



## Studies on the controllable transformation of ferrihydrite

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### ABSTRACT

Ferrihydrite was prepared by two different procedures. Ferrihydrite-1 was prepared by dropping NaOH solution into Fe(III) solution. Ferrihydrite-2 was prepared by adding Fe(III) and NaOH solutions into a certain volume of water simultaneously. Our earlier results obtained at  $\sim 100$  °C have shown that the structure of ferrihydrite-2 favors its solid state transformation mechanism. Further research reveals that the structure of ferrihydrite-2 favors its dissolution re-crystallization mechanism at a temperature of  $\leq 60$  °C. Based on the transformation mechanism of ferrihydrite at different temperatures, the controllable transformation from ferrihydrite to various iron (hydr)oxides such as lepidocrocite, goethite, hematite and magnetite can be achieved by adjusting the pH, transformation temperature, transformation time, the amount of Fe(II) as well as the preparation procedures of ferrihydrite. The results in the present paper give a nice example that the transformation of a precursor can be controlled with the help of mechanism.

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### 1. Introduction

Ferrihydrite is one of the distinct minerals in the family of oxides, hydroxides and oxyhydroxides of Fe, which occurs naturally and can also be easily synthesized. Due to its metastable property, ferrihydrite can transform into more thermodynamically stable species with time [1,2]. Usually, it was thought that the transformation products of ferrihydrite were goethite and hematite [1,3]. For example, Schwertmann et al. [4] found that two-line ferrihydrite kept under water at temperatures of 4–30 °C and at pHs 2–12 transformed into goethite and/or hematite. Comparing with the transformation from ferrihydrite to goethite and hematite, there are very few studies on the transformation from ferrihydrite to lepidocrocite because it was usually thought that lepidocrocite is an oxidation product of  $\text{Fe}^{2+}$  [5a]. To our knowledge, Cornell and Schneider [6] reported that lepidocrocite can form from ferrihydrite in the presence of L-cysteine. Ristić et al. [7] prepared lepidocrocite, goethite and hematite particles by hydrolysis of  $\text{Fe}^{3+}$  solution.

In recent years, our group has investigated the transformation of ferrihydrite in the presence of trace Fe(II) [8–11]. It was found that ferrihydrite, prepared by using  $\text{FeCl}_3$  as a raw material and

NaOH as a precipitator, can transform to the mixture of lepidocrocite and goethite at temperatures below 80 °C [8]. The rapid dissolution of ferrihydrite in the presence of Fe(II) is responsible for the formation of lepidocrocite. More recently, we prepared ferrihydrite by two different mixing procedures of  $\text{FeCl}_3$  and NaOH solution [9]. In Ref. [9], ferrihydrite-1 is prepared by adding NaOH solution into Fe(III) solution until a desired pH under vigorous stirring. Ferrihydrite-2 is prepared by adding NaOH solution and Fe(III) solution simultaneously into a certain volume of water under vigorous stirring and the rate of adding two solutions is controlled by maintaining a desired pH. The results obtained at  $\sim 100$  °C showed that, comparing with ferrihydrite-1, the structure of ferrihydrite-2 favors the solid state transformation mechanism and the formation of hematite [11]. To our surprise, further investigation reveals that the dissolution of ferrihydrite-2 in the presence of Fe(II) at a temperature of  $\leq 60$  °C occurs more rapidly than that of ferrihydrite-1. That is, the structure of ferrihydrite-2 favors the dissolution of ferrihydrite and the formation of lepidocrocite. Actually, the transformations from ferrihydrite to lepidocrocite, goethite, hematite and magnetite in the presence of Fe(II) are competitive to each other. Based on our knowledge on the transformation mechanism of ferrihydrite at different conditions, the controllable transformation from ferrihydrite to a single product (e.g. lepidocrocite, goethite, hematite or magnetite) was investigated in detail in this paper. We hope that these results can give a nice example by controlling the transformation of the precursors to prepare the goal products.

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## 2. Experimental methods

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH) of analytical purity and distilled water were used. The ferric salt solutions were filtered through a  $0.22 \mu\text{m}$  Millipore filter to remove any particulate contaminants before use.

Ferrihydrite was prepared by different procedures described in Ref. [11].

**Procedure 1.** 6.0 mol/L NaOH solution was added into 50 mL of Fe(III) solution (1.0 mol/L) until a desired pH varying from 5 to 9 under vigorous stirring (The gel formed in this system was named as ferrihydrite-1.), followed by the addition of Fe(II) solution ( $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02-0.5$ ) to the above mixture. The pH of the system was again adjusted to 7 by a dilute NaOH solution (1.0 mol/L). At the same time, the total volume of the system was adjusted to 100 mL.

