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Structural and magnetic properties of the products of the transformation of ferrihydrite: Effect of cobalt dications

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ABSTRACT

The effect of cobalt dications on the transformation of 2-line ferrihydrite (2LF) has been studied. The products of the transformation reaction were characterized by X-ray diffraction, Mössbauer spectroscopy (MS), transmission electron microscopy (TEM), magnetometry, and first-order reversal curve (FORC) diagrams. It was found that the concentration of cobalt dications plays an important role on the structural and magnetic properties of the products; i.e., for low cobalt concentrations, cobalt-substituted hematite is formed, while higher concentrations promote the formation of cobalt-substituted magnetite. Structural results revealed that formation of other iron oxide polymorphs is avoided and residual 2LF is always present in the final products. In this way, hematite/2LF and magnetite/2LF nanocomposites were formed. For all the samples, magnetic measurements yielded non-saturated hysteresis loops at a maximum field of 12 kOe. For cobalt-substituted hematite/2LF samples, FORC diagrams revealed the presence of multiple single-domain (SD) components which generate interaction coupling between SD with low and high coercivity. Moreover, for cobalt-substituted magnetite/2LF samples, the FORC diagrams revealed the components of wasp-waist hysteresis loops which consist of mixtures of SD and superparamagnetic particles. One of the goals of the present study is the rigorous, experimental documentation of ferrihydrite/hematite mixtures as a function of reaction conditions for use as analytical standards research.

1. Introduction

Currently, there are several methods for the synthesis of iron oxide (IO) nanoparticles (NPs). One of them is the ferrihydrite transformation pathway; many IO-NPs may be obtained through this route, such as goethite, lepidocrocite, hematite and magnetite [1–6]. The transformation to a specific IO polymorph depends on several factors such as the conditions of 2-line ferrihydrite (2LF) synthesis (for example, the counter anions in ferric/ferrous salts [7]), and the conditions established during the transformation of 2LF [1–4].

In absence of additives, the transformation of 2LF is very slow and forms mixtures of polymorphs [7]. In order to control and accelerate the 2LF transformation, the use of dications such as Fe [1,8], Cu [2], Mn [9], Ni [10], Zn [11] and Co [3] have been proposed. In these cases, the atomic ratio of dications/Fe(III) is very important. For example, for Fe(II)/Fe(III) with an atomic ratio of 0.02, pH =7, T=95 °C, under N_2 atmosphere, the formation of hematite has been reported [4]. However, if the Fe(II)/Fe(III) atomic ratio is increased, 2LF may transform to mixtures of lepidocrocite, goethite and magnetite [1,12].

Currently, the transformation pathways from ferrihydrite to more crystalline IO polymorphs are subjects of intense research in different fields, for example, material science, chemistry, environmental science, geochemistry, and biology [13,14]. Although the effect of cobalt dications on the 2LF transformation has been studied, the properties and applications of the products of the transformation is an open issue. In this context, the aim of this work is to characterize the products of the transformation of 2LF using cobalt dications as an additive. The transformation reactions were done with different Co(II)/Fe(III) atomic ratios, using a pH buffer. The complete transformation of ferrihydrite to crystalline iron oxides can be quite slow, with there being a great interest in faster and more efficient methods of effecting the transition and the detailed documentation in general of the use and study of iron

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Table 1
Samples prepared with different Co(II)/Fe(III) atomic ratios, the lattice parameters are listed for each sample; the lattice parameters for the rhombohedral crystal structure of hematite are *a* and *b*, and for the cubic crystal structure of magnetite, the *a* parameter is shown.

Sample	Co (II)/Fe (III) atomic ratio (%)	Lattice parameters *a*, *c* (Å)
C0	0	5.031, 13.758
C05	0.5	5.034, 13.771
C1	1	5.035, 13.773
C3	3	5.036, 13.767
C15	15	8.393

oxide mixtures in research [15–17]. As shown by the timescale in the present investigation, there is value in studying both the yields of the ferrihydrite/hematite polymorphs and their ratios to be used as standards. In order to characterize the products of the transformation of 2LF using cobalt as an additive, several techniques have been used.

2. Experimental details

All chemicals used were of analytical grade. The 2LF NPs were prepared by dissolving $FeCl_3 \cdot 6H_2O$ (8 g) in 100 mL of deionized water. Then, under constant stirring 6.0 M NaOH (6 mL) were added, and in order to get a pH between 7.8–8.0, some drops of 1.0 M NaOH were added. For the transformation reactions, the freshly prepared 2LF suspensions were stirred for 10 min. After this time, $CoCl_2 \cdot 6H_2O$ at different Co(II)/Fe(III) atomic ratios (0%, 0.5%, 1%, 3%, 5%, 15% and 20%) were added, and the reaction media was carefully adjusted to pH 8 with 1.0 M NaOH solution. Subsequently, a pH buffer of 1 M $NaHCO_3$ (5 mL) was added. The reaction was stirred at 95 °C for 2 h in open atmosphere. The products of these reactions were then washed and named as indicated in Table 1.

