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The transformation of ferrihydrite in the presence of trace Fe(II): The effect of the anionic media

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ABSTRACT

The transformation from ferrihydrite to various iron oxides and iron oxyhydroxides has been given much attention not only in environmental science and geochemistry but also in biology and material science. This laboratory study attempted to investigate Fe(II)-induced transformation of ferrihydrite in sulfate-rich medium. The results indicate that the transformation in sulfate-rich medium differs from that in Cl^- medium in the species, the amount and the morphology of products and transformation rate. Lepidocrocite is a main ingredient in the product in Cl^- medium at room temperature (RT), while goethite is the only product in SO_4^{2-} medium at RT. Goethite particles obtained in Cl^- medium are star-like but rod-like in SO_4^{2-} medium. The transformation rate in the latter medium is obviously slower than that in the former medium. The formation of lepidocrocite depends on both the ionic strength of the system and the dissolution rate of ferrihydrite.

1. Introduction

Ferrihydrite is a common product that forms over the earth's surface under several environmental conditions. Due to its high surface area and intrinsic reactivity, ferrihydrite serves as a dominant sink for numerous metals (e.g., As) and nutrients (e.g., P). Ferrihydrite is also considered the most (bio)available Fe(III) (hydr)oxide for dissimilatory iron reducing bacteria (DIRB) and thus greatly influences the global cycling of carbon [1]. Ferrihydrite is often used as a precursor to prepare hematite, goethite [2,3]. Considering the importance of ferrihydrite in material science, geochemistry, biology, environmental science, etc., the study on ferrihydrite has been paid more attention [4–9].

Because of its metastable property, ferrihydrite can transform into more thermodynamically stable species. The transformation is affected by such factors as the temperature, the concentration, pH value, anionic type as well as all kinds of additives, etc. Generally, the conversion of ferrihydrite is slow in the absence of catalysts. Strong reductants (e.g., cysteine) induce interfacial electron transfer to structural Fe(III), thus stimulating dissolution and subsequent re-precipitation as a thermodynamically more stable phase [10]. Due to strong reducing capacity, Fe(II) also induces the dissolution and the subsequent conversion of ferrihydrite [11,12]. Furthermore, the rate and products of transformation of ferrihydrite vary with the preparation conditions of ferrihydrite as well as the anionic media. For example, the results obtained by Schwertmann et al. [13] indicated that ferrihydrite, prepared by the hydrolysis of 0.1 M $Fe(NO_3)_3$ solution at pH 7 or by oxidizing of 0.1 M $FeCl_2$ solution at pH 6.5, transformed into goethite or/and hematite at pH 2–12. $Fe(NO_3)_3$ was still used as a starting material to prepare ferrihydrite and lepidocrocite was formed in the presence of L-cysteine in the study of Cornell and Schneider [10]. Jang et al. [11] investigated the effects of Zn(II), Fe(II), NO_3^- or SO_4^{2-} on the transformations of hydrous ferric oxide by Mossbauer spectroscopy. Their results showed that the products of the transformation of ferrihydrite in SO_4^{2-} medium were the mixture of lepidocrocite and goethite, and only goethite was obtained in Cl^- medium. Our group has explored the transformation of ferrihydrite in the presence of trace Fe(II) [12,14–17]. It was found that Fe(II) can catalyze the transformation of ferrihydrite even at a low temperature (e.g., room temperature (RT)). The transformation time as well as the species and the amount of products have a close relationship with the initial pH, the temperature as well as anionic media. More interestingly, our results were different from those obtained by Jang et al. [11] even under the similar conditions. That is,

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lepidocrocite and goethite were formed in Cl^- medium [16] and the formation of lepidocrocite was restrained in SO_4^{2-} medium. The differences between ours and Jang's results should be attributed to the formation condition of ferrihydrite. These results indicate that a minor change in the preparing condition of ferrihydrite can cause great changes in the transformation product of ferrihydrite. On the other hand, these results infer the complexity and diversity of products of transformation of ferrihydrite.

The aim of present paper is to investigate the transformation of ferrihydrite in the presence of trace Fe(II) and SO_4^{2-} ions under various conditions. The investigations focus on the effect of transformation rate of ferrihydrite, the heating rate of ferrihydrite and ionic strength of the system on the transformation mechanism of ferrihydrite.

