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Journal of Solid State Chemistry 180 (2007) 2121–2128

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Fe(II)-induced transformation from ferrihydrite to lepidocrocite and goethite

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Received 3 December 2006; received in revised form 17 March 2007; accepted 26 March 2007
Available online 28 March 2007

Abstract

The transformation of Fe(II)-adsorbed ferrihydrite was studied. Data tracking the formation of products as a function of pH, temperature and time is presented. The results indicate that trace of Fe(II) adsorbed on ferrihydrite can accelerate its transformation obviously. The products are lepidocrocite and/or goethite and/or hematite, which is different from those without Fe(II). That is, Fe(II) not only accelerates the transformation of ferrihydrite but also leads to the formation of lepidocrocite by a new path. The behavior of Fe(II) is shown in two aspects—catalytic dissolution–reprecipitation and catalytic solid-state transformation. The results indicate that a high temperature and a high pH(in the range from 5 to 9) are favorable to solid-state transformation and the formation of hematite, while a low temperature and a low pH are favorable to dissolution–reprecipitation mechanism and the formation of lepidocrocite. Special attentions were given to the formation mechanism of lepidocrocite and goethite.

Keywords: Ferrihydrite; Fe(II); Catalysis; Dissolution–reprecipitation; Solid-state transformation; Lepidocrocite; Goethite

1. Introduction

The chemistry of iron oxyhydroxides including the species, structure as well as the transformation among them is very rich. Almost all these phases can be formed from solutions giving rise to a puzzling chemistry, and because of the great diversity of physicochemical conditions in the environment (acidity, redox conditions, bacterial activity, temperature, salinity, presence of organic or inorganic ligands…), practically all the iron oxide phases can be found in the natural environment [1]. The idea that iron chemistry in aqueous medium is a nice example of chemical versatility is not exaggerated.

Up to now, 16 iron compounds were founded or synthesized. These compounds are either oxides, hydroxides or oxide hydroxides. Their stability varies with species. A metastable species is apt to transform with time to a more thermodynamically stable one. The numerous interconversions between iron oxides and iron oxyhydroxides reflect the complexity of reactions in this system. In fact, the pathways from ferrihydrite to various iron oxides and iron oxyhydroxides of increasing thermodynamic stability are still partly known. To our knowledge, a large effort has been made to study the transformation from ferrihydrite to goethite and hematite [2,3], the adsorption of some ions on ferrihydrite [4,5] as well as the dissolution of ferrihydrite [6,7], while very few studies have explicitly investigated the transformation from ferrihydrite to lepidocrocite [8]. Even some authors thought that lepidocrocite is never formed from ferric species [1]. Certainly, lepidocrocite is usually thought to be an oxidation product of Fe^{2+} [9] and very few papers reported the formation of lepidocrocite from ferric species [10]. The results obtained by Schwertmann et al. [11] indicated that ferrihydrite transforms into goethite or/and hematite at pH 2–12, and no lepidocrocite is detected. Cornell and Schneider [8] found that lepidocrocite can form from ferrihydrite only in

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0022-4596/$ - see front matter © 2007 Published by Elsevier Inc.
doi:10.1016/j.jssc.2007.03.022

the presence of L-cysteine. However, lepidocrocite is not detected in the presence of such organic ligands as cysteamine or glutathione, etc.

Recently, we have studied the transformation mechanism from 2-line ferrihydrite to hematite in the presence of trace of Fe(II) at 100 °C [12]. It is found that Fe(II) adsorbed on ferrihydrite, as a catalyst, can accelerate the formation of hematite. The preliminary study at low temperatures less than 100 °C reveals that Fe(II) still obviously accelerates the transformation of ferrihydrite. More interestingly, the products obtained in the presence of Fe(II) are different from those obtained in the absence of Fe(II). That is, in the current system, Fe(II) induced a new formation path of lepidocrocite from ferrihydrite. The present investigation considers the effect of Fe(II) adsorbed on the transformation of ferrihydrite at lower temperatures (in the range from room temperature (RT) to 100 °C). Particular attention was given to the transformation mechanism from ferrihydrite to lepidocrocite and goethite.

