



The transformation of ferrihydrite in the presence of trace Fe(II): The effect of the ammonia, amine and the coordination ions of Fe(III)

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ARTICLE INFO

Article history:

Received 29 April 2009

Received in revised form

10 November 2009

Accepted 19 December 2009

Available online 4 January 2010

Keywords:

Ferrihydrite

Fe(II)

Ammonia

Amine

Complexation

Lepidocrocite

Goethite

ABSTRACT

This work examined Fe(II)-induced transformation of ferrihydrite in the presence of ammonia, amine and the coordination ions of Fe(III). Our earlier results showed that ferrihydrite transformed into the mixture of lepidocrocite, goethite and/or hematite in the presence of trace Fe(II) and absence of ammonia and similar species. However, the formation of lepidocrocite was restrained when using ammonia as precipitants. When introducing some amines (e.g. ethanolamine and diethanolamine) and some coordination ions (e.g. F^- and $C_2O_4^{2-}$ ions) into the reaction system, a similar effect on the transformation of ferrihydrite was found. Probably, the complexes formed between Fe(III) and those additives favor the formation of goethite. At the same time, the introduction of these additives hinders Fe(II) from interacting with ferrihydrite, which makes the catalytic dissolution of ferrihydrite be limited, thus, the formation of lepidocrocite be restrained.

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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, which makes it be often used as a precursor to prepare hematite, goethite, etc. [1,2]. As for the transformation of ferrihydrite, there has been considerable research interest in investigating the effect of various factors such as the temperature, pH value, anionic type as well as all kinds of additives on the transformation of ferrihydrite, so that the transformation from ferrihydrite to various products is able to be controlled [3–11].

Our group has explored the transformation of ferrihydrite in the presence of trace Fe(II) [9–14]. It was found that Fe(II) can catalyze the transformation of ferrihydrite even at a low temperature (e.g. room temperature (RT)). In fact, the transformation of ferrihydrite in the presence of trace Fe(II) is a very complicated process. A little change in the condition for preparing ferrihydrite can cause a great difference in the transformation of ferrihydrite. Our previous results indicated that the transformation

time as well as the species and the amount of products have a close relationship with the initial pH, the temperature, the heating rate as well as anionic media [13,14]. Further investigation shows that the transformation of ferrihydrite prepared using $NH_3 \cdot H_2O$ as a precipitant is different from that using NaOH. The aim of the present work is to evaluate the affecting rules of ammonia, amine as well as some coordination ions of Fe(III) on the transformation of ferrihydrite. The obtained results again display the versatility of iron chemistry in aqueous medium.

2. Experimental

$FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, NaOH, LiOH, KOH, $NH_3 \cdot H_2O$, $C_6H_{12}N_4$, $H_2NCH_2CH_2OH$, $HN(CH_2CH_2OH)_2$, $N(CH_2CH_2OH)_3$, $Na_2C_2O_4$ and NaF of analytical purity and distilled water were used. The ferric 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. [13]. Briefly, 6.0 mol/L $NH_3 \cdot H_2O$ (or LiOH, NaOH, KOH) solution was added into Fe^{3+} solution (50 mL 1.0 mol/L) until pH 7 under vigorous stirring, followed by the addition of trace Fe^{2+} solution ($n_{Fe(II)}/n_{Fe(III)} = 0.02$) to the above mixture. The pH of the system was again adjusted to 7 with a dilute $NH_3 \cdot H_2O$ (or LiOH, NaOH, KOH) 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 in all stages. Gel-like

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precipitate was formed in the reaction solution, then the suspensions were aged in closed polypropylene bottles at different temperatures from RT to 100 °C for a certain time varying from 30 min to 7 days. The products were washed with distilled water and dried at RT.

The additives (e.g. $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$, $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, $\text{Na}_2\text{C}_2\text{O}_4$ and NaF) were introduced into the system according to the following procedures. The mixture of ferric solution and a certain amount of additives was precipitated by NaOH (6.0 mol/L) firstly. The subsequent procedures are the same as the above ones. As for $\text{C}_6\text{H}_{12}\text{N}_4$, a certain amount of $\text{C}_6\text{H}_{12}\text{N}_4$ solution was added to the system to precipitate the ferric solution under vigorous stirring firstly. Then NaOH (6.0 mol/L) solution was added until pH 7.