2. Experimental

Ferric sulfate ($Fe_2(SO_4)_3 \cdot xH_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$) and sodium hydroxide (NaOH) of analytical purity and distilled water were used. The ferric salt solution was filtered through a 0.22 μm Millipore filter to remove any particulate contaminants before use.

Ferrihydrite was prepared using the procedures described in Ref. [16]. Briefly, 6.0 mol/L NaOH solution was added into Fe^{3+} salt solution (50 mL 1.0 mol/L) until pH 5–9 under vigorous stirring, followed by the addition of trace Fe^{2+} solution ($n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$) to the above mixture. The pH of the system was adjusted to 5–9 again with a dilute NaOH solution (1.0 mol/L). The total volume of the system was adjusted to 100 mL. The experiment was carried out under nitrogen gas and oxygen-free distilled water was used in all stages. When gel-like precipitate formed in reaction solution, part of sample was removed to be subjected to X-ray diffraction (XRD) characterization. Then the remained suspensions aged in closed polypropylene bottles at different temperatures from RT to 100 °C for a certain time varying from 30 min to 2 days. The products were washed with distilled water and dried at RT.

The XRD patterns (Bruker D8 ADVANCE) of the particles were recorded using Cu $K\alpha$ radiation. When the products were a mixture of goethite and hematite, the component of the products was estimated by Evaluation Software installed on the X-ray diffractometer according to the 110 XRD peak of goethite and the 104 peak of hematite. For TEM (Hitachi H-7500) analysis, a drop of diluted nanoparticle ethanol solution was put onto a copper grid and dried naturally. Scanning electron micrographs (SEM) were obtained with a Hitachi H-570. The samples were dispersed in ethanol using an ultrasonic treatment.

3. Results and discussion

3.1. The effect of Fe(II) on the transformation of ferrihydrite at RT

Ferrihydrite ($C_{\mathrm{Fe(III)}} = 0.5$ mol/L, pH = 7) aged at RT for 2 days in the presence or absence of Fe(II). XRD patterns of the samples are shown in Fig. 1. As can be seen from Fig. 1, ferrihydrite has transformed into goethite in the presence of trace Fe(II) while no detectable change is founded in the control system without Fe(II), which indicates that Fe(II) accelerates the transformation of ferrihydrite. Moreover, it was found that the products obtained in sulfate-rich medium are different from those in chloride medium [16].

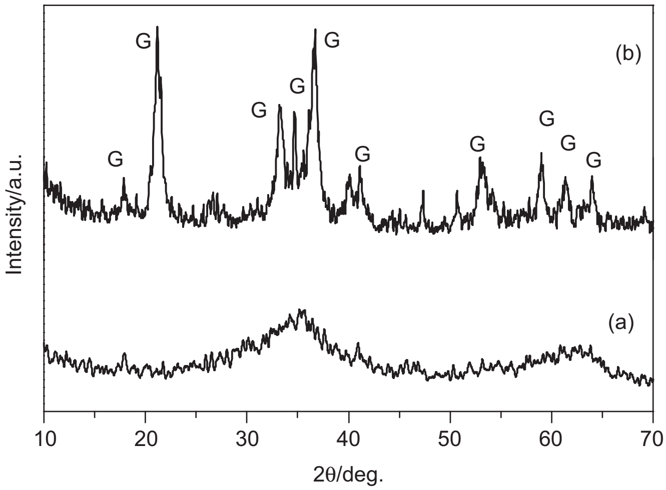

Fig. 1. XRD patterns of the samples obtained both in the presence and absence of Fe(II) (pH = 7, G: α-FeOOH; (a) $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0$ and (b) $n_{\mathrm{Fe(II)}}/n_{\mathrm{Fe(III)}} = 0.02$).