**Procedure 2.** NaOH solution (6.0 mol/L) and 25 mL of Fe(III) solution (2.0 mol/L) were added simultaneously into 40 mL of water at RT under vigorous stirring. The rate of adding two solutions was controlled by maintaining a desired pH 7 varying from 5 to 9 with accuracy of better than 0.5 pH unit. The gel formed was named as ferrihydrite-2. Then Fe(II) solution ( $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02-0.5$ ) was added into the system and the pH of the system was again adjusted to the desired value by dilute NaOH solution (1.0 mol/L). At the same time the total volume of the system was adjusted to 100 mL.

The experiments were carried out under nitrogen gas and oxygen-free distilled water was used in all stages. The slurry formed in the above two systems was aged in closed polypropylene bottles at different temperatures from 0 to  $80^\circ\text{C}$  for a certain time varying from 0.7 h to 2 d. The products were washed with distilled water and dried at about  $70-80^\circ\text{C}$ .

X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker diffractometer D8 ADVANCE using a  $\text{CuK}\alpha$  radiation, where the reaction product consisted of a mixture of goethite and hematite, the proportion of each compound was estimated by EVA software installed on X-ray diffractometer according to 110 XRD peak of goethite, the 104 peak of hematite. Field emission scanning electron microscopy (FESEM) was obtained with S-4800. Infrared (IR) spectra were obtained using FTIR-8900 Fourier transform IR spectroscopy. The spectra were acquired over the range of  $4000$  and  $400 \text{ cm}^{-1}$ . The specific surface area was evaluated by nitrogen adsorption-desorption isotherm measurements at 77 K (Micromeritics ASAP2020).

The concentration of Fe(III) ions in solution was determined spectrophotometrically by using 1,10-phenanthroline after reducing Fe(III) ions to Fe(II) ions with hydroxylamine [12].

## 3. Results and discussion

### 3.1. The transformation comparison of ferrihydrites prepared by different procedures

Fig. 1 presents XRD patterns of the products obtained from ferrihydrite-1 and ferrihydrite-2 at  $60^\circ\text{C}$  and different pHs. As shown in Fig. 1, both the ferrihydrites transformed to hematite at pH 9. In ferrihydrite-1 system, the proportion of hematite to goethite in the products obtained at pH 8.3 is about 60:40 (Fig. 1A). However, in ferrihydrite-2 system, the proportion at pH 8.3 is about 85:15 (Fig. 1B). There is little difference in the species and amount of the products obtained from ferrihydrite-1 and ferrihydrite-2 at pH 7. However, a large difference was detected

for the transformation of ferrihydrite-1 and ferrihydrite-2 at pHs 5 and 6. In ferrihydrite-1 system, only a little goethite was detected at pH  $\sim 5$  and 6, while ferrihydrite-2 has transformed into almost pure phase lepidocrocite. Our previous results showed that the catalytic behavior of Fe(II) is shown in two aspects—the catalytic dissolution re-crystallization and the catalytic solid state transformation [13]. A low pH (in the range from 5 to 9) favors the catalytic dissolution of ferrihydrite. The results in Fig. 1 probably indicate that the catalytic dissolution process of ferrihydrite-2 occurs easily, because a fast dissolution rate of ferrihydrite will lead to the formation of lepidocrocite [8].

