Materials Chemistry and Physics 163 (2015) 88–98

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Controlled phase formation of nanocrystalline iron oxides/hydroxides in solution – An insight on the phase transformation mechanisms

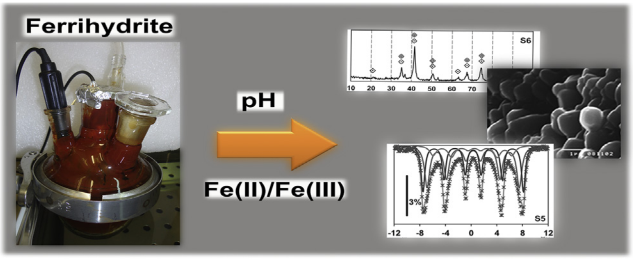
Jorge Pedrosa [a], Benilde F.O. Costa [b], António Portugal [a], Luisa Durães [a, *]

[a] CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
[b] CFisUC, Department of Physics, Faculty of Sciences and Technology, University of Coimbra, Rua Larga, P-3004-516 Coimbra, Portugal

HIGHLIGHTS

- Study of the effect of pH and Fe(II)/Fe(III) ratio in iron oxides/hydroxides.
- Iron(II) proves to have a catalytic effect.
- pH of 4 inhibits the catalytic effect of iron(II).
- pH of 7 and 12 promote phase transformation.
- The predominant mechanism is defined by the amount of Fe(II).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 October 2014
Received in revised form
8 May 2015
Accepted 5 July 2015
Available online 20 July 2015

Keywords:
Magnetic materials
Nanostructures
Chemical synthesis
Phase transition
Crystal growth
Mossbauer spectroscopy

ABSTRACT

In this work, the effect of pH in the formation of iron oxides/hydroxides obtained by chemical precipitation, as well as the influence of the presence of Fe(II) in the phases formation process were studied. Iron(III) chloride nonahydrated and iron(II) chloride tetrahydrated were used as precursors and sodium hydroxide as a base to adjust the pH and to promote the hydrolysis and condensation reactions. Syntheses were performed at three pH values – 4, 7 and 12 – and two Fe(II)/Fe(III) molar ratios – 0.02 and 0.5. The obtained phases were observed by SEM, showing agglomerates of nanometric crystallites ranging from ~1 to ~15 nm in size. The iron oxides/hydroxides identification/quantification was performed by the combined use of FTIR, XRD and Mössbauer spectroscopy. It was concluded that at low pH the catalytic effect of Fe(II) in the transformation of ferrihydrite is inhibited independently of the Fe(II) amount. In alkaline medium and at low concentration of Fe(II), goethite was formed. A Fe(II)/Fe(III) ratio of 0.5, for pH of 7 or 12, led to the simultaneous formation of magnetite and goethite. Thus, the extent of the transformation mechanisms – topotactic and reconstructive – is strongly influenced by the pH and the Fe(II)/Fe(III) ratio. In alkaline conditions, the predominant mechanism is defined by the ratio of Fe(II)/Fe(III) – a higher ratio favors the topotatic transformation of ferrihydrite in magnetite, while a low ratio leads to a dominant reconstructive mechanism.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Iron oxides have been used by cavemen as coloring agents. Today, after thousands years of progress and technology development, multiple advanced applications have emerged, due to the unique catalytic, magnetic, sorption, and optical properties, among other characteristics, exhibited by the iron oxide based materials. Overviews of the broad applicability given to iron oxides, which can range from industrial, environmental, biological and medical fields, are given by Cornell and Schwertmann [1], Machala *et al.* [2], Faraji

---

* Corresponding author.
E-mail address: luisa@eq.uc.pt (L. Durães).

http://dx.doi.org/10.1016/j.matchemphys.2015.07.018
0254-0584/© 2015 Elsevier B.V. All rights reserved.

et al. [3] and Mohapatra and Anand [4].

Iron oxides/hydroxides are an important group of minerals. In the majority of these compounds, iron is in a trivalent state of oxidation. Exceptions are FeO and $Fe(OH)_2$, in which iron is present exclusively in a divalent state. A mixture of both states of oxidation (Fe(III) − Fe(II)), appears in other compounds namely Fe_3O_4 [1].

Iron oxides/hydroxides are usually crystalline, being schwertmanite and ferrihydrite exceptions with a low degree of crystallinity [4]. The most unstable form of iron oxide is ferrihydrite. Due to its metastable nature, it can be transformed into more thermodynamically stable species [5], being thus an important precursor for iron oxides of higher crystallinity.

Ferrihydrite particles can be generally prepared by adding alkali to a Fe(III) salt solution. Nevertheless, the synthesis method is quite sensitive to the process conditions, such as the type and concentration of the iron salt, pH, temperature, and aging time. Consequently, ferrihydrite with different degrees of crystallinity is obtained. These different degrees can be interpretated by XRD patterns, and can vary from two to six lines, corresponding the two lines to the less ordered structure [6]. When freshly precipitated, ferrihydrite exhibits a very small size, typically a few nanometers in diameter. Accordingly, it is highly reactive due to its high surface area [7].

Synthesis of iron oxides tailored for various applications has been a challenging area.

