition time at 300°C. The sample reaches a maximum of about 39 emu/g for an annealing time of about 8 h; no further increment was observed because the ferric citrate is completely decomposed into a mixture of maghemite and hematite, as reflected by the X-ray diffraction pattern. This is also confirmed by the gradual reduction with the decomposition time of the paramagnetic contribution at the center of the Mössbauer spectra associated to residual ferric citrate see insert.

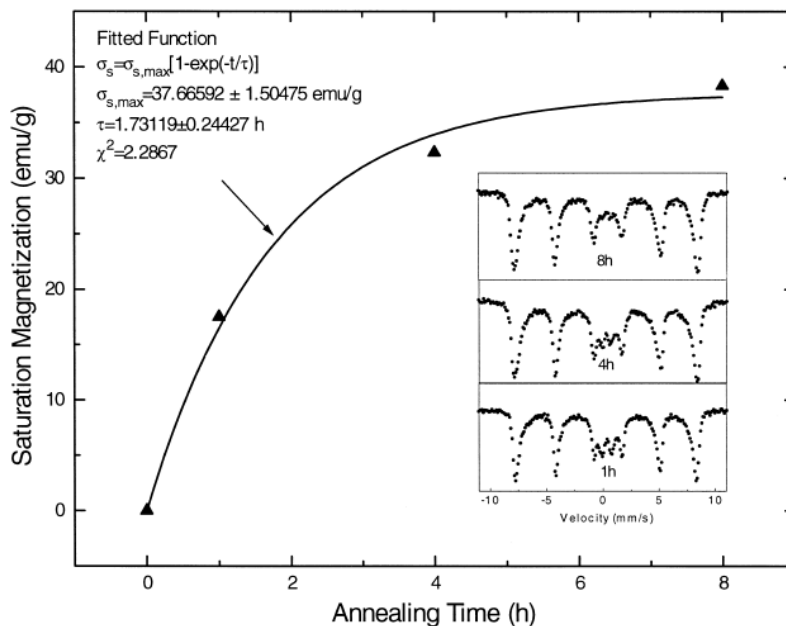


Fig. 4. Evolution of ferric citrate with annealing time at 300°C in oxygen atmosphere.

Fig. 5 shows the Mössbauer spectra collected at room temperature and at liquid nitrogen temperature for the sample annealed 8 h at 300°C. In Fig. 5(a), the broad lines of the magnetic sextets and their smooth inner slopes, along with the central paramagnetic component, suggest the existence of a wide size distribution of the obtained iron oxides, reaching the superparamagnetic dimensions and leading to relaxation effects. This is confirmed by an almost elimination of the central doublet at 77 K, and a better definition of the magnetic contribution.

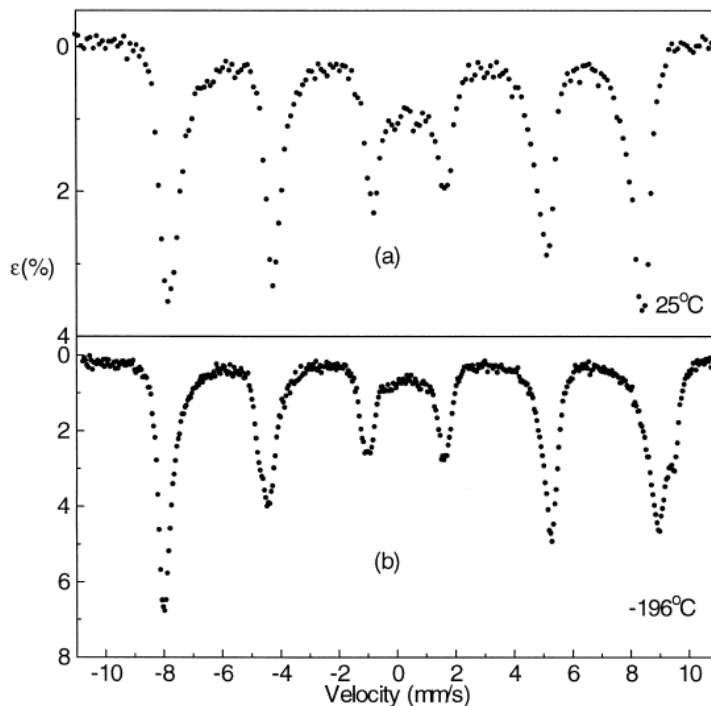


Fig. 5. Mössbauer absorption spectra measured at: (a) 25°C and (b) -196°C of ferric citrate decomposed during 8 h at 300°C.

Conclusions

n-Hydrated ferric citrate isothermally decomposes at 300°C into a mixture of maghemite and hematite. The decomposition is complete for an annealing time of 8 h with about 90 wt.% of the product particles having a size smaller than 1 μm; the specific saturation magnetization was 39 emu/g. A certain fraction of the particles reach a nanometric scale and show a superparamagnetic behavior at room temperature. The low temperatures involved in the heat treatments of this organic precursor is a promising perspective to attain small sized magnetic powders for a wide scope of applications. An optimization of the sample procedure is in course.

References

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