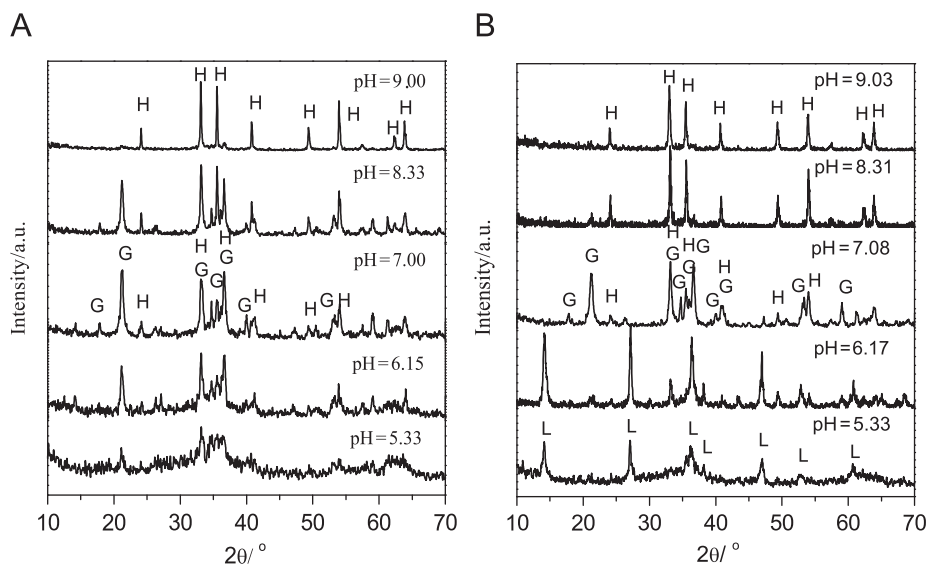
To understand the above results, the two ferrihydrites were aged at  $60^\circ\text{C}$  and pH 6. The changes of the concentration of Fe(III) ions in solution with time were determined (Fig. 2). Fig. 2 indicates that the concentration of Fe(III) ions dissolving into solution from ferrihydrite-2 is larger than that from ferrihydrite-1, which reveals that ferrihydrite-2 dissolves more easily than ferrihydrite-1 under the same conditions. That is, the microstructure of ferrihydrite-2 is favorable for its catalytic dissolution re-crystallization mechanism at a temperature of  $\leq 60^\circ\text{C}$ . This is consistent with the conclusions obtained from Fig. 1.

To further reveal the reason that the transformation rate of ferrihydrite-2 is faster than that of ferrihydrite-1 under the same conditions, the dissolution-time curves of the two ferrihydrites in 3.0 mol/L of HCl solution at RT were determined and the result is shown in Fig. 3. As shown in Fig. 3, ferrihydrite-2 dissolves more slowly than ferrihydrite-1 under same conditions. We have known that the size of ferrihydrite-2 aggregate is smaller than that of ferrihydrite-1 [11]. Theoretically, the dissolving rate of ferrihydrite-2 in HCl solution should be larger than that of ferrihydrite-1. However, the fact is reverse. We deduced that ferrihydrite-2 is probably more compact than ferrihydrite-1.

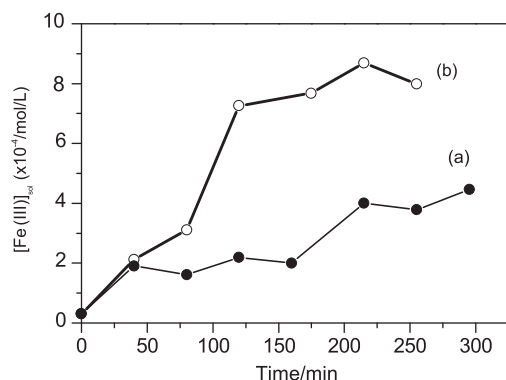
To further confirm this conclusion, the specific surface areas of the two ferrihydrites were determined and the results were shown in Table 1. Theoretically, the specific surface area of the ferrihydrite-2 should be larger than that of ferrihydrite-1. However, the BET specific area of ferrihydrite-2 is less than that of ferrihydrite-1. Interestingly, the  $t$ -plot micropore area of ferrihydrite-2 is also less than that of ferrihydrite-1, which indicates that less micropores exist in ferrihydrite-2 aggregates; that is, ferrihydrite-2 is more compact.

The differences between the two ferrihydrite aggregates in the transformation at low temperatures can be explained based on the above results. Firstly, those Fe(II) added into the reaction system are adsorbed on the surface of ferrihydrite aggregate. Secondly, the electron transfer between adsorbed Fe(II) and interfacial Fe(III) occurs and this electron transfer is continually repeated. We imagine this electron transfer process proceed batch by batch. After the first batch of electron transfer between Fe(II) and Fe(III) occurs, the original Fe(II) ion is oxidized to be Fe(III) ion and enters into the solution. At the same time, the original Fe(III) lying on the surface of ferrihydrite is reduced to be Fe(II) and subsequently the next batch of electron transfer between newly formed Fe(II) and Fe(III) lying in the second surface occurs. The electron transfer between Fe(II) and Fe(III) in ferrihydrite-2 aggregate should occur more easily than in ferrihydrite-1 due to its higher compaction degree. That is, the catalytic dissolution rate of ferrihydrite-2 aggregate in the presence of trace Fe(II) is larger than that of ferrihydrite-1 under the same conditions. A fast dissolution rate of ferrihydrite leads to the formation of lepidocrocite [8].