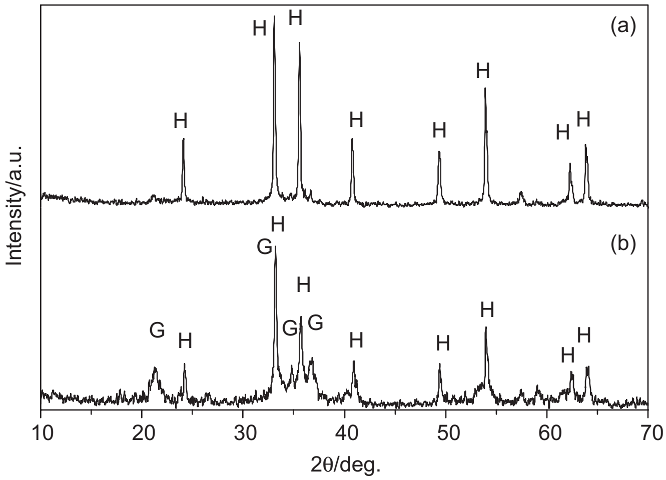

Fig. 2. XRD patterns of the product obtained at 80 °C and different pH values (G: goethite, H: hematite, (a) pH = 9, $t = 40$ min and (b) pH = 7, $t = 3.5$ h).

3.2. The effect of pH and temperature on the transformation of ferrihydrite

Fe(II) exists in different forms at different pH values. In the range of pH 5–9 there are four forms of Fe(II), namely Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$ and $Fe(OH)_3^-$. Our earlier research [12] showed that $Fe(OH)^+$ can catalyze the dissolution of ferrihydrite and $Fe(OH)_2$ can induce the solid-state transformation from ferrihydrite to hematite. According to the data of Smith and Martell [18] and Intsirveili et al. [19], $FeOH^+$ is the main species at pH 7 and $Fe(OH)_2$ dominates at pH 9. Therefore, the two systems with pH 7 and 9 were chosen to study the transformation of ferrihydrite. Fig. 2 shows the XRD patterns of the products aged at 80 °C. The results reveal that not only the transformation time of ferrihydrite at pH 7 (3.5 h) is different from that at pH 9 (40 min) but also the products differ from each other. Pure phase hematite is obtained at pH 9, while the product obtained at pH 7 is a mixture of goethite and hematite. It is known that goethite precipitates from ferrihydrite following the dissolution re-precipitation mechanism [10], while the formation of hematite follows both the dissolution re-precipitation and the solid-state transformation [12]. Those results further confirm the conclusion that $Fe(OH)^+$ can catalyze the dissolution of ferrihydrite and $Fe(OH)_2$ catalyzes the solid-state transformation from ferrihydrite to hematite.

XRD patterns of the products obtained at RT and different pH values are shown in Fig. 3. Aging for 2 days at RT, ferrihydrite transforms to goethite at pH 7 and no detectable change is found at pH 9. The reasons for these results are as follows. On the one hand, the dissolution rate of ferrihydrite is very slow due to the small proportion of $FeOH^+$ at pH 9. On the other hand, the transformation temperature is so low that hematite cannot precipitate in such a short time. However, the amount of $FeOH^+$ is so large at pH 7 that it can catalyze the dissolution of ferrihydrite even at a low temperature, which results in the formation of goethite.

The transformation time, the species and the amount of products obtained at different temperatures were listed in Table 1. The results in Table 1 indicate that the rate of the transformation of ferrihydrite increases with rising temperature. Pure goethite was obtained at $T \leqslant 40\,^{\circ}C$. The amount of goethite in the products decreases with rising temperature at $40\,^{\circ}C < T < 80\,^{\circ}C$. Once the temperature reaches 100 °C, pure hematite precipitates. According to the literature data [10], the mechanism of transformation from ferrihydrite to goethite is a dissolution re-precipitation process and that from ferrihydrite to hematite includes both the dissolution re-precipitation and the solid-state transformation [12]. The above results show that a high temperature is favorable for the solid-state transformation as well as the formation of hematite and a low temperature favors the dissolution re-precipitation mechanism as well as the formation of goethite.

Comparing the transformation of ferrihydrite at pH 9 with that at pH 7, it is found that the transformation rate of the former is less than that of the latter at $T \leqslant 40\,^{\circ}C$ while the transformation rate of the former is larger than that of the latter at $T > 60\,^{\circ}C$. Moreover, the proportion of hematite in the products at pH 9 and $T > 60\,^{\circ}C$ is obviously larger than that at pH 7. It is deduced that a high pH in the range of pH 5–9 is favorable for the formation of hematite as well as the solid-state transformation and a low pH favors the formation of goethite as well as the dissolution re-precipitation.

