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Structural and magnetic characterization of synthetic ferrihydrite nanoparticles

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ABSTRACT

Ferrihydrite is a generic term for various poorly ordered Fe(III) oxyhydroxides which are naturally occurring as nanocrystals and are believed to constitute the ferric core of ferritine, the main iron storage protein in biological systems. Unlike other iron oxides, the exact structure and composition of ferrihydrite is still a matter of debate. In this work, we have prepared and characterized the two main forms of ferrihydrite referred to as 2-lines and 6-lines, on the basis of the number of reflections observed in the (X-ray) diffraction pattern. Thermal and textural properties have been studied; structural characterization has been performed by X-ray diffraction, transmission electron microscopy and X-ray absorption spectroscopy (EXAFS and XANES). The structure of the two forms results to be quite similar. The study of the magnetic properties indicates that the small differences between the 2-lines and 6-lines ferrihydrite samples are mainly caused by the different weight of the magnetic spins located on the particle surface, related to the different nanoparticles mean size.

1. Introduction

Ferrihydrite is a poorly crystalline Fe (III) oxyhydroxide whose particles have nanometric dimensions, usually around 2–6 nm [1,2]. As it is a natural occurring mineral commonly found in soils, sediments, mine wastes and aquatic sediments, it has been an important subject of research in soil and environmental science [3,4]. Moreover, ferrihydrite is frequently found as precursor in the formation of iron oxides [5,6] and the small size of the nanoparticles make them useful as catalysts and as adsorbents of many toxic ions [7]. Recently, ferrihydrite has gained renewed attention due to his importance in biomedical research as it forms the core of ferritin, a protein used to sequester and store iron by plants and animals [8,9]. Therefore, research has been devoted to the development of synthetic routes to prepare pure ferrihydrite with tailored morphology and texture both because natural ferrihydrite is difficult to isolate and contains impurities and also in order to gain insights on the formation of nanocrystals in biological media (biomineralization).

Regardless of the synthetic method, ferrihydrite is formed by poorly crystalline and highly dispersed nanoparticles. Due to its poor crystallinity, X-ray diffraction (XRD) patterns consist of few, broad reflections. On the basis of the number of peaks observed in the XRD patterns, two ferrihydrite varieties with different degree of order can be distinguished, defined as 6-lines and 2-lines. The 6-lines ferrihydrite is more ordered and the XRD pattern consists of six well-defined peaks; the 2-lines ferrihydrite is very poorly crystallised and the XRD pattern consist of two broad peaks. However, forms with variable number of XRD peaks occur in both natural and synthetic ferrihydrite. As a consequence of variable crystallinity and water content, the stoichiometry is not well defined: the most reported formula is $5Fe_2O_3{\cdot}9H_2O$ [3] but more complex formulas as $Fe_5HO_8{\cdot}4H_2O$ and $2FeOOH{\cdot}26H_2O$ have also been proposed [10,11]. The exact atomic structure of ferrihydrite is not fully established and is still matter of debate [12] and in particular, due to the poor crystallinity and uncertainty of the composition and stoichiometry, the definition of a structural model for ferrihydrite is particularly challenging. However, several attempts of determining a structural model for 6- and 2-lines ferrihydrite have been made, which differ for the iron site occupancies and the amount of octahedrally and tetrahedrally coordinated iron [10–19].

Important information on the differences between 6-lines and 2-lines ferrihydrite nanoparticles can be inferred by their magnetic behavior. Ferrihydrite is usually considered as an antiferromagnetic material [20]. However, low-temperature magnetic characterization of 6-lines ferrihydrite nanoparticles [21], clearly indicates superparamagnetic behavior [22,23]. Authors consider the occurrence of superparamagnetic behavior a consequence of the nanometric size of the ferrihydrite magnetic domains. More recently, Rancourt et al. [24] proposed that uncompensated spin moments located at nanoparticles surface act as source of the small

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ferromagnetic moments measured in samples constituted by 2-line ferrihydrite nanoparticles. Very interestingly, a recent investigation on the magnetic properties of 6-lines ferrihydrite nanoparticles indicates a strong dependency of the magnetic parameters on particle size [25].