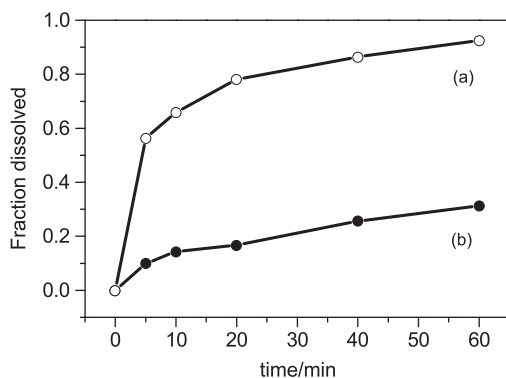
We have reported the transformation of ferrihydrite-1 prepared by using  $\text{Fe}_2(\text{SO}_4)_3$  as raw material and NaOH as a precipitator (named as  $\text{SO}_4^{2-}$  system) in the presence of trace Fe(II) [10]. It was found that only goethite can be obtained. Similar



**Fig. 1.** XRD patterns of the products obtained at 60 °C and different pHs by ageing (A) ferrihydrite-1 and (B) ferrihydrite-2 for 5 h. L:  $\gamma$ -FeOOH, G:  $\alpha$ -FeOOH and H:  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



**Fig. 2.** Changes in concentration of Fe(III) ions in solution with time: (a) ferrihydrite-1 and (b) ferrihydrite-2,  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ , pH=7.

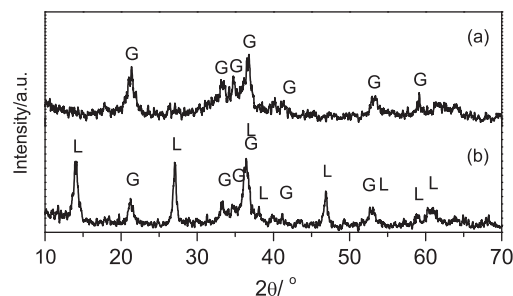


**Fig. 3.** The dissolution–time curves for (a) ferrihydrite-1 and (b) ferrihydrite-2 in 3.0 mol/L of HCl solution at RT. Fraction dissolved gives the ratio of the amount of dissolved ferrihydrite to the total amount of added ferrihydrite.

results were obtained when using FeCl<sub>3</sub> as raw material and NH<sub>3</sub> · H<sub>2</sub>O as a precipitator (named as NH<sub>3</sub> · H<sub>2</sub>O system) [11]. The slow dissolution rate of ferrihydrite-1 both in SO<sub>4</sub><sup>2-</sup> and NH<sub>3</sub> · H<sub>2</sub>O systems is responsible for these results. To further confirm the conclusion that ferrihydrite-2 dissolves more easily than ferrihydrite-1 in the presence of trace Fe(II), the transformation of ferrihydrite-2 prepared both in SO<sub>4</sub><sup>2-</sup> and NH<sub>3</sub> · H<sub>2</sub>O systems was studied. Fig. 4 presents XRD patterns of the products obtained in

**Table 1**  
BET surface area and *t*-plot micropore area of the two ferrihydrites.

	Ferrihydrite-1	Ferrihydrite-2
BET surface area (m <sup>2</sup> /g)	277.4269	252.3703
<i>t</i> -plot micropore area (m <sup>2</sup> /g)	124.1498	41.2340
<i>t</i> -plot external surface area (m <sup>2</sup> /g)	153.2771	211.1363

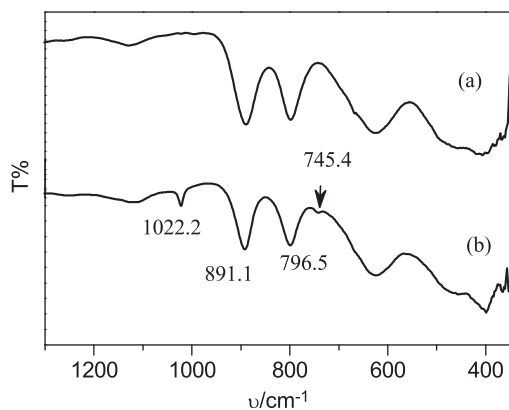


**Fig. 4.** XRD patterns of the products obtained in SO<sub>4</sub><sup>2-</sup> system at 25 °C by ageing (a) ferrihydrite-1 and (b) ferrihydrite-2 for 2 d (pH=7,  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ , L:  $\gamma$ -FeOOH and G:  $\alpha$ -FeOOH).

