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

JOURNAL OF SOLID STATE CHEMISTRY

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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.

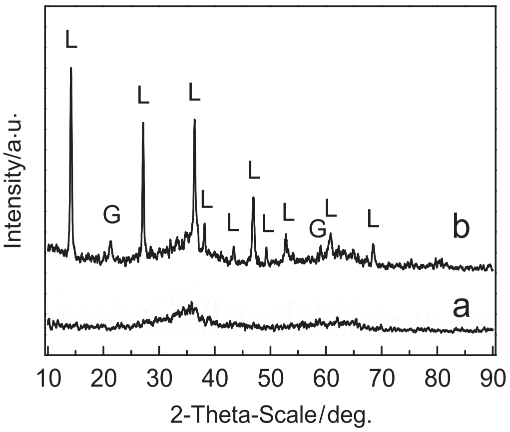

Fig. 1. XRD patterns of the samples obtained both in the presence and absence of Fe(II) ((a) $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0$, (b) $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$; G: goethite, L: lepidocrocite).

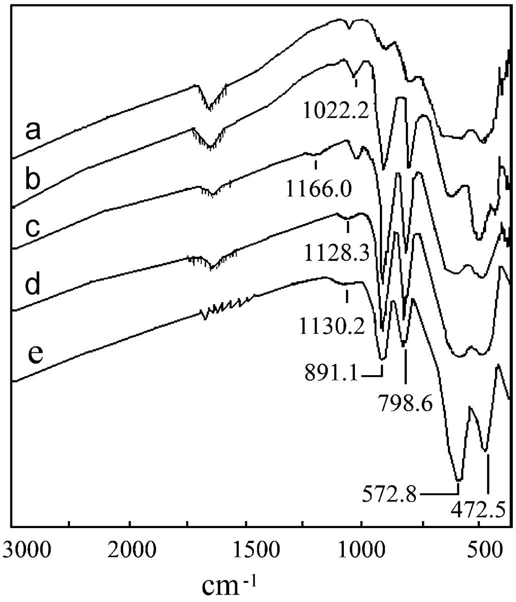

Fig. 2. IR images of the product ($C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, aging at 60 °C for 5 h and (a) pH = 5.35, (b) pH = 6.15, (c) pH = 7.05, (d) pH = 8.33, and (e) pH = 9.0, respectively).

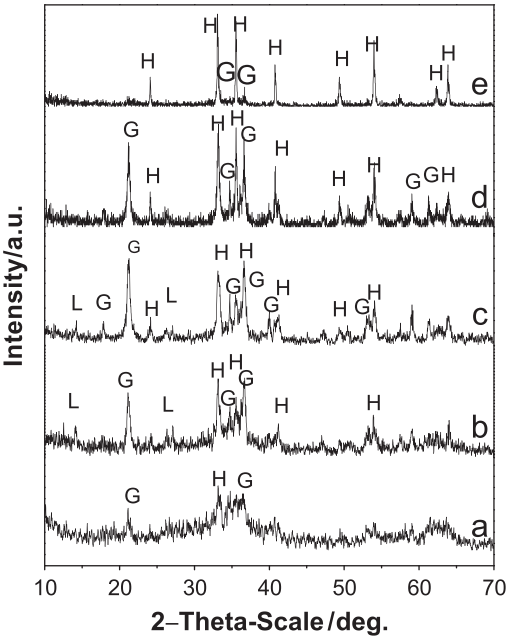

Fig. 3. XRD patterns of the product ($C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, aging at 60 °C for 5 h, (a) pH = 5.35, (b) pH = 6.15, (c) pH = 7.05, (d) pH = 8.33, (e) pH = 9.0; H: hematite, G: goethite, L: lepidocrocite, respectively).

3.2. Effect of pH on the transformation of ferrihydrite

Ferrihydrite with different pHs was aged in a water bath at 60 °C for 5 h. IR spectra and XRD patterns of the samples are shown in Figs. 2 and 3, respectively. In Fig. 2, the bands at 1022.2 and 1166.0 cm^{-1} can be ascribed to γ-FeOOH and the bands at 891.1 and 798.6 cm^{-1} to α-FeOOH, and the bands at 572.8 cm^{-1} and 472.5 cm^{-1} to α-Fe_2O_3 [9]. From Figs. 2 and 3, it is easily found that the pH of ferrihydrite has a great influence on the composition of the product. The product consists of γ-FeOOH, α-FeOOH and α-Fe_2O_3 at pH $\leqslant 7$ and only α-FeOOH and α-Fe_2O_3 are found in the product at pH > 7.