The XRD patterns (Bruker D8 ADVANCE) of the particles were recorded using $\text{CuK}\alpha$ radiation. When the products were a mixture of lepidocrocite, goethite and hematite, the composition of the products was estimated by Evaluation Software installed on the X-ray diffractometer according to the 110 peak of goethite, the 020 peak of lepidocrocite and the 104 peak of hematite. Infrared (IR) spectra were obtained using FTIR-8900 Fourier transform IR spectroscopy. The spectra were acquired over the range of 4000 and 400 cm^{-1} .

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 [15].

3. Results and discussion

3.1. The effect of precipitants on the transformation of ferrihydrite

Ferrihydrites prepared by using LiOH, NaOH, KOH or $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitants were aged at 40 °C for 5 h in the presence of Fe(II). XRD patterns of the samples are shown in Fig. 1. As can be seen from Fig. 1a–c, when using LiOH, NaOH and KOH as precipitants, the products are the mixture of lepidocrocite and goethite, which indicates that Li^+ , Na^+ and K^+ ions do not appear to impact the transformation of ferrihydrite. Only goethite is obtained when using $\text{NH}_3 \cdot \text{H}_2\text{O}$ as a precipitant, which probably means that NH_4^+ ions or NH_3 influences the transformation of ferrihydrite.

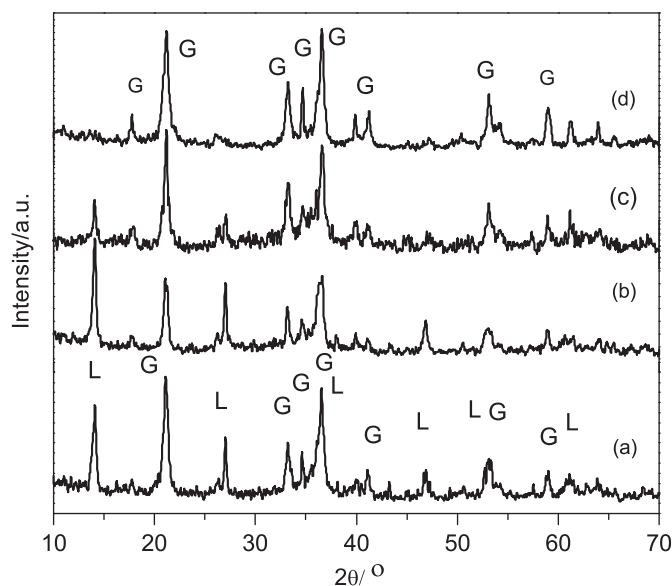


Fig. 1. XRD patterns of the products obtained by using different precipitants. Ferrihydrites were aged at 40 °C for 5 h. (a) LiOH, (b) NaOH, (c) KOH, (d) $\text{NH}_3 \cdot \text{H}_2\text{O}$. L: $\gamma\text{-FeOOH}$, G: $\alpha\text{-FeOOH}$, pH=7.

3.2. The transformation comparison of ferrihydrites prepared by NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$

The transformations of ferrihydrite prepared using NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$ as precipitants were studied at different temperatures. XRD patterns of the products are shown in Fig. 2 and changes of the proportion of various species in the products with temperature in the two media in Fig. 3. Fig. 2 indicates that the transformation product is goethite at 25–40 °C and the mixture of goethite and hematite is obtained at 60–80 °C in the $\text{NH}_3 \cdot \text{H}_2\text{O}$ medium (Fig. 2a). However, under the same conditions lepidocrocite with little goethite is obtained at 25–40 °C and the mixture of goethite, lepidocrocite and hematite is obtained at 60–80 °C in the NaOH medium (Fig. 2b). There are no obvious differences between the two systems at 100 °C. That is, only one product hematite is formed both in NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$ media.