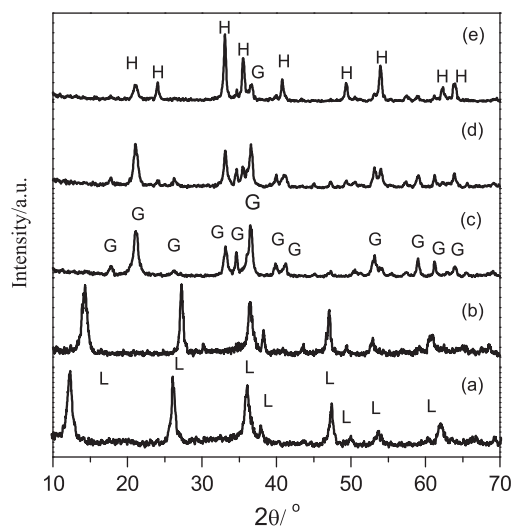
SO<sub>4</sub><sup>2-</sup> system. As shown in Fig. 4, only goethite was obtained when using ferrihydrite-1 as a precursor while lepidocrocite was detected beside goethite in ferrihydrite-2 system. Fig. 5 presents IR spectrum of the products obtained in NH<sub>3</sub> · H<sub>2</sub>O system. In Fig. 5 the bands at 1022.2 and 745.4 cm<sup>-1</sup> can be ascribed to lepidocrocite and the bands at 891.1 and 796.5 cm<sup>-1</sup> to goethite [5b]. Fig. 5a showed that only goethite can be obtained in NH<sub>3</sub> · H<sub>2</sub>O system when using ferrihydrite-1 as a precursor. Lepidocrocite beside goethite was found in the transformation products of ferrihydrite-2.

### 3.2. The controllable transformation from ferrihydrite to lepidocrocite, goethite, hematite and magnetite

It has been known that the formation of lepidocrocite from ferrihydrite was completed by a dissolution re-crystallization mechanism [7]. That is to say, the factors which favor the dissolution of ferrihydrite will favor the formation of lepidocrocite.



**Fig. 5.** IR spectrum of the products obtained in  $\text{NH}_3\text{H}_2\text{O}$  system at 25 °C by ageing (a) ferrihydrite-1 and (b) ferrihydrite-2 for 1 d ( $\text{pH}=7$ ,  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ ).

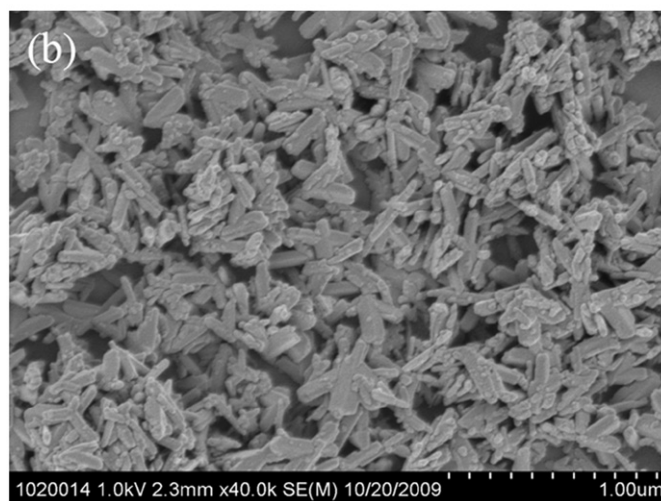
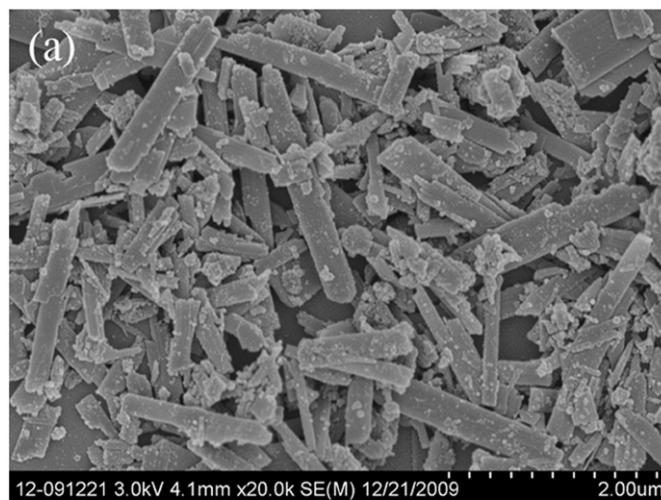


**Fig. 6.** XRD patterns of the products by ageing ferrihydrite-2 at (a) 0 °C for 2 d, (b) 25 °C for 1 d, (c) 40 °C for 1 d, (d) 60 °C for 5 h and (e) 80 °C for 0.7 h ( $\text{pH}=7$ ,  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ , L:  $\gamma\text{-FeOOH}$ , G:  $\alpha\text{-FeOOH}$  and H:  $\alpha\text{-Fe}_2\text{O}_3$ ).