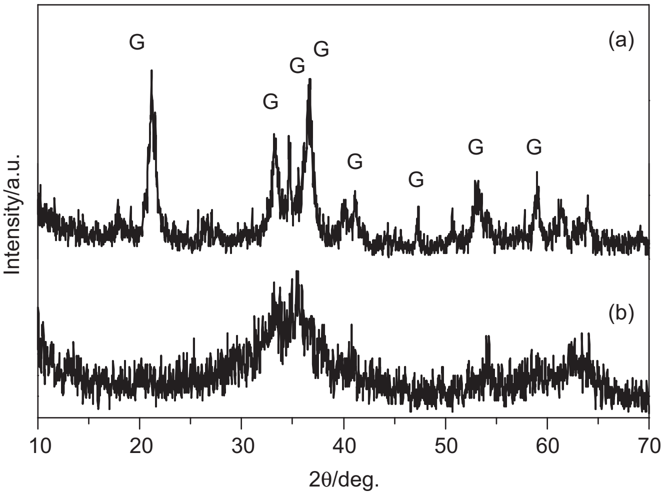

Fig. 3. XRD patterns of the products obtained at RT and different pH values (G: goethite, H: hematite, (a) pH = 7, $t = 2$ days and (b) pH = 9, $t = 2$ days).

Table 1
The changes in the reaction time, species or amount of products with temperature ($n_{Fe(II)}/n_{Fe(III)} = 0.02$, pH = 7)

Temperature (°C)	Reaction time	Product	
		α-FeOOH (%)	α-Fe_2O_3 (%)
RT	2 days	100	0
40	1 day	100	0
60	8 h	39	61
80	3.5 h	16	84
100	0.5 h	0	100

3.3. The effect of heating rate of ferrihydrite on its transformation

The preliminary experimental results indicated that the heating rate has an influence on both the transformation rate and the products. In order to investigate the influence, the ferrihydrites are prepared at 80 °C (named as process-1) and RT (denoted as process-2), then aged at 80 °C. The results show that the transformation time in process-1 is about 40 min. XRD pattern (Fig. 4a) confirms that the product is pure hematite phase. The transformation time in process-2 is about 3.5 h and the product is a mixture of goethite and hematite (Fig. 4b). The proportion of hematite to goethite in the products is about 21:4. These results show that the formations of hematite and goethite are competitive during the dissolution re-precipitation process. A high temperature is favorable for the formation of hematite. In the meantime, the two mechanisms are also competitive to each other. A high temperature favors the solid-state transformation. Moreover, the results in Fig. 4 reveal that the rate of transformation in the solid-state transformation process is faster than that in the dissolution re-precipitation process. When energy meets the need for forming hematite, hematite particles precipitate rapidly by the solid-state transformation. This result is of significance for the synthesis of hematite.

Fig. 5 shows the pH–t curves both in processes-1 and -2. Under the same conditions, the pH values decrease from 7.0 to 5.9 in process-1 while the pH values decrease by about 3.4 pH units in process-2. If ΔpH is converted to the concentration of H^+ ions released in the reaction process by the formula $[H^+] = (10^{-pH})_{final} - (10^{-pH})_{initial}$, the concentration of H^+ ions is about 1.16×10^{-6} mol/L in process-1 and that is about 3.16×10^{-3} mol/L in process-2. The decrease of pH in the transformation of ferrihydrite indicates that the dissolution re-precipitation process happens in the current system [16]. The reasons for the decrease in pH are as follows. Firstly, some H^+ ions are probably adsorbed on the surface of ferrihydrite. As the reaction proceeds, these ions are desorbed from ferrihydrite into solution, which causes the

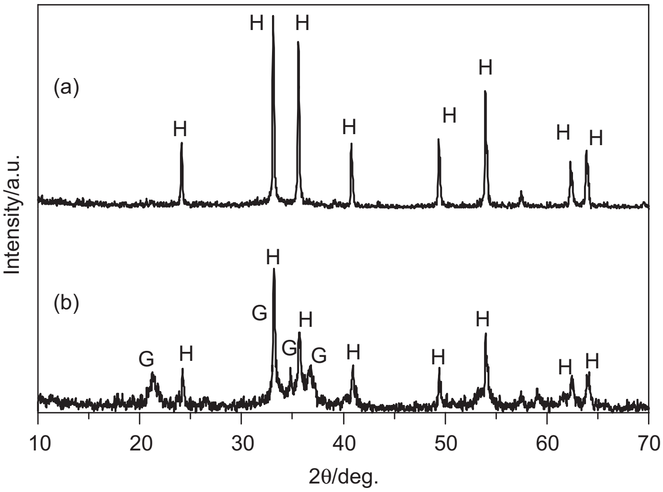

Fig. 4. XRD patterns of products obtained at 80 °C (pH = 7, $n_{Fe(II)}/n_{Fe(III)} = 0.02$, (a) process-1 and (b) process-2; H: hematite, G: goethite).