Cornell et al. [16] thought that the transformation from ferrihydrite to lepidocrocite and goethite was a dissolution re-precipitation process. Penn et al. [17] demonstrated that goethite was formed from ferrihydrite by oriented aggregation. In our reaction system, the two mechanisms should coexist, as Fe(II) can accelerate obviously the dissolution of ferrihydrite [9,10] and the rapid dissolution of ferrihydrite can result in the transformation from ferrihydrite to lepidocrocite [13]. The formation of hematite from ferrihydrite in the presence of trace Fe(II) was completed by both the solid state transformation mechanism and the dissolution re-precipitation mechanism. But the solid state transformation mechanism predominates [10]. According to our previous results [13], a high temperature in the range of RT to 100 °C favors the solid-state transformation mechanism and the formation of hematite. A low temperature favors the dissolution re-precipitation mechanism and the formation of lepidocrocite. The results in Figs. 2 and 3 probably indicate that $\text{NH}_3 \cdot \text{H}_2\text{O}$ influences mainly the dissolution re-precipitation processes.

Fig. 4 presents the XRD patterns of ferrihydrite prepared by both $\text{NH}_3 \cdot \text{H}_2\text{O}$ and NaOH. There are no obvious differences detected between the two ferrihydrites. In their IR spectra (Fig. 5), the bands at $\sim 1618.2\text{ cm}^{-1}$ can be ascribed to the bending vibrations of structural $-\text{OH}$ group in ferrihydrite as well as sorbed H_2O [18]. The stretching modes of vibration of O–H in water display bands near 3300 cm^{-1} (Those data are not shown.). The bands at $\sim 1402.2\text{ cm}^{-1}$ (Fig. 5a) are assigned to NH_4^+ ions or NH_3 [18]. This result implies that some NH_4^+ ions or NH_3 were introduced into the aggregate of ferrihydrite during its formation process. The region between 1450 and 800 cm^{-1} probably contains the $\nu_3\text{C}-\text{O}$ stretching modes of adsorbed carbonate because ferrihydrite is very susceptible to CO_2 from air [2,18,19]. The bands at $450\text{--}700\text{ cm}^{-1}$ are attributed to Fe–O stretching vibration. Comparing to the ferrihydrite prepared by NaOH, the bands at $450\text{--}700\text{ cm}^{-1}$ in the ferrihydrite prepared by $\text{NH}_3 \cdot \text{H}_2\text{O}$ shift approximately of $15\text{--}18\text{ cm}^{-1}$ to higher wavenumber due to the presence of NH_4^+ or NH_3 despite the XRD (Fig. 4) showing that there is no difference in crystal structure between the two samples. The above results probably suggest that there are some differences in the microstructure of the two ferrihydrites because factors such as the degree of crystallinity, shape, and extent of particle aggregation, each of these changes influence the infrared spectrum of iron oxide minerals [2].

Fig. 6 shows the changes of the concentration of Fe(III) ions in solution with the reaction time. It can be seen that the dissolution rate of the ferrihydrite prepared by $\text{NH}_3 \cdot \text{H}_2\text{O}$ is slower than that by NaOH, which is consistent with the fact that the formation of lepidocrocite is restrained in $\text{NH}_3 \cdot \text{H}_2\text{O}$ medium. It has been known that lepidocrocite is formed from some low-molecular-weight species such as $\text{Fe}(\text{OH})_2^{2+}$, $\text{Fe}(\text{OH})_2^+$ or $\text{Fe}_2(\text{OH})_4^{2+}$ and goethite from the polymer of Fe(III) [20] or the oriented