The color is considered to be a useful indicator for the transformation of ferrihydrite. By naked-eye observation, the color changes from dark brownish at pH 5 to yellow at pH 7 and to red at pH 9 (Supporting Information). The content for various crystalline products is listed in Table 1.

It is obvious that the content of α-Fe_2O_3 in the product increases with rising pH of ferrihydrite. The content of α-Fe_2O_3 reaches about 94% at pH 9. The total for γ-FeOOH and α-FeOOH at pH 7 is the highest during the pH range from 5 to 9. On a comparison of the data of Schwertmann et al. [11] with the above results, we deduced that the transformation mechanism in the presence of Fe(II) is different from that without Fe(II). In order to understand the action of Fe(II), the percentage of Fe(II) adsorbed on the ferrihydrite and the transformation time from ferrihydrite to hematite at different pHs were determined. The results are shown in Fig. 4.

As shown in Fig. 4, the transformation rate from ferrihydrite to hematite in the presence of Fe(II) increases with rising pH in the range of 5–7 and it almost keeps unchangeable at pH 7–9. In fact, the results obtained at above 60 °C are similar to that in Fig. 4. According to the report of Инцкирвели [16] and the data in Fig. 4, the above experimental results can be given a reasonable explanation. First, only Fe(II) adsorbed on the ferrihydrite can catalyze its transformation. At pH 5, because most of Fe(II) exists in solution the transformation rate is slow. With increasing pH, the percentage of Fe(II) adsorbed on ferrihydrite increases, which leads to the increase of transformation rate. At pH 7–9, more than 95% of Fe(II) is adsorbed on the ferrihydrite, so the transformation rate is big enough. Second, usually the formation of γ-FeOOH and α-FeOOH from ferrihydrite is considered to be a

Table 1
The composition of the crystalline product obtained at different initial pHs ($n_{Fe(II)}/n_{Fe(III)} = 0.02$, $C_{Fe(III)} = 0.5\,mol/L$, aging at 60 °C for 5 h)

Initial pH	Lepidocrocite(%)	Goethite(%)	Hematite(%)
5.35	—	—	—
6.15	11	37	52
7.05	7	47	46
8.33	0	40	60
9.00	0	6	94

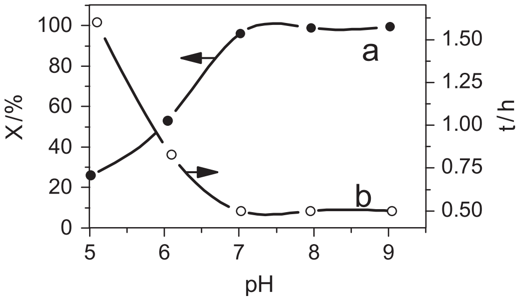

Fig. 4. The percentage of Fe(II) adsorbed on ferrihydrite and the transformation time change with its pH ($C_{Fe(III)} = 0.5\,mol/L$, $n_{Fe(II)}/n_{Fe(III)} = 0.02$).

dissolution/reprecipitation process [8]. At pH 7, about 50% of Fe(II) exists in the form of $FeOH^+$, and $FeOH^+$ has been confirmed to accelerate the dissolution of ferrihydrite [12], which is responsible for the fact that the percentage of γ-FeOOH and α-FeOOH obtained in the current system is rather high. At pH 9, most of the Fe(II) exists in the form of $Fe(OH)_2$, and $Fe(OH)_2$ can catalyze a solid-state transformation of ferrihydrite [12], which leads to the result that hematite dominates in the product.

3.3. Effect of temperature on the transformation of ferrihydrite

Ferrihydrite(pH 7 and $n_{Fe(II)}/n_{Fe(III)} = 0.02$) was aged at different temperatures until it was completely transformed into other crystalline products. The results indicate that the transformation rate of ferrihydrite increases with rising temperature and the composition of the crystalline product has closed relationship to the aging temperature of ferrihydrite (Fig. 5). The changes of the content of various crystalline products with the aging temperature of ferrihydrite are shown in Fig. 6.