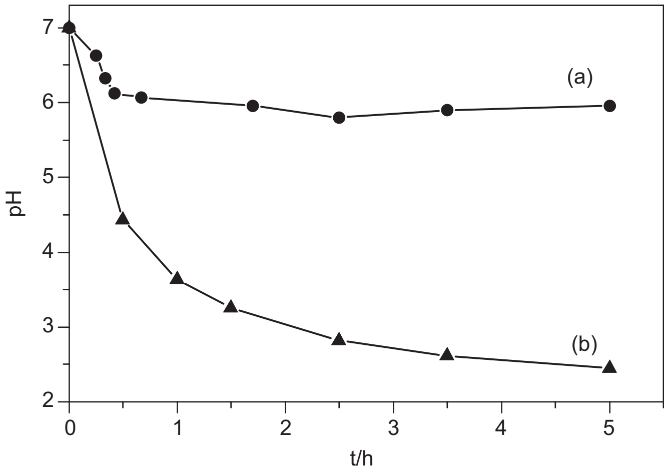

Fig. 5. The curves of pH versus reaction time: (a) process-1 and (b) process-2.

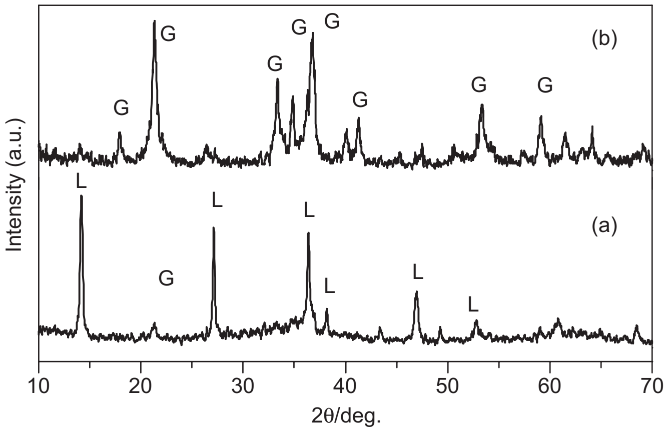

Fig. 6. XRD patterns of products obtained at RT (a) in Cl^- medium for 1 day and (b) in SO_4^{2-} medium for 2 days ($pH = 7$, $n_{Fe(II)}/n_{Fe(III)} = 0.02$; L: lepidocrocite, G: goethite).

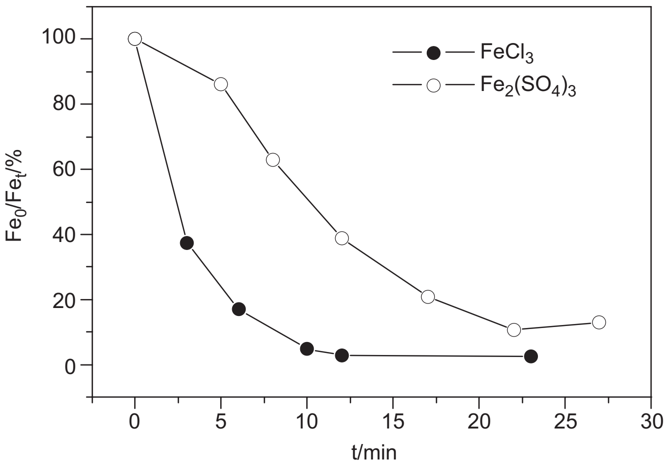

Fig. 7. The fraction of the unconverted ferrihydrite versus reaction time in different anionic media ($pH = 7$, $n_{Fe(II)}/n_{Fe(III)} = 0.02$, the reaction temperature is 100 °C).