Our earlier results indicated that a low temperature (in the range from room temperature (RT) to 100 °C) favors the dissolution recrystallization mechanism [8]. We also found that Fe(II) existing in the form of  $\text{FeOH}^+$  can catalyze the dissolution of ferrihydrite [13] and the proportion of  $\text{FeOH}^+$  is the highest at pH 7 [14]. Figs. 1 and 2 reveal that the microstructure of ferrihydrite-2 is favorable to its catalytic dissolution. As such, we chose ferrihydrite-2 as a precursor and studied its transformation at pH 7 and different temperatures. XRD patterns of the products are shown in Fig. 6.

Fig. 6 reveals that the transformation from ferrihydrite-2 to lepidocrocite, goethite and hematite can be controlled by adjusting the reaction temperature and time. Pure lepidocrocite was obtained at 0 °C by ageing ferrihydrite-2 for 2 d and at 25 °C for 1 d. Pure goethite was obtained when ageing ferrihydrite-2 at 40 °C for 1 d. The product obtained by ageing ferrihydrite-2 at 80 °C for 0.7 h was hematite with little goethite. Fig. 7 presents SEM photos of those products. As shown in Fig. 7, the as-prepared lepidocrocite is lath-like particles and goethite is “Y”-like or star-like particles.

Increasing the amount of Fe(II) should be favorable to the formation of lepidocrocite because Fe(II) can catalyze the dissolu-



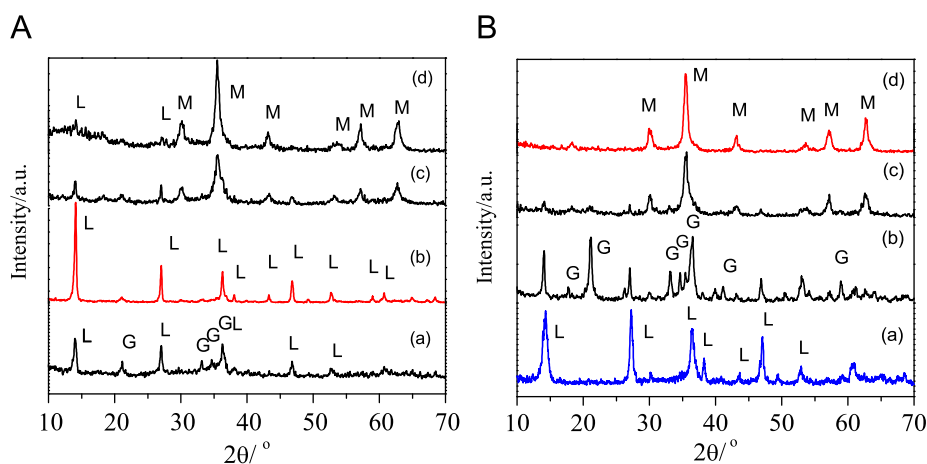
**Fig. 7.** SEM photos of the products obtained by ageing ferrihydrite-2: (a) lepidocrocite: 25 °C for 1 d and (b) goethite: 40 °C for 1 d ( $\text{pH}=7$ ,  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ ).

tion of ferrihydrite. As such, the transformation of the two ferrihydrites at 25 °C and different  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}$  molar ratios was investigated. Fig. 8 presents the XRD patterns of the products obtained from the two ferrihydrites. It can be seen that ferrihydrite-1 transformed to the mixture of lepidocrocite and goethite at  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$  (Fig. 8Aa) and the mixture of lepidocrocite and magnetite was obtained at  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.3\text{--}0.5$  (Fig. 8Ac and Ad). However, lepidocrocite was obtained (Fig. 8Ab). Fig. 8Ba indicates that pure lepidocrocite can be obtained by ageing ferrihydrite-2 at 25 °C and  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$  for 1 d. Moreover, we noticed that only magnetite can be detected by ageing ferrihydrite-2 at 25 °C and  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.5$  for 1 d (Fig. 8Bd), which means that the transformation from ferrihydrite to magnetite can also be controlled.