In the present work, we have synthesized 2-lines and 6-lines ferrihydrite by controlled hydrolysis of a ferric salt; the effect of temperature and pH on the synthesis was studied. The outcome of preparation parameters on the structure and purity of the resultant powders was also investigated. Thermal analysis was used to evaluate water content, N_2 physisorption at 77 K and transmission electron microscopy (TEM) were used to investigate textural properties of the powders, morphology and dimension of nanoparticles. Structural information on 2-lines and 6-lines ferrihydrite were obtained using X-ray diffraction and X-ray absorption spectroscopy (EXAFS and XANES) at Fe K-edge. X-ray absorption spectroscopy [26] is a powerful tool for studying disordered materials, being element specific and sensitive to the local structure. EXAFS gives information on bond distances and coordination numbers of shells surrounding the absorbing iron atom (and therefore on the coordination polyhedra); XANES provides information on oxidation state and site-symmetry of the absorbing atom, in particular on the presence of tetrahedrally or octahedrally coordinated iron.

Finally, a comparison of the magnetic behavior of 2-lines and 6-lines ferrihydrite nanoparticles is reported.

2. Experimental

2.1. Materials

Synthetic 2-lines and 6-lines ferrihydrites will be thereafter named as 2-Fh and 6-Fh, respectively.

2-Fh was prepared adding dropwise a 0.1 M solution of KOH (Analyticals) to 50 mL of solution 0.1 M of $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich, 98%) under constant stirring until pH 7–8 was reached. The solution was centrifuged and the precipitate obtained was repeatedly washed with distilled water and dried at 45 °C for 24 h [3].

6-Fh was prepared as follows: 200 mL of a 0.025 M solution of $Fe(NO_3)_3{\cdot}9H_2O$ were pre-heated under stirring at 75 °C for about 20 min; the solution was then cooled at room temperature for 15 min and immersed in an ice bath for additional 15 min. The solution was then titrated at room temperature with NaOH 0.01 M until pH 7 and centrifuged. The precipitate obtained was repeatedly washed with distilled water and then dried in an oven at 45 °C for 24 h [27].

The above synthetic routes refer to the optimized conditions for directing the hydrolysis of an iron (III) salt in a controlled environment. The synthesis is particularly sensitive to parameters such as concentration, temperature and pH. In particular, the synthesis of 6-Fh seems to be more sensitive to the preparation conditions than that of 2-Fh.

2.1.1. Effect of temperature

The synthesis performed by heating the iron nitrate solution at 75 °C leads to 6-Fh if the 0.025 M solution of $Fe(NO_3)_3{\cdot}9H_2O$ is used and to goethite if a more concentrated solution (0.1 M) is used. Therefore, the synthesis of 6-Fh requires the hydrolysis of a dilute solution of $Fe(NO_3)_3{\cdot}9H_2O$ and the heating of the solution. It should be noted that heating induces a progressive colour variation of the solution from yellow to gold-red. This suggests that the formation of 6-Fh starts from high molecular weight polymerized iron oxyhydroxides species which are formed by heating and are precipitated by addition of a base. The formation of this metastable phase seems to rely on a gradual formation of polymerized iron oxyhydroxides species by using a dilute solution and inducing precipitation very slowly.

The synthesis performed at room temperature leads to 2-Fh using either 0.025 M or 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$ solution. Formation of 2-Fh occurs more rapidly than 6-Fh and it seems to precipitate from less polymerized oxyhydroxides species, as no heating of the solution is required for the precipitation.

2.1.2. Effect of pH

The hydrolysis of $Fe(NO_3)_3{\cdot}9H_2O$ has to be induced by controlled increase of the pH of the solution by addition of a base. The pH has to be increased in such a way to obtain the precipitation of the desired oxyhydroxide, avoiding the precipitation of more stable iron hydroxides. If the pH is too high, the most stable hydroxide, goethite, is formed. In particular, a pH between 7 and 9 is necessary for the synthesis of 2-Fh, whereas the pH range is wider for the synthesis of 6-Fh ($2 < pH < 8$).