Figs. 5 and 6 showed that lepidocrocite is the main crystalline product (about 90%) at pH 7 and at temperature ⩽40 °C. A pure phase of hematite is obtained at 100 °C and the content of α-FeOOH in the product is the highest at about 60 °C. Because the formation of γ-FeOOH and α-FeOOH from ferrihydrite is a dissolution/reprecipitation process [8] and hematite is formed by both dissolution/reprecipitation and solid-state transformation in the presence of Fe(II) [12], the above results reveal that a higher temperature will conduce to the solid-state transformation of ferrihydrite and a lower temperature will conduce to the dissolution/reprecipitation mechanism.

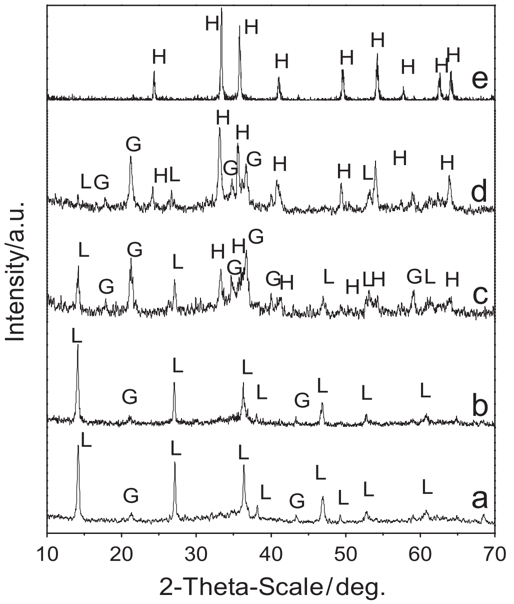

Fig. 5. XRD patterns of the samples obtained at different temperatures ($n_{Fe(II)}/n_{Fe(III)} = 0.02$, $C_{Fe(III)} = 0.5\,mol/L$, pH = 7, (a) RT, (b) 40 °C, (c) 60 °C, (d) 80 °C, (e) 100 °C; H: hematite, G: goethite, L: lepidocrocite, respectively).

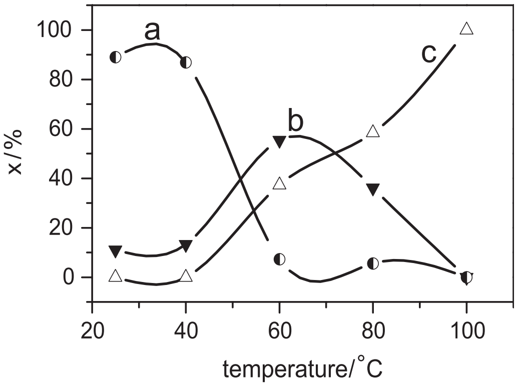

Fig. 6. The relationship between the amount of various products and the aging temperature of ferrihydrite ((a) lepidocrocite, (b) goethite, (c) hematite, $C_{Fe(III)} = 0.5\,mol/L$, pH = 7, $n_{Fe(II)}/n_{Fe(III)} = 0.02$)).

3.4. Effect of reaction time on the products

The preliminary experimental results indicate that the composition of the product also changes with the reaction time. The transformation process of ferrihydrite (pH 7) at 60 °C was studied in detailed. The results are shown in Fig. 7.

As shown in Fig. 7, various crystalline products such as lepidocrocite, goethite and hematite begin to form in a very short time in the presence of trace of Fe(II). It is found that the amount of lepidocrocite begins to decrease after 5 h and its XRD peaks disappear at 2 days. This is because

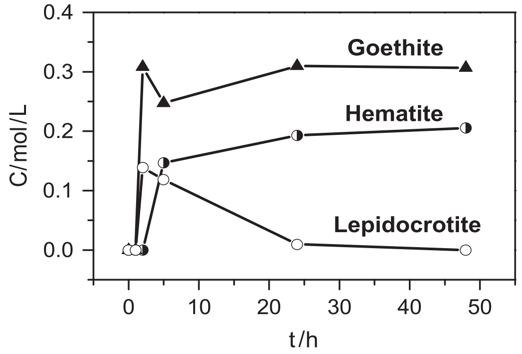

Fig. 7. The change of the amount of the crystalline products with reaction time ($n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, $C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, pH = 7).

lepidocrocite is less thermodynamically stable than goethite and hematite and can be transformed into the more stable species under appropriate conditions. The transformation process from lepidocrocite to goethite or hematite was also detected by TEM (Fig. 8). Usually, synthetic 2-ferrihydrite particles are 2- to 3-nm sized [11]. Lath-like lepidocrocite can be detected at 26 min (Fig. 8a) and its amount gradually increases with transformation time (Fig. 8b). However, it almost cannot be detected at 1 day in Fig. 8c (star-like particles in Fig. 8b and c are goethite.). This result also reveals the further transformation of lepidocrocite, which is consistent with that obtained by XRD.