decrease of pH. Secondly, Fe(II) can catalyze the dissolution of ferrihydrite. The species dissolved in solution may be $Fe(OH)^{2+}$ and/or $Fe(OH)_2^+$ and/or Fe^{3+}, depending on the pH of the reaction system [20]. Those monomeric Fe(III) ions, such as $Fe(OH)_2^+$, dissolved in the solution can condense to form polymers in which the Fe(III) ions are bridged by OH– groups (reaction 1) or O^{2-} ions (oxolation, reaction 2):

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

$$[\mathrm{Fe(OH)_2}^+]_n \rightarrow [\mathrm{FeO(OH)}]_n + n\mathrm{H}^+ \tag{2}$$

Reactions (1) and (2) reveal that the formation of polymers is accompanied by de-protonation. The latter reason indicates that Fe(II) catalyzes the dissolution of ferrihydrite. Because ferrihydrite prepared at 80 °C was dissolved more difficultly than that prepared at RT [20], the dissolution re-precipitation mechanism was restrained in process-1, thus the solid-state transformation and the formation of hematite dominate. It is known that the solid-state transformation is completed within the aggregation of the ferrihydrite and this process is accompanied by dehydration, which leads to a little pH decrease (Fig. 5a). In contrast, the dissolution re-precipitation occurs to some degree in process-2, which results in the formation of goethite as well as a great pH decrease (Fig. 5b). When ferrihydrite is prepared at 0 °C and aged at 80 °C, the proportion of hematite to goethite in the product reaches about 1:1, which further support the above conclusion.

3.4. *The effect of anionic species on the transformation of ferrihydrite*

Fig. 6 shows the XRD patterns of the products obtained both in Cl^- and SO_4^{2-} media. The mixture of lepidocrocite and goethite is obtained in Cl^- medium and goethite was the only product in SO_4^{2-} medium. The results also show that the rate of transformation at different temperatures varies with anionic species. For example, the transformation from ferrihydrite to the crystalline product at RT is finished in about 1 day in Cl^- medium and 2 days in SO_4^{2-} medium. The similar result was obtained at 100 °C (Fig. 7). As can be seen from Fig. 7, the extent of transformation of ferrihydrite at different time intervals is given by the ratio of Fe_0/Fe_t, where Fe_0 is soluble iron (i.e. the unconverted ferrihydrite. The concentration of the unconverted ferrihydrite was determined by the method used by Sugimoto et al. [21]) and Fe_t is the total iron in the system. Based on the data obtained by Cornell and Giovanoli [22], a high ionic strength can retard the transformation reaction. When $FeCl_3$ and $Fe_2(SO_4)_3$ are used as starting materials, respectively, the ionic strength in Cl^- medium is less than that in SO_4^{2-} medium at the same concentration of Fe(III) (0.5 mol/L). In fact, the rate of transformation of ferrihydrite in SO_4^{2-} medium is slower than that in Cl^- medium in the current system, which means that our conclusion is consistent with that of Cornell and Giovanoli. In addition, the differences between the two systems in the rate of transformation also contribute to the species of products. Schwertmann et al. [13] indicated that ferrihydrite transforms into goethite or/and hematite at pH 2–12. Our earlier results [16] showed that ferrihydrite transforms into lepidocrocite or/and goethite at pH 5–9 at RT in trace Fe(II) medium. The reason of the difference between the results of Schwertmann and ours is due to that the fast rate of dissolving ferrihydrite in the presence of trace Fe(II) controls the formation of lepidocrocite by the dissolution re-precipitation mechanism. In the current experimental system, a high ionic strength in SO_4^{2-} medium retards the dissolving of ferrihydrite. Thus, the formation of lepidocrocite is also retarded.