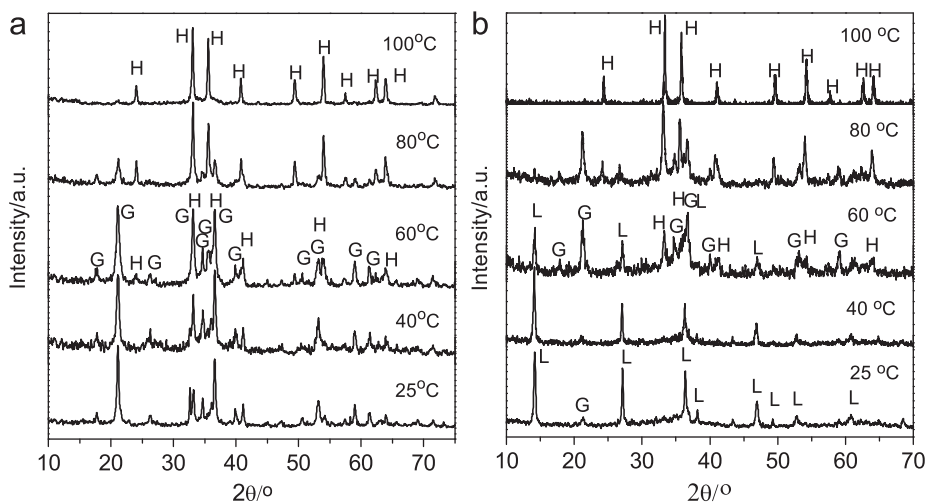


Fig. 2. XRD patterns of the products obtained at pH 7 and different temperatures using (a) $\text{NH}_3 \cdot \text{H}_2\text{O}$ and (b) NaOH as precipitants. L: $\gamma\text{-FeOOH}$, G: $\alpha\text{-FeOOH}$, H: $\alpha\text{-Fe}_2\text{O}_3$.

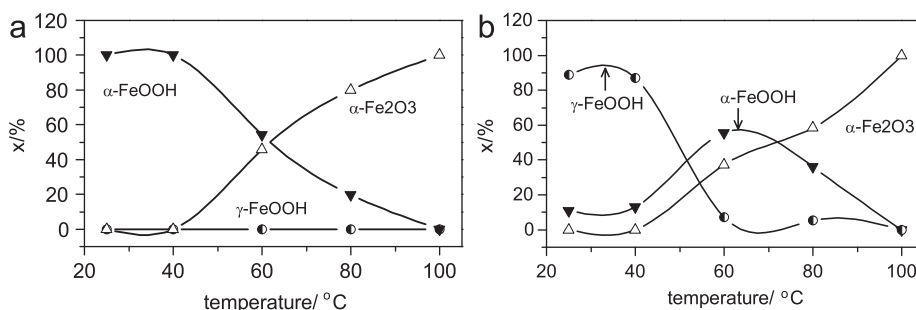


Fig. 3. Changes of the proportion of various species in the products with temperature using (a) $\text{NH}_3 \cdot \text{H}_2\text{O}$ and (b) NaOH as precipitants.

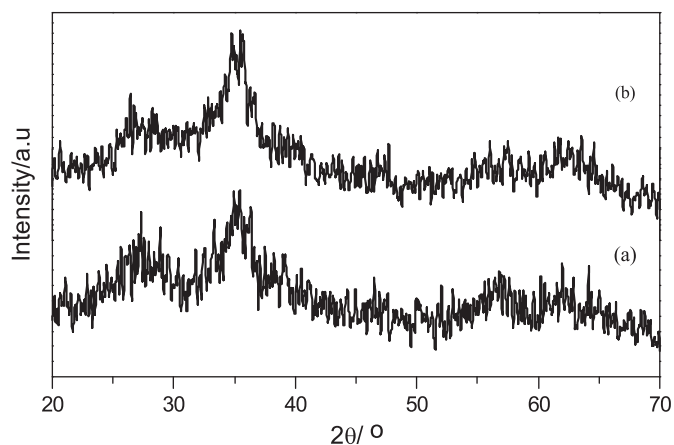


Fig. 4. XRD patterns of ferrihydrites prepared at pH 7 and RT using (a) $\text{NH}_3 \cdot \text{H}_2\text{O}$ and (b) NaOH as precipitants.

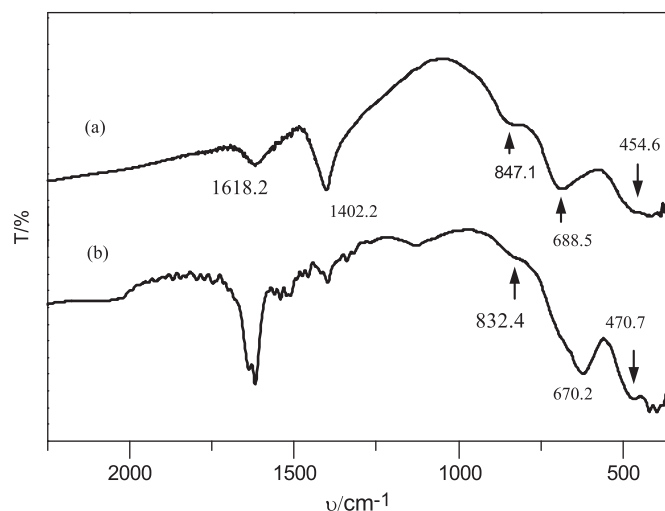


Fig. 5. IR patterns of ferrihydrites prepared at pH 7 and RT using (a) $\text{NH}_3 \cdot \text{H}_2\text{O}$ and (b) NaOH as precipitants.