When the amount of lepidocrocite decreases, the amount of hematite or goethite increases with the reaction time until it almost remains invariable (Fig. 7). Usually goethite is considered to be one of the thermodynamically most stable iron oxyhydroxides at ambient temperature and is, therefore, the first oxide to form and also the end member of many transformations. However, there is another viewpoint about the transformation of goethite. Flynn [17] thought that the stability of goethite relative to hematite and water is uncertain. ΔG^0_{298} for reaction (1) is 0 ± 1 kJ/mol:

$$\alpha\text{-FeOOH} \rightarrow \tfrac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \tfrac{1}{2}\text{H}_2\text{O}. \qquad (1)$$

After analyzing the dependence of ΔG of reaction (1) on the particle size, Langmuir [18] has concluded that the effect of particle size on ΔG becomes significant (exceeding 5 kJ/mol) for particle size $<10^{-1}\,\mu$m. Based on the above viewpoint, during the reaction it is possible that very small goethite particles transform into hematite particles. Once the goethite particles grow up to be bigger particles, the above transformation from goethite to hematite becomes almost impossible because goethite needles ca. 50 nm long need hydrothermal treatment at 160–180 °C to convert to hematite in 1 week [11].

3.5. The transformation mechanism from ferrihydrite to lepidocrocite and goethite in the presence of trace of Fe(II)

Dissolution of Fe(III) oxyhydroxides is of importance in oceanographic and limnological cycles iron. The various pathways of reductive dissolution of Fe(III) oxyhydroxides are discussed and assessed on the basis of laboratory experiments [6,7]. Some organic ligands such as L-cysteine, etc. can be adsorbed on the surface of Fe(III) oxyhydroxides, leading to partial reduction of interfacial ferric ions during interaction with those ligands and conversion of ferrihydrite into a mixed valence iron(II)–iron(III) compound, which dissolved more readily than the original material [8]. Our present work shows that the essential part of reductive dissolution of Fe(III) oxyhydroxides in the presence of those organic ligands is that Fe(II) accelerates its dissolution process.

The transformation mechanism from ferrihydrite to hematite in the presence of traces of Fe(II) has been discussed in our earlier investigation [12]. More attention in the current work was paid to the transformation mechanism from ferrihydrite to lepidocrocite and goethite in the presence of Fe(II). As we proposed in our earlier work, $\mathrm{FeOH^+}$ can accelerate the dissolution of ferrihydrite. Species dissolved into solution may be $\mathrm{Fe(OH)_2^+}$ or/and $\mathrm{Fe(OH)^{2+}}$, which depends on the pH of the reaction system [9]. The experimental results confirm that the magnitude of the concentration of Fe(III) dissolved into solution is only 10^{-4} mol/L [19], which means this Fe(III) solution is a dilute one. Murphy et al. [10,20] thought that goethite or akaganeite is formed from the polymer of Fe(III) and lepidocrocite from low-molecular-weight species in the hydrolysis of Fe(III). According to the viewpoint of Murphy as well as the model of the Fe(III) hydrolysis–precipitation process suggested by Dousma and De Bruyn [21] and Dousma et al. [22] and Tang and Stumm [23], we propose the following schemes for interpreting our experimental results.

$$\text{Ferrihydrite}\ \underset{\text{Dissolved into solution}}{\overset{\text{In the presence of Fe(II)}}{\longrightarrow}} \left\{\begin{array}{l} \mathrm{Fe(OH)_2^{+}} \\ \mathrm{Fe(OH)^{2+}} \end{array}\right. \left\{\begin{array}{l} \underset{\text{formation}}{\overset{\text{Direct}}{\longrightarrow}}\ \gamma-\mathrm{FeOOH} \\ \mathrm{Fe_2(OH)_2^{4+}} \leftrightarrow \mathrm{Fe_3(OH)_4^{5+}} \leftrightarrow \text{polymerization} \\ \leftrightarrow \mathrm{Fe}_x\mathrm{O}_z\mathrm{(OH)}_y^{(3x-2z-y)+} \rightarrow \alpha\text{-FeOOH} \end{array}\right.$$