Moreover, the result obtained in the current system is different from that reported by Jang et al. [11] although the transformation of ferrihydrite in their system was carried out both in SO_4^{2-} media and in the presence of Fe(II). The reason is probably attributed to the preparation condition of ferrihydrite. In the experiment of Jang, ferrihydrite was prepared in 3 days while the ferrihydrite

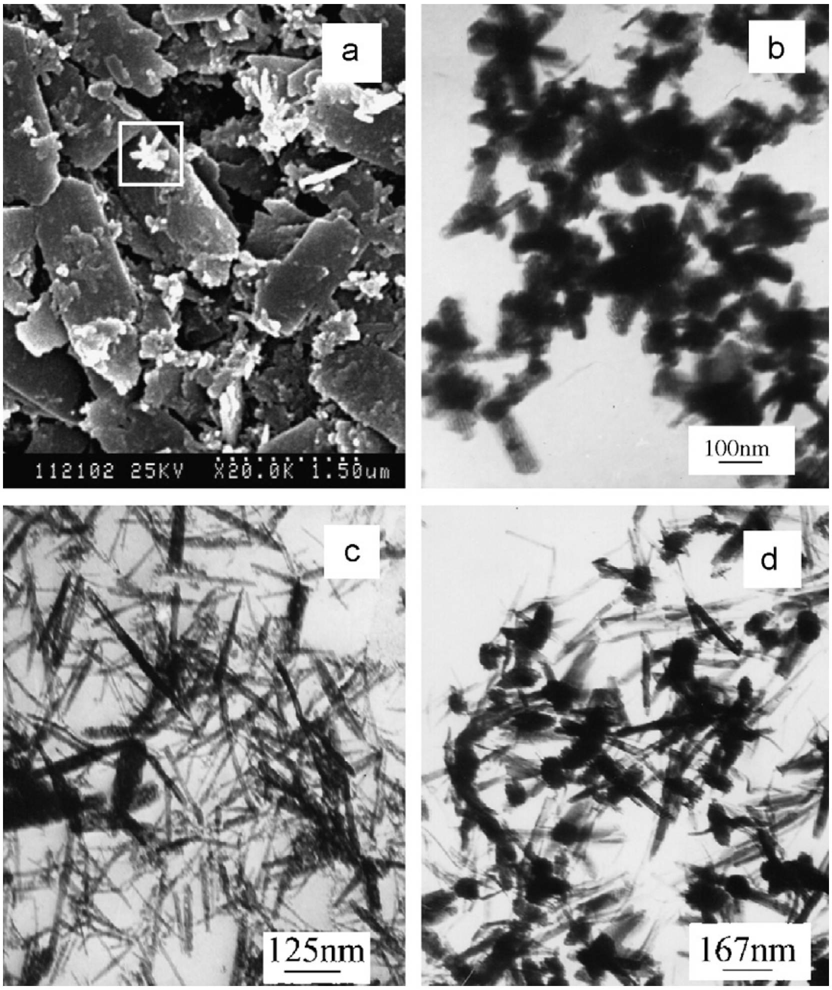

Fig. 8. TEM or SEM images of products obtained (a and b) in Cl^- media and (c and d) in SO_4^{2-} media ($pH = 7$, $n_{Fe(II)}/n_{Fe(III)} = 0.02$; (a) RT, (b) 60 °C, (c) RT and (d) 60 °C).

was prepared in 0.5–1 h in our current system. These results indicate the complexity and diversity of transformation in iron oxide family.

Fig. 8 shows TEM images of the products obtained in Cl^- and SO_4^{2-} media. Plate-like particles are lepidocrocite obtained in Cl^- medium (Fig. 8a) and star-like particles are goethite formed in Cl^- medium (Fig. 8b and white box in Fig. 8a). Goethite particles obtained in SO_4^{2-} medium are needle-like or rod-like (Fig. 8c and d). These results further indicate the effect of anionic species on the transformation of ferrihydrite.

4. Conclusions

The transformation from ferrihydrite to various iron oxides and/or iron oxyhydroxides in sulfate-rich system was investigated. The results indicate that anionic species has an influence not only on the species, the amount as well as the morphology of products but also on the transformation rate of ferrihydrite. Lepidocrocite predominates in the product at RT in Cl^- medium while goethite is the main product in SO_4^{2-} medium. Goethite particles obtained in Cl^- medium is star-like while rod-like in SO_4^{2-} medium. The transformation rate in the latter system is obviously slower than that in the former system, which is attributed to the difference in the ionic strength between the two systems. Moreover, a high temperature, a high pH and a fast heating rate in the range of 7–9 are favorable for the solid-state transformation of ferrihydrite in solution as well as the formation of hematite, while a low temperature, a low pH and a low heating rate favor the dissolution re-precipitation mechanism as well as the formation of goethite.

Acknowledgments

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