The ceramic method, based on the direct reaction of powder mixtures, has been one of the most widely used techniques for the production of iron oxides. This type of synthesis requires high temperatures and small particle sizes of the raw materials. However, this method is a rather crude approach, compared to other new methods, like wet chemistry methods [8]. The wet approach allows a better size and composition control of the final products. However, even with a careful choice/control of conditions (pH, concentrations, temperature, mixing method, *etc.*), the obtained phases morphology still depends strongly on the competition between nucleation, growth, aggregation and adsorption of impurities. In many cases, the synthesis is carried out by the transformation of other iron oxide precursor particles, due to the impossibility to directly precipitate a specific iron phase [4].

In these last few years, some studies have been published about the transformation of ferrihydrite in more stable phases, especially from Liu and co-workers. Liu *et al.* [5,9–14], found that the presence of iron(II) can clearly accelerate the transformation of ferrihydrite into different iron phases. High pH and fast heating rates favor the topotactic transformation of ferrihydrite in solution as well as the formation of hematite, while a low pH and low heating rates favor the dissolution/re-precipitation mechanism of ferrihydrite as well as the formation of goethite [11].

When the pH of a mixture of ferrihydrite and Fe(II) ions is raised from 5 to 9, the ferrihydrite is rapidly transformed into hematite particles at 100 °C. The adsorption of Fe(II) and electron transfer between Fe(II) and Fe(III) accelerates the dissolution/reprecipitation mechanism and the topotactic transformation. It is thought that Fe(II), in the forms of $FeOH^+$ and $Fe(OH)_2$, plays the role of a catalyst [9].

Saric *et al.* [15] have concluded that iron oxides/hydroxides obtained by precipitation in $FeCl_3$ solutions were strongly dependent on the experimental conditions. Powders obtained by precipitation with NaOH at pH 4.2 and 4.4 and aging at 90 °C contained α-Fe_2O_3 as a single phase. When the pH of the system increased to 6.5, the precipitation of α-FeOOH particles was observed.

In this work, a systematic study of the effect of pH in the phases of iron oxides/hydroxides obtained by chemical precipitation was performed. Iron(III) chloride nonahydrated was used as precursor, water as solvent, and sodium hydroxide as a base to promote the precipitation reactions and adjust the pH. In addition, the effect of adding to the system different amounts of Fe(II) was also studied. Iron(II) chloride tetrahydrated was used either as a source of iron(II) ions for the iron oxide phase and to test its catalytic effect. The syntheses were carried out at three different pH levels (acid, neutral, alkaline) at two different molar ratios of iron(II)/iron(III) (0.02 and 0.5). A detailed description of the chemical and growth mechanisms involved in the synthesis of iron oxides/hydroxides, and particularly the effect of the presence of Fe(II) in the transformation of phases, is also presented based on a review of the open literature (Section 2).

The materials obtained in this work were characterized by several chemical and structural analytical techniques in order to identify the formed iron phases and to discuss the probable mechanisms of phases' transformation/growth. In this context, the Mössbauer spectroscopy was of great value and helped to clarify the samples composition in terms of iron phases and their amounts. For the first time in this context, the phase conversion was quantified giving a clear indication of the predominant transformation mechanisms.

This work is a contribution for an improved understanding and control of the iron oxides/hydroxides formation by chemical precipitation, in order to allow the tailoring of the produced phases for subsequent applications.

2. Overview on the phenomena of the iron oxides/hydroxides growth and chemical transformation

The hydrolysis and condensation chemistry of transition metals compounds in solution to produce metal oxides/hydroxides is well documented in the literature, such as in Livage *et al.* [16] and Jolivet [17]. Metal alkoxides can be used as precursors, but many of the alkoxides are difficult to obtain, expensive and sensitive to moisture, heat and light, making long term storage difficult. Metal salts are cheaper and easier to handle than metal alkoxides [18].

A metal salt, when in aqueous solution, converts into ionic species and the cations (M^{Z+}) suffer solvation by water molecules according to:

$$M^{Z+} + H_2O \rightarrow [M - OH_2]^{Z+} \tag{1}$$

$[M(OH_2)_n]^{Z+}$ species are formed, where the oxygen atoms of water are directed toward the metal cation (Livage, 1993). For example, iron cations form hexacoordinated aquo complexes – $[Fe(OH_2)_6]^{Z+}$ [19].

Water behaves as a Lewis base, and the solvation process leads to the formation of a partially covalent bond, involving some electron transfer from the water molecule to the metal cation. This transference increases the positive partial charge on hydrogen atoms, weakening the O—H bond and, as a consequence, the water molecule becomes more acidic. According to the magnitude of the electron transfer, a deprotonation can take place as follows:

$$[M - OH_2]^{Z+} \leftrightarrow [M - OH]^{(Z-1)+} + H^+ \leftrightarrow [M - O]^{(Z-2)+} + 2H^+ \tag{2}$$

In a noncomplexing aqueous media, a whole set of more or less deprotonated species can be present. Three kinds of ligands can be identified, an aquo ligand (OH_2), a hydroxo ligand (OH) and an oxo ligand (O). The formula of any inorganic precursor after hydrolysis can be summarized as $[MO_NH_{2N-h}]^{(Z-h)+}$, being N the coordination number and h the hydrolysis ratio. The hydrolysis ratio depends on the pH of the solution and the oxidation state of the metal cation. This dependence can be represented in a charge-pH diagram (Fig. 1).

Download English Version:

https://daneshyari.com/en/article/1521059

Download Persian Version:

https://daneshyari.com/article/1521059

Daneshyari.com