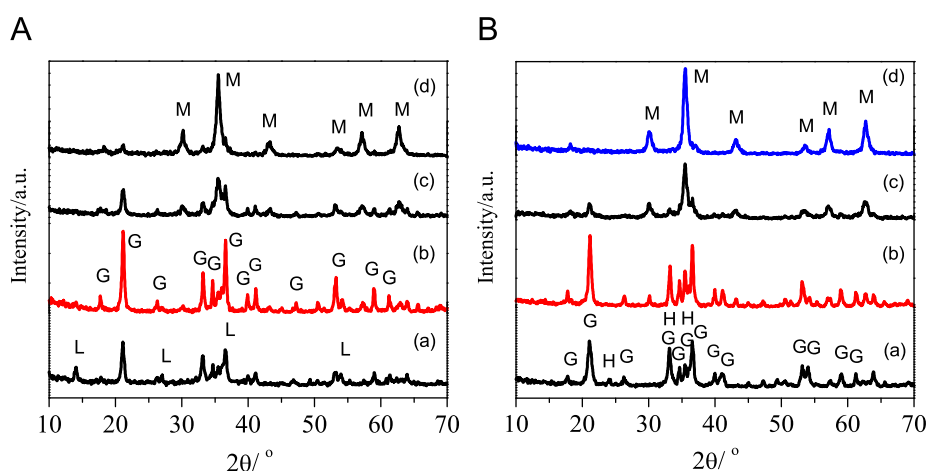
Fig. 9 presents XRD patterns of the products obtained by ageing the two ferrihydrites at pH 7 and 60 °C for 5 h. The results show that both ferrihydrite-1 and ferrihydrite-2 transformed to goethite at  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.1$  (Fig. 9Ab and Bb) and ferrihydrite-2 transformed to magnetite at  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.5$  (Fig. 9Bd).

Fig. 1 indicates that both ferrihydrite-1 and -2 can transform to pure hematite particles at pH 9 and 60 °C by ageing them for 5 h. Moreover, our earlier results showed that hematite particles with different size and surface state can be obtained by boiling and refluxing the two ferrihydrites for 0.5–2 h [9,13].





**Fig. 8.** XRD patterns of the product by ageing (A) ferrihydrite-1 and (B) ferrihydrite-2 at 25 °C for 1 d. (Aa, Ba)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ , (Ab, Bb)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.1$ , (Ac, Bc)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.3$ , (Ad, Bd)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.5$  pH=7, L:  $\gamma$ -FeOOH; G:  $\alpha$ -FeOOH and M:  $\text{Fe}_3\text{O}_4$ .



**Fig. 9.** XRD patterns of the product by ageing (A) ferrihydrite-1 and (B) ferrihydrite-2 at pH 7 and 60 °C for 5 h. (Aa, Ba)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$ , (Ab, Bb)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.1$ , (Ac, Bc)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.3$ , (Ad, Bd)  $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.5$  pH=7, L:  $\gamma$ -FeOOH; G:  $\alpha$ -FeOOH; H:  $\alpha$ - $\text{Fe}_2\text{O}_3$  and M:  $\text{Fe}_3\text{O}_4$ .

**Table 2**

The transformation conditions from ferrihydrite to various iron (hydr)oxides.

No.	Precursor	System	pH	Temperature (°C)	$n_{\text{Fe(II)}}/n_{\text{Fe(III)}}$	Time	Product
1	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	0	0.02	2 d	$\gamma$ -FeOOH
2	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	25	0.02	1 d	$\gamma$ -FeOOH
3	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	6.17	60	0.02	5 h	$\gamma$ -FeOOH
4	Ferrihydrite-1	$\text{Cl}^- + \text{NaOH}$	7	25	0.10	1 d	$\gamma$ -FeOOH
5	Ferrihydrite-1	$\text{Cl}^- + \text{NaOH}$	7	60	0.10	5 h	$\alpha$ -FeOOH
6	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	60	0.10	5 h	$\alpha$ -FeOOH
7	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	40	0.02	1 d	$\alpha$ -FeOOH
8	Ferrihydrite-1	$\text{SO}_4^{2-} + \text{NaOH}$	7	25	0.02	2 d	$\alpha$ -FeOOH
9	Ferrihydrite-1	$\text{Cl}^- + \text{NH}_3 \cdot \text{H}_2\text{O}$	7	40	0.02	5 h	$\alpha$ -FeOOH
10	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	25	0.50	1 d	$\text{Fe}_3\text{O}_4$
11	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	7	60	0.50	5 h	$\text{Fe}_3\text{O}_4$
12	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	9	60	0.02	5 h	$\alpha$ - $\text{Fe}_2\text{O}_3$
13	Ferrihydrite-2	$\text{Cl}^- + \text{NaOH}$	5–9	~100	0.02	0.5–2 h	$\alpha$ - $\text{Fe}_2\text{O}_3$
14	Ferrihydrite-1	$\text{Cl}^- + \text{NaOH}$	5–9	~100	0.02	15–60 min	$\alpha$ - $\text{Fe}_2\text{O}_3$
15	Ferrihydrite-1	$\text{Cl}^- + \text{NaOH}$	9	60	0.02	5 h	$\alpha$ - $\text{Fe}_2\text{O}_3$