In the initial stage of catalytic dissolution of ferrihydrite, the main Fe(III) species dissolved into solution are monomers $\mathrm{Fe(OH)_2^+}$ or/and $\mathrm{Fe(OH)^{2+}}$. With time, there are two processes of precipitation. One is the process of direct precipitation from monomer or dimmer that leads to the formation of γ-FeOOH. The other is the process of forming dimmer, then trimer …, then polymers and finally

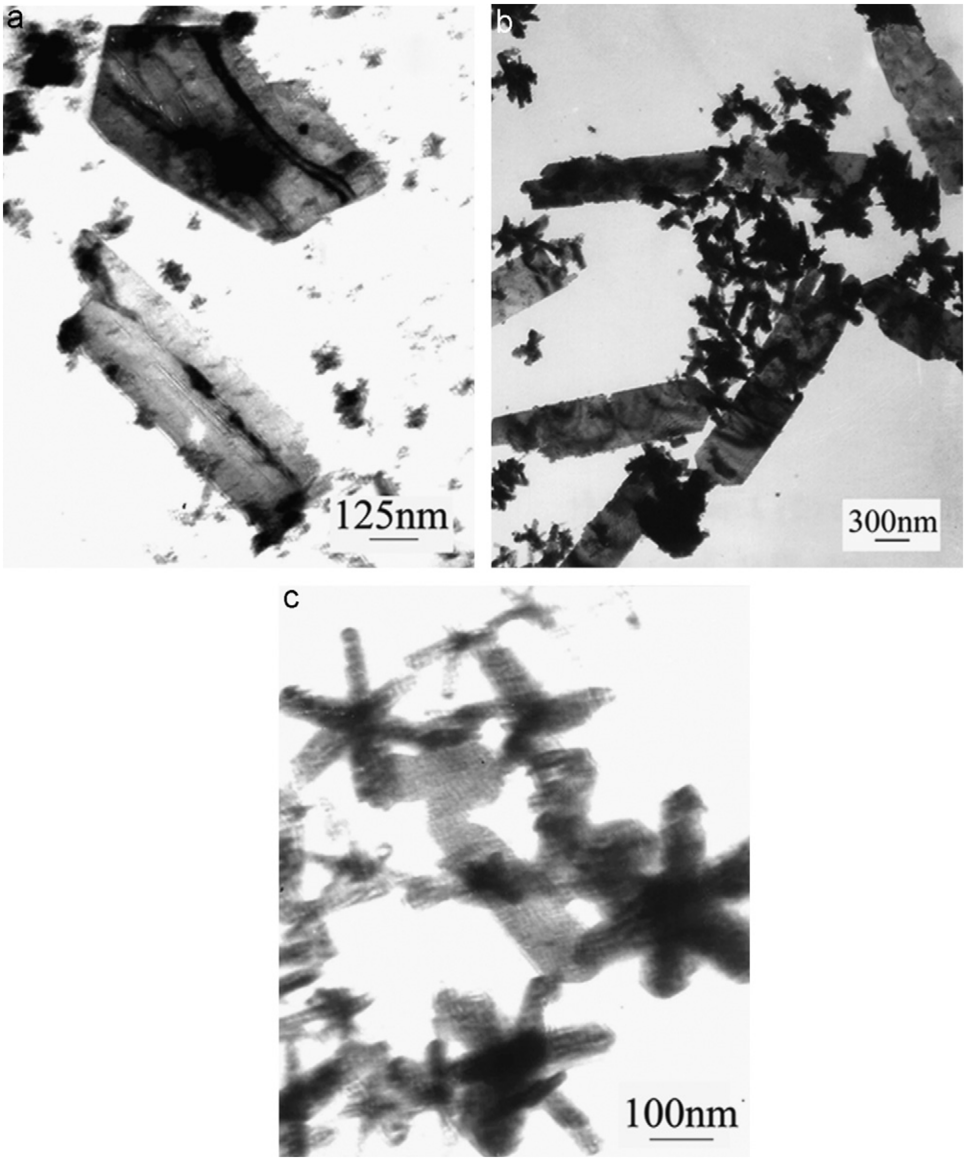

Fig. 8. TEM images of the samples obtained at different times at 60 °C ($n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, $C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, pH = 7, aging at 60 °C, (a) $t = 26\,\mathrm{min}$, (b) $t = 1\,\mathrm{h}$, (c) $t = 1$ day).