aggregation of ferrihydrite [17]. In the same reaction system, the formations of lepidocrocite and goethite in solution are competitive to each other. In the NaOH medium, Fe(II) ions catalyze ferrihydrite to dissolve rapidly into solution in forms of Fe(OH)_2^+ , Fe(OH)_2^+ or $\text{Fe}_2(\text{OH})_4^+$ ions, which leads to the formation of lepidocrocite [13]. However, the situation is relative complicated when $\text{NH}_3 \cdot \text{H}_2\text{O}$ using as a precipitant. Andreeva et al. [21] thought that during the dissolution of ferrihydrite, most probably, an complexes of the type $[\text{Fe}(\text{OH})_4]^- \cdot \text{NH}_4^+$ was formed and $[\text{Fe}(\text{OH})_4]^- \cdot \text{NH}_4^+$ favored the formation of goethite. However, NH_4^+ has no more lone electron pair located on nitrogen, so it

cannot give rise to metal complexes. We inferred that the complexes $[\equiv\text{Fe}^{\text{III}}(\text{OH})_n(\text{NH}_3)_m]^{3-n}$ formed between Fe(III) ions and NH_3 molecule favored the formation of polymer of Fe(III) , thus, the formation of goethite instead of the nucleation of lepidocrocite. On the other hand, the coordination between Fe(III) and NH_3 hinders more or less Fe(II) from interacting with the ferrihydrite aggregate surface, which makes the dissolution of ferrihydrite be inhibited, that is, the formation of lepidocrocite be

inhibited. Anyway, the introduction of NH_3 molecule favored the formation of goethite. The following results further support this conclusion.

3.3. The effect of amine on the transformation of ferrihydrite

Fig. 7 presents the XRD patterns of the products obtained in the presence of different amounts of hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$). As shown in Fig. 7, with the increase in the amount of hexamethylenetetramine, the formation of lepidocrocite is retarded. When the concentration of hexamethylenetetramine reached 0.9 mol/L, lepidocrocite was not detected in the product (Fig. 7c). IR spectra of the products give a similar conclusion (Fig. 8). In Fig. 8, the bands at ~ 889.1 and ~ 796.4 cm^{-1} are attributed to δ_{OH} in plane bending vibration and γ_{OH} out of plane bending vibration of goethite, respectively. The band at ~ 621.9 and ~ 479.2 cm^{-1} are assigned to Fe–O stretching vibration. Comparing Figs. 8a and c with 8b, it was found that the intensity of the band (~ 621.9 cm^{-1}) in Fig. 8b is larger than those in Fig. 8a and c. This is probably related to the crystallinity of the samples [20].

Subsequently, ethanolamine, diethanolamine and triethanolamine were introduced into the reaction system, respectively. Fig. 9 presents the XRD patterns of the products. As can be seen in Fig. 9, ethanolamine and diethanolamine show a similar effect to $\text{C}_6\text{H}_{12}\text{N}_4$ (Fig. 9a and b), that is, the formation of lepidocrocite is retarded. However, when triethanolamine was introduced after an aging time of 7 days the final product was ferrihydrite (Fig. 9c).

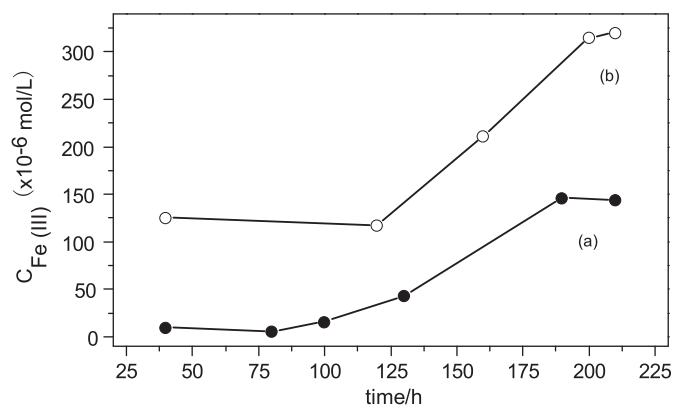


Fig. 6. The concentration Fe(III) ions in solution versus the reaction time: (a) $\text{NH}_3 \cdot \text{H}_2\text{O}$ system and (b) NaOH system. Ferrihydrite was prepared at pH 7 and aged at 40 °C.