X-ray diffraction (XRD) was conducted to evaluate the structural characteristics of the products. A Philips diffractometer X′Pert with Cu(Kα) radiation in a 2-theta range of 20–80° was used. A semi-quantitative phase analysis as well as the average crystallite size were obtained by Rietveld refinement of the XRD patterns using the MAUD program v. 2.33 [18]. For high-resolution transmission electron microscopy (HR-TEM) observations, the samples were suspended in ethanol and ultrasonicated for 3 min. Subsequently, a drop of the suspension was carefully put onto a copper grid, dried naturally, and analyzed in a Jeol ARM200F. Mössbauer spectra were measured at room temperature (RT) in a Mössbauer system by Wissel Instruments, with a data acquisition system MB-MCA 3/1 and a ^{57}Co source. The fitting of the hyperfine parameters were done in the NORMOS-90 package [19]. The magnetic properties were measured at RT in an alternating gradient magnetometer (AGM Micromag 2900) manufactured by Princeton Measurements; 180 first-order reversal curves (FORC's) were obtained, and the FORC diagrams were processed and analyzed with the FORCinel software package [20].

3. Results and discussion

3.1. X-ray diffraction

The role of cobalt dications on the crystal structure of the products obtained from the 2LF transformation was followed by XRD. Fig. 1(a) shows the XRD patterns of the samples. The transformation to hematite was detected for Co(II)/Fe(III) atomic ratios from 0% to 5%. It can be seen that all the diffractions match very well with the trigonal hematite phase (JCPDS Card No. 89–598), the determined lattice parameters for the samples are close to the hematite standard (*a* =5.038 Å and *c* =13.776 Å) (Table 1). It is worthwhile to mention here that the diffraction pattern for C5 is too weak and diffuse to yield any rigorous interpretable or comparable data. Otherwise, the magnetite phase was formed when the Co(II)/Fe(III) atomic ratios were higher (C15). For this sample, all the diffractions match with the magnetite phase (JCPDS Card No. 89–688), the calculated lattice parameter was 8.393 Å for C15, whose value is close to the parameter for standards of magnetite (8.406 Å) and cobalt ferrite (8.396 Å) -JCPDS Card No. 88–2152.

From the XRD patterns, it can be concluded that the addition of $NaHCO_3$ to the 2LF transformation reaction promotes the formation of hematite in 2 h (C0 sample); in contrast, when the $NaHCO_3$ is not used, hematite is partially formed after 24 h [21,22]. The addition of

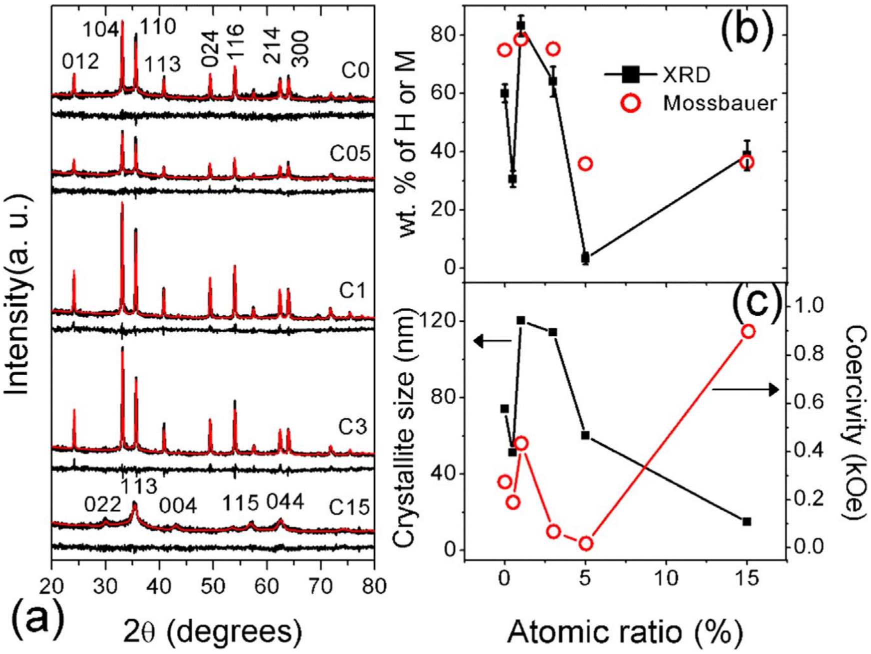

Fig. 1. (a) XRD patterns of the samples C0, C05, C1, C3, and C5 samples are indexed to hematite JCPDS Card No. 89-598. Otherwise, the C15 sample is indexed to magnetite JCPDS Card No. 89-688. (b) Weight % of hematite (H) or magnetite (M) as a function of the cobalt atomic ratio determined by XRD and Mossbauer spectroscopy. (c) Crystallite size of hematite or magnetite, and coercivity of the samples as a function of the cobalt atomic ratio.