forming α-FeOOH. The two processes are in competition with each other. Which process dominates depends on the transformation temperature of ferrihydrite. At a low temperature, the former, that is, the formation of γ-FeOOH dominates. A high temperature is favorable to polymerization that leads to the formation of α-FeOOH. Once the temperature is so high that it meets the need of energy for forming hematite, α-Fe_2O_3 particles begin to form by both solid-state transformation and dissolution/reprecipitation.

The above deduction is confirmed by the mechanism for the formation hydrolytic polymer suggested by Flynn [17] and our further experimental results. Flynn thought the formation of polymer involves condensation of monomer:

$$[\mathrm{FeOH}]_2{}^{+}]_n + \mathrm{Fe}^{3+} + 2\mathrm{H_2O} \rightarrow [\mathrm{FeOH}]_2{}^{+}]_{n+1} + 2\mathrm{H}^{+}, \quad (2)$$

$$\begin{aligned} &2[\mathrm{Fe(OH)_2}\ (\mathrm{H_2O})_{(4-2p)/2}(\mathrm{OH})_{2p/2}{}^{(1-p)+}]_n \text{ (single chain)} \\ &\rightarrow [\mathrm{Fe(H_2O)}\ (\mathrm{OH})_{2/2}\ \mathrm{O}_{3/3}]_{2n} \text{ (double chain)} \\ &+ 2n(1-p)\ \mathrm{H}^{+} + 2n\mathrm{H_2O}. \qquad (3) \end{aligned}$$

It is obvious that the formation of polymer is accompanied by dehydrogenation. In fact, the pH of the system decreases with reaction time (Fig. 9). The lower the transformation temperature the more slowly the pH decreases. This is consistent with the fact that a low temperature is favorable to the formation of γ-FeOOH.

The above conclusion is also supported by Stranski's rule. Stranski's rule states that the least stable phase nucleates first, because the interfacial energy requirements are less stringent. When various phases may form and later disappear, the bigger the solubility of one species the

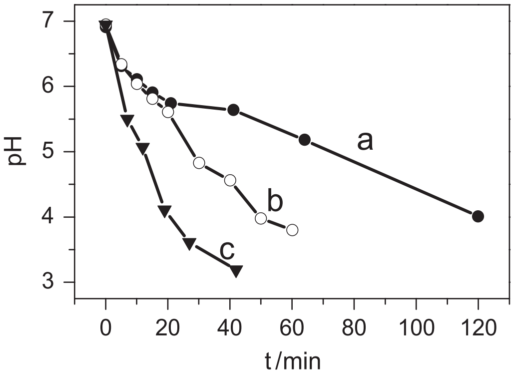

Fig. 9. Changes of pH of the reaction system with time at different temperatures ($n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, $C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, pH = 7, (a) 60 °C, (b) 70 °C, (c) 80 °C).

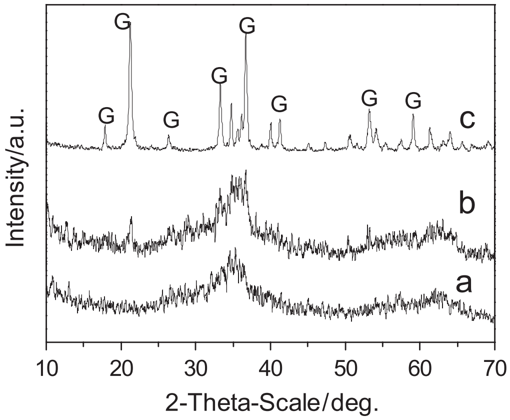

Fig. 10. XRD patterns of samples obtained at different temperatures and reaction times ($n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$, $C_{\mathrm{Fe(III)}} = 0.5\,\mathrm{mol/L}$, pH = 9, (a) RT for 1 day, (b) 40 °C for 5 h, (c) 40 °C for 1 day; G: goethite).