Furthermore, the results obtained in the current work are of significance in the following two aspects. Firstly, because the transformation condition of ferrihydrite (pH 5–9) in the current system is similar to that in natural environment, the conclusion obtained in the present work will be helpful for us to understand the widespread existence of lepidocrocite and goethite in nature. Secondly, because ferrihydrite is an oxidation product of Fe(II) [13] and is detected in the corrosion product of iron [14], it is possible that the results obtained in the current work can help us to create a new cognition for the corrosion mechanism of iron.

2. Experimental

2.1. Starting compounds

Analytically pure $FeCl_3 \cdot 6H_2O$ and NaOH (Tianjin Kaitong Chemical Com.) were used as reagents without further purification. The ferric salt solutions were filtered through a 0.22 μm Millipore filter to remove any particulate contaminants before use.

2.2. Experimental processes

Prior to synthesis, pure nitrogen gas (99.99%) was passed through all solutions used, respectively, in order to remove dissolved oxygen gas. Ferrihydrite was prepared by the following procedures: 6.0 mol/L NaOH solution was added into Fe(III) salt solution (50 ml 1 mol/L) until pH 5–9 under the condition of vigorous stirring. When the pH of the system was adjusted to a desired pH, the agitation was continued for an additional 10 min followed by adding trace of Fe(II) solution ($n_{Fe(II)}/n_{Fe(III)} = 0.02$) into the system. The pH of the system was adjusted once again with a dilute NaOH solution and at the same time the total volume of each system was adjusted to 100 ml. All stages of the preparation were carried out under nitrogen, using degassed distilled water. In this mixed system, a gel-like deposit formed. X-ray diffraction (XRD) shows that this product is 2-line ferrihydrite. Then the suspensions were held in closed polypropylene bottles and aged at different temperatures from RT to 100 °C for a predetermined time varying from 30 min to 2 days with the reaction conditions. The products were washed with distilled water and dried at RT.

The percentage of Fe(II) adsorbed on ferihydrite at different pHs was determined by the following procedures. After preparing ferrihydrite, a certain amount of Fe(II) solution ($n_{Fe(II)}/n_{Fe(III)} = 0.02$) was added. The pH of the suspension was adjusted to a given pH by adding a dilute NaOH solution. After 30 min equilibration time (The above stages were carried out under nitrogen.), the suspension was centrifuged at 4000 rpm. The concentration of Fe(II) in the supernatant was determined spectrophotometrically by using 1,10-phenanthroline [15]. According to the data of the concentration of Fe(II) in the supernatant and the total concentration of Fe(II) added into the system, the percentage of Fe(II) adsorbed on ferihydrite can be calculated. When the concentration of Fe(II) in solution is too little to be determined by spectrophotometry (e.g. at $pH \geqslant 7$), the concentration of Fe(II) in solution can be estimated by K_{sp} of $Fe(OH)_2$.

XRD patterns were collected on a Bruker D8 ADVANCE diffractometer with Cu$K\alpha$ radiation. When the reaction product consisted a mixture of goethite, and/or lepidocrocite and/or hematite, the proportion of each compound was estimated by Evaluation Software installed on X-ray diffractometer according to 1 1 0 XRD peak of goethite, the 1 0 4 peak of hematite and the 0 2 0 peak of lepidocrocite. Infrared (IR) spectra were conducted over the range 400–3500 cm^{-1} with a FTIR-8900 Fourier transform IR spectroscopy. The sample powder (4 mg) was uniformly mixed with 160 mg of ground KBr powder in an agate mortar with a pestle. Transmission electron micrographs (TEMs) were obtained with a Hitachi H-7500. The samples were dispersed in ethanol using an ultrasonic treatment.

3. Results and discussion

3.1. The accelerating action of Fe(II) on the transformation of ferrihydrite at a low temperature

Ferrihydrite (pH 7) was aged at RT for 1 day in the presence or absence of Fe(II). XRD patterns of the samples are shown in Fig. 1. It can be seen in Fig. 1 that ferrihydrite has transformed into lepidocrocite and goethite in the presence of trace of Fe(II), while no detectable change is founded in the control system without Fe(II). The result reveals Fe(II) has obvious accelerating action on the transformation of ferrihydrite even at RT.