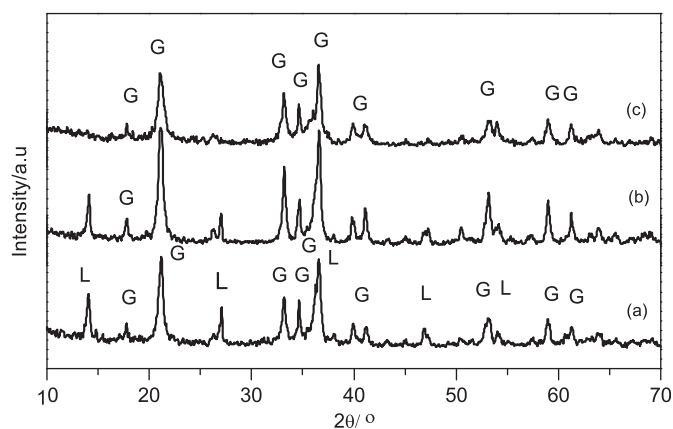


Fig. 7. XRD patterns of the products obtained by ageing ferrihydrite at 40 °C and pH 7 for 6 h in the presence of $\text{C}_6\text{H}_{12}\text{N}_4$. (a) $C_{\text{C}_6\text{H}_{12}\text{N}_4} = 0.15$ mol/L, (b) $C_{\text{C}_6\text{H}_{12}\text{N}_4} = 0.3$ mol/L, (c) $C_{\text{C}_6\text{H}_{12}\text{N}_4} = 0.9$ mol/L. L: γ -FeOOH, G: α -FeOOH.

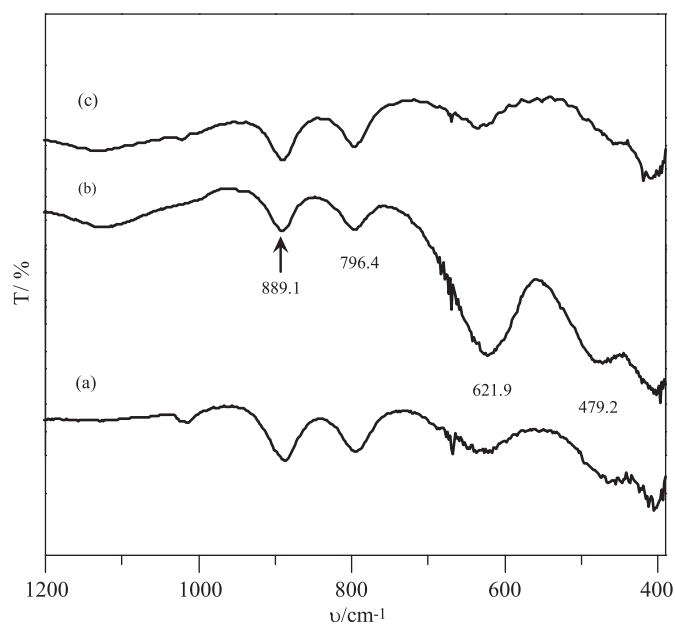


Fig. 8. IR spectra of the products obtained by ageing ferrihydrite at (a) 25 °C for 48 h, (b) 40 °C for 6 h and (c) 60 °C for 1.5 h. $C_{\text{C}_6\text{H}_{12}\text{N}_4} = 0.9$ mol/L, $C_{\text{Fe(III)}} = 0.5$ mol/L, pH = 7, $n_{\text{Fe(II)}}/n_{\text{Fe(III)}} = 0.02$.