bigger its initial precipitation rate [24]. According to the thermodynamic data of lepidocrocite, goethite and hematite, the order of solubility of them is $S_{\mathrm{lepidocrocite}} > S_{\mathrm{goethite}} \geqslant S_{\mathrm{hematite}}$ [9]. These data indicate that the initial precipitation rate for lepidocrocite is the biggest among them. Once lepidocrocite begins to grow, ferrihydrite whose solubility is more than that of lepidocrocite, acts as a reservoir that releases Fe(III) ions. With rising temperature, the formation of crystalline products becomes faster. On the one hand, the polymerization of Fe(III) is accelerated, which is favorable to the formation of goethite. On the other hand, lepidocrocite also can be transformed to goethite or hematite. This is consistent with the fact that the content of lepidocrocite in the product decreases with rising temperature. The transformation rate of ferrihydrite in the absence of Fe(II) is much slower than that in the presence of Fe(II). That is, the concentration of Fe(III) dissolved into solution in the absence of Fe(II) is lower than that in the presence of Fe(II). Thus, it is difficult to reach the saturation concentration of Fe(III) for forming lepidocrocite, so those Fe(III) ions are apt to form polymers which lead to the formation of goethite.

Moreover, it is easily found that a high pH should be favorable for the polymerization of Fe(III) according to Eqs. (2) and (3), which means that a high pH will be favorable for the formation of goethite. The results obtained at pH 9 and RT~40 °C confirm the conclusion.

Fig. 10 shows the XRD patterns of the samples obtained by aging ferrihydrite (pH 9) at different temperatures and different times. Compared Figs. 10a and b with Figs. 5a and b, we noticed that the transformation rate of ferrihydrite at pH 9 at a low temperature is much slower than that at pH 7. This fact is explained as follows. Because the percentage of Fe(II) in the form of $\mathrm{FeOH^{+}}$ at pH 9 is so low that the catalytic dissolution process of ferrihydrite proceeds very slow. When the reaction time of ferrihydrite at pH 9 at 40 °C was prolonged to 1 day, the transformation of ferrihydrite was completed. XRD patterns reveal that the product obtained is goethite instead of the mixture of lepidocrocite and goethite. This result is consistent with the above analysis.

Based on the experimental results obtained in the current work, we can further understand the wide existence of the iron oxides and iron oxyhydroxides in natural environment and the corrosion product of iron. On the one hand, in nature most iron oxyhydroxides exist in near neutral pH environment. When some reducing agents coexist with them and trace of Fe(III) is reduced into Fe(II), it is possible to trigger the above catalytic process leading to the formation of various FeOOH species. On the other hand, it has been reported that ferrihydrite is one of corrosion products of iron [14]. Once Fe(II) and ferrihydrite coexist in the same system, the as-proposed mechanism can explain the formation of lepidocrocite and goethite.

4. Conclusions

In the presence of trace of Fe(II), ferrihydrite transforms to lepidocrocite, goethite and/or hematite rapidly, whereas in the absence of Fe(II), not only the transformation rate of ferrihydrite is very slow but also the transformation products don't include lepidocrocite. The experimental results show that the transformation temperature, the initial pH and the transformation time of ferrihydrite have great influence on its transformation rate or transformation mechanism. The transformation rate increases with rising temperature. A high temperature in the range from RT to 100 °C is favorable for the formation of hematite, while a low temperature is favorable for the formation of lepidocrocite. A high pH in the range of pH 5–9 is favorable for the formation of hematite, while a low pH is favorable for the formation of lepidocrocite and goethite. The reason for the formation of lepidocrocite from Fe(II)-adsorbed ferrihydrite is that Fe(II) can accelerate the dissolution of ferrihydrite, which makes a great deal of monomers $\mathrm{Fe(OH)_2^{+}}$ or/and $\mathrm{Fe(OH)^{2+}}$ dissolve into solution in a short time. Thus, it is easy to reach the saturation concentration of Fe(III) for forming lepidocrocite in the presence of a trace of Fe(II).

Acknowledgments

This work was supported by the Chinese Hebei Province Foundation of Natural Science Research (B2006000130 and E2006000167) and the Doctor Foundation of Hebei Normal University (L2005B15).

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.03.022.

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