#### 4. Conclusions

The controllable transformation of ferrihydrite was achieved by adjusting pH, temperature, time and the level of Fe(II) as well as the preparing procedure of ferrihydrite. The transformation conditions from ferrihydrite to various (hydr)oxides are summarized in Table 2. Obviously, for the transformation from ferrihydrite to lepidocrocite, the factors such as a lower temperature (e.g.

0–25 °C), a neutral pH value and a rapid dissolution rate of ferrihydrite (e.g. the structure of ferrihydrite-2 and a high level of Fe(II)) are favorable. As for the transformation from ferrihydrite to goethite, a moderate temperature (e.g. 40–60 °C) and a neutral pH value are the important factors in  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and NaOH system. Both using  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  to replace  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to replace NaOH can lead to the formation of pure goethite. When using ferrihydrite to prepare magnetite, the structure of

ferrihydrate-2, the introduction of enough Fe(II) and a temperature of  $\leq 60$  °C are favorable. Moreover, both ferrihydrate-1 and ferrihydrate-2 can transform to hematite rapidly at pH 5–9 and  $\sim 100$  °C in the presence of trace Fe(II). When the transformation was completed at 60 °C, a high pH (e.g. pH 9) and a long reaction time are necessary.

It must be pointed out that the transformation from ferrihydrate to single product can be completed under other conditions besides the ones discussed in the present paper because the inter-conversion between iron (hydr)oxides is very complicated. Actually, it is the complicated conversion in iron (hydr)oxides system that exhibits the chemical versatility.

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#### References

- [1] Y. Cudennec, A. Lecerf, J. Solid State Chem. 179 (2006) 716–722.
- [2] M. Ristić, E. De Grave, S. Music, S. Popovic, Z. Orehovec, J. Mol. Struct. 834–836 (2007) 454–460.
- [3] D.J. Burleson, R.L. Penn, Langmuir 22 (2006) 402–409.
- [4] U. Schwertmann, J. Friedl, H. Stanjek, J. Colloid Interface Sci. 209 (1999) 215–223.
- [5] R.M. Cornell, U. Schwertmann, in: The Iron Oxides, second ed., Wiley, New York, 2003 (a: p. 5; b: pp. 143–145.).
- [6] R.M. Cornell, W. Schneider, Polyhedron 8 (1989) 2829–2836.
- [7] M. Ristić, S. Musić, M. Godec, J. Alloy Compd. 417 (2006) 292–299.
- [8] H. Liu, P. Li, M.Y. Zhu, Y. Wei, Y.H. Sun, J. Solid State Chem. 180 (2007) 2121–2128.
- [9] H. Liu, P. Li, B. Lu, Y. Wei, Y.H. Sun, J. Solid State Chem. 182 (2009) 1767–1771.
- [10] H. Liu, H. Guo, P. Li, Y. Wei, J. Solid State Chem. 181 (2008) 2666–2671.
- [11] H. Liu, L.J. Yang, M.R. Ma, P. Li, Y. Wei, J. Solid State Chem. 183 (2010) 542–546.
- [12] Wuhan University compilation group, Experiment of Analytical Chemistry, High Education Publishing Company, Beijing, 1987, p. 354.
- [13] H. Liu, Y. Wei, Y.H. Sun, J. Mol. Catal. A Chem. 226 (2005) 135–140.
- [14] L.N. Intsrveili, I.V. Kolosov, G.M. Varshar, Inorg. Chem. Russia 20 (1975) 2388–2391.