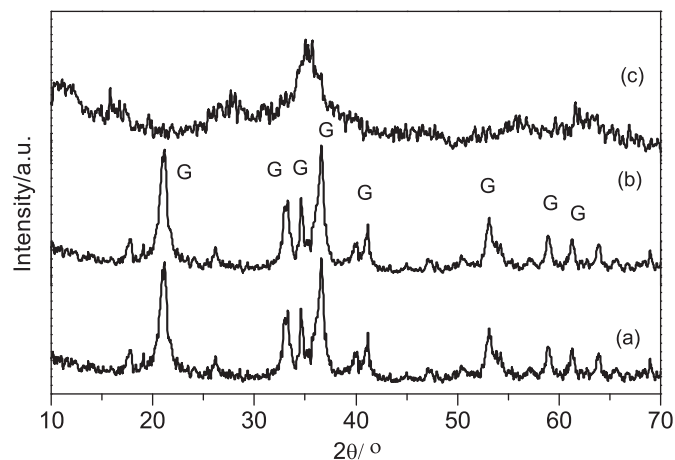


Fig. 9. XRD patterns of the products by ageing ferrihydrite at 40 °C and pH 7 in the presence of ethanolamine, diethanolamine and triethanolamine. (a) $C_{\text{ethanolamine}} = 1.0$ mol/L, $t = 44$ h, (b) $C_{\text{diethanolamine}} = 0.2$ mol/L, $t = 40$ h, (c) $C_{\text{triethanolamine}} = 0.1$ mol/L, $t = 7$ days.

Comparing the transformation of ferrihydrite with and without amine, whichever amine is introduced, the transformation becomes difficult and even it does not occur (e.g. the introduction of triethanolamine). We thought that these amines and ammonia are similar in their effect on the transformation of ferrihydrite. On the one hand, the complexes $[\equiv\text{Fe}^{\text{III}}(\text{OH})_n\text{A}_m]^{3-n}$ (Here A represents amines) formed between Fe(III) ions and amine molecule favored the formation of polymer of Fe(III), thus, the formation of goethite. The differences in the different amines probably come from the steric hindrance of the complexes of Fe(III) with amines. The steric hindrance for primary amine is the least, so the formation of polymer is the easiest, thus the formation of goethite is the easiest. The steric hindrance for tertiary amine is the largest and its introduction completely inhibits the transformation of ferrihydrite. On the other hand, the introduction of amine hinders Fe(II) from reaching the ferrihydrite

surface or from interacting with the ferrihydrite aggregate surface. Thus, the rapid dissolution of ferrihydrite in the presence of Fe(II) was greatly hindered. That is to say, the formation of lepidocrocite is hindered and ferrihydrite transforms to goethite.

3.4. The effect of coordination ions on the transformation of ferrihydrite

It is well known that F^- and $C_2O_4^{2-}$ ions have complexation with Fe(III). Li et al. [22] found that on the surface of iron oxides, oxalic acid is first adsorbed by iron oxide particles to form iron oxide–oxalate complexes of $[≡Fe^{III}(C_2O_4)_n]^{3-2n}$. Therefore, we deduce that it is possible that F^- and $C_2O_4^{2-}$ ions have also significant influence on the transformation of ferrihydrite. Fig. 10 presents XRD patterns of the products obtained in the presence of $C_2O_4^{2-}$ ions. As we deduced, $C_2O_4^{2-}$ ions were observed to retard the formation of lepidocrocite. The results obtained by introducing F^- ions show a similar effect (Fig. 11).

The possible reasons are thought as follows. In the presence of some coordination ions such as $C_2O_4^{2-}$ and F^- ions, Fe(III) ions dissolved from ferrihydrite into solution exist in form of the

complexes $[≡Fe^{III}(C_2O_4)_n]^{3-2n}$ or $[≡Fe^{III}F_n]^{3-n}$ instead of the form of $Fe(OH)^{2+}$, $Fe(OH)_2^+$ or $Fe_2(OH)_2^{2+}$. Those complexes are favorable for the formation of polymer and then goethite. At the same time, the interaction between Fe(II) and ferrihydrite aggregate, that is, the rapid dissolution of ferrihydrite is limited, which favors the oriented aggregation mechanism and the formation of goethite favorable. In a word, when Fe(III) co-existed with some coordination ions, ferrihydrite is subjected to transform into goethite.