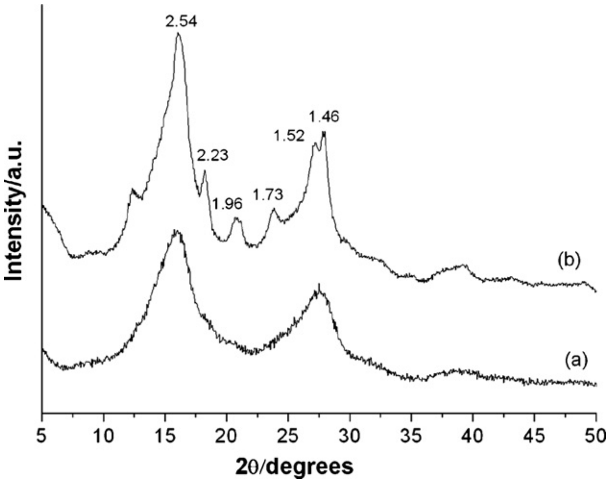

Fig. 1. XRD diffraction patterns (Mo Kα radiation) for (a) 2-Fh, (b) 6-Fh.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Siemens D500 with Mo Kα radiation ($\lambda = 0.709$ Å), operating at 50 kV and 35 mA. Scans were performed over an angular range $2\vartheta = 4$–$52°$. Thermogravimetric and differential thermal analysis (TGA and DTA) were carried out using a 851 Mettler Toledo TGA/SDTA at a heating rate of 10 °C min^{-1} in the range of 25–1000 °C in O_2 atmosphere. About 15 mg of samples were used in an alumina crucible. TEM micrographs were recorded on a JEOL 200CX microscope operating at 200 kV. N_2 physisorption isotherms at 77 K were collected on a Sorptomatic 1990 System (Fisons Instruments) after sample outgassing at 200 °C for 10 h. The X-ray absorption spectroscopy experiments (EXAFS and XANES) were carried out on station 9.3 of the SRS, Daresbury Laboratory, U.K. Data were collected at room temperature using a Si(1 1 1) monochromator at the Fe (7112 eV) K-edge. Samples with a suitable and highly uniform optical thickness were prepared from powders. Samples were dispersed in an inert solvent and then filtered onto polyethylene supports.

Measurements of static magnetizations and hysteretic behavior of the samples were performed on a Quantum Design MPMS SQUID magnetometer, equipped with a superconducting magnet producing fields up to 50 kOe. Zero-field-cooled (ZFC) magnetizations were measured by cooling samples in zero magnetic field and then by increasing the temperature in an applied field of 50 Oe, while field-cooled (FC) curves were recorded by cooling the samples in the same field of 50 Oe. The field dependence of the magnetization (hysteresis loop) was recorded up to 50 kOe, at $T = 5$ K. All the results have been normalized with respect to the total mass of the sample.

2.3. EXAFS and XANES data analysis

The program Viper [28] was used to sum the data, identify the beginning of the absorption edge, fit pre- and post-edge backgrounds, and hence to obtain the normalized absorbance as a function of the modulus of the photoelectron wavevector k. The modular package DL_EXCURV [29], based on the EXCURV98 code, was used in the final stage of data processing to model the experimental $\chi(k)$ in order to extract structural information. The fitting was carried out in k space using the range 2.5–13 $Å^{-1}$. The structural parameters were obtained by nonlinear least squares fitting in k-space with a k^3 weighting of the total experimental EXAFS spectra to emphasize the high-energy part of the spectrum. Fourier Transform (FT) of EXAFS data corrected for phase-shift shows peaks that correspond to local atom correlations. The positions of the peaks (R) correspond to bond distances between the central and the backscatterers atoms while the amplitudes are related to the coordination number (N) and to the static and thermal disorder (σ) of the atoms around the absorber. The typical errors in fitting are about ±0.01 Å in R_i and about 10% in $2\sigma_i^2$ and N_i. The quality of the fit can be judged from the normalized sum of residuals (R-factor). Reasonable EXAFS fits of single shells typically have values of R-factor around 20%.

The XANES spectra were processed in the usual way to obtain normalized absorbance [30]. XANES at the K-edge involves the excitation of a 1s photoelectron into low-lying empty states at the central atom with p-type symmetry. The K-edge XANES spectra in transition metal oxides and oxyhydroxides have sharply rising main absorption edge, with main absorption edge peak(s) of high intensity, and a notable drop in intensity after the main absorption edge peak. In addition, oxides and oxyhydroxides may show a small pre-edge peak if the excited atom site has a lack of centrosymmetry (*e.g.* tetrahedral sites). The XANES pre-edge spectra have been analysed using the "fingerprint" method, by comparing spectra from ferrihydrite