4. Conclusions

- The products obtained by using NaOH, LiOH, KOH and $NH_3 \cdot H_2O$ as precipitants are different under the same conditions. The introduction of ammonia into the reaction system is responsible for those differences. The results showed that the effect of ammonia on the transformation of ferrihydrite works at low temperatures.
- Some amines (e.g. ethanolamine, diethanolamine and hexamethylenetetramine) and some coordination ions (e.g. F^- and $C_2O_4^{2-}$ ions) have similar effects on the transformation of ferrihydrite to ammonia. However, the introduction of triethanolamine completely inhibits the transformation of ferrihydrite.
- The common point for ammonia, amines and the coordination ions of Fe(III) ions in the effect on the transformation of ferrihydrite is the formation of complexes of Fe(III) $[≡Fe^{III}(OH)_nA_m]^{3-n}$ (Here A represents ammonia or amines), $[≡Fe^{III}(C_2O_4)_n]^{3-2n}$ and $[≡Fe^{III}F_n]^{3-n}$, which favors ferrihydrite transforming to goethite instead of lepidocrocite.

Acknowledgments

This work was supported by a Grant from the Natural Science Foundation of China (20877021) and Hebei Province (E2007000276) and Ph.D. Programs Foundation and Key Programs of Hebei Normal University (L2005B15 and L2007z06).

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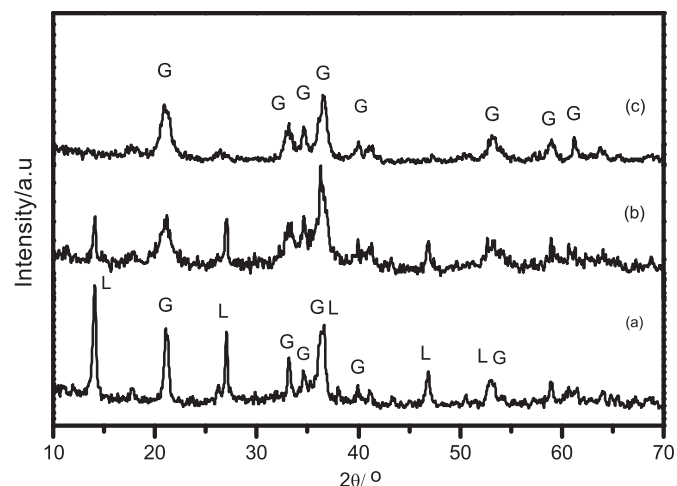


Fig. 10. XRD patterns of the products by ageing ferrihydrite at 40 °C and pH 7 in the presence of $C_2O_4^{2-}$ ions. (a) $C_{Na_2C_2O_4} = 0$ mol/L, $t = 5$ h, (b) $C_{Na_2C_2O_4} = 0.0125$ mol/L, $t = 24$ h, (c) $C_{Na_2C_2O_4} = 0.025$ mol/L, $t = 48$ h. L: γ -FeOOH, G: α -FeOOH.

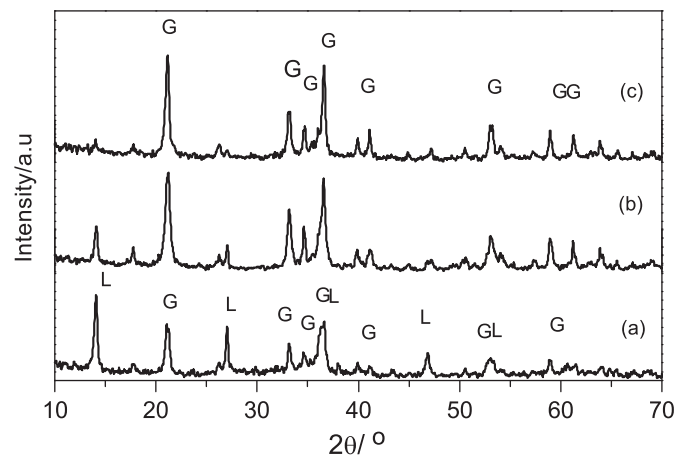


Fig. 11. XRD patterns of the product by ageing ferrihydrite at 40 °C and pH 7 in the presence of F^- ions. (a) $C_{F^-} = 0$ mol/L, $t = 5$ h, (b) $C_{F^-} = 0.1$ mol/L, $t = 48$ h, (c) $C_{F^-} = 0.15$ mol/L, $t = 72$ h. L: γ -FeOOH, G: α -FeOOH.