



Comparison study on transformation of iron oxyhydroxides: Based on theoretical and experimental data

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ABSTRACT

We have investigated the catalytic transformation of ferrihydrite, ferroxhyte, and lepidocrocite in the presence of Fe(II). In this paper, the transformation from akaganeite and goethite to hematite in the presence of trace Fe(II) was studied in detail. The result indicates that trace Fe(II) can accelerate the transformation of akaganeite and goethite. Compared with the transformation of other iron oxyhydroxides (e.g., ferrihydrite, ferroxhyte, lepidocrocite, and akaganeite), a complete transformation from goethite to hematite was not observed in the presence of Fe(II). On the basis of our earlier and present experimental results, the transformation of various iron oxyhydroxides was compared based on their thermodynamic stability, crystalline structure, transformation mechanism, and transformation time.

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1. Introduction

The chemistry of iron oxyhydroxides, including their species and structure as well as the transformation between them, is very rich. To date, 16 iron compounds are either found in nature or synthesized in the laboratory [1]. The stability of these compounds varies with species. Ferrihydrite, ferroxhyte, lepidocrocite, akaganeite, goethite, and hematite are very important iron (hydr)oxides. Among them, from a thermodynamical point of view, hematite is the most stable species (Table 1) [2–6]. Iron oxyhydroxides can transform to hematite under appropriate conditions. In fact, such transformations have been reported [7–10].

The transformation from various iron oxyhydroxides to hematite is classified into two kinds of reaction. One is the thermal transformation that takes place in the dry state and only at elevated temperatures. The thermally induced transformation mechanism is still a controversial subject and very different primary crystallization products can be identified depending on the atmosphere, heating conditions, sample weight, material thickness, and sample character [11]. The other transformation takes place in the liquid phase. Many studies have shown that the convertibility from iron oxyhydroxides to hematite in liquid phase depends on the precursor's reactivity. The reactivity is very high for two-line ferrihydrite, which transforms to hematite even at 4 °C, although

several years are needed for the transformation to occur at this temperature for the transformation of ferrihydrite to occur [8]. Ferroxhyte, a poorly crystalline iron oxyhydroxide, can transform to a more stable iron oxyhydroxide or oxide [9]. Lepidocrocite can transform into hematite and its reactivity depends on its crystalline [10]. Compared with ferrihydrite and ferroxhyte, akaganeite and goethite are well-crystallized species and their transformation to hematite can only occur under very specific conditions. Sugimoto et al. [12] reported that the time necessary for the complete transformation of akaganeite into hematite is about 7 days at 100 °C. Goethite, a more stable phase, is even less reactive. Goethite needles that are ca. 50 nm long need hydrothermal treatment at 160–180 °C to convert to hematite in one week [8].

Two mechanisms have been proposed with regard to the transformation of different iron species: the dissolution re-precipitation mechanism and the solid-state transformation mechanism or topotactic transformation. The dissolution re-precipitation mechanism is achieved only in the liquid phase while a solid-state or topotactic transformation occurs both in liquid phase (e.g., the transformation from ferrihydrite to hematite) [13] and in solid state (e.g., the transformation from lepidocrocite to maghemite by thermal dehydration) [7]. For the solid-state or topotactic transformation, there is an agreement in the structure of precursor and final product. In this case, kinetic phenomena are more important than laws of thermodynamics to explain the experimental results found [7]. A dissolution re-precipitation process depends on the solubility and dissolution rate of the precursor, in which there is no structural relationship between the precursor and the final product.

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Table 1
The Gibbs free energy of formation for different iron oxides.

Species	Gibbs free energy of formation: $\Delta_f G^\circ(298.15\text{ K})/\text{kJ/mol}$
2-Line ferrihydrite	-708.5 ± 2.0
Feroxyhyte	-478.1 ± 2.0
Lepidocrocite	-480.1 ± 1.4
Akaganeite	-481.7 ± 1.3
Goethite	-498.8
Hematite	-742.2

Recently, our group investigated the transformation of various iron oxyhydroxides and found that the introduction of trace Fe(II) species can clearly accelerate the transformation of ferrihydrite, feroxyhyte, and lepidocrocite [9,10,13]. To further understand the action of Fe(II) as a catalyst, this paper investigates in detail the transformation from akaganeite and goethite to hematite in the presence of trace Fe(II). The transformation of various iron oxyhydroxides is also compared based on experimental results, thermodynamic stability, crystalline structure, and transformation mechanism.

2. Experimental methods

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and NaOH of analytical purity and distilled water were used. The ferric salt solutions were filtered through a 0.22 μm Millipore filter to remove any particulate contaminants before use.

Akaganeite was prepared using ferric chloride as raw material following the procedure described in ref. [14]. Briefly, FeCl_3 solution was adjusted to the concentration of $[\text{Fe}^{3+}] (< 0.1\text{ mol/L})$ and was aged at 80 °C for 8 h, leading to hydrolysis and producing yellow suspensions. The yellow deposit was confirmed as akaganeite using X-ray diffraction (XRD). To increase the concentration of akaganeite suspension, some of the supernatant was removed after centrifugation. The final concentration of akaganeite suspension was 0.3 mol/L.

Goethite was prepared using ferric sulfate as raw material according to the procedure described in ref. [15]. Briefly, 6.0 mol/L NaOH solution was added into 50 mL of $\text{Fe}_2(\text{SO}_4)_3$ solution (1.0 mol/L) and vigorously stirred until a desired pH varying around 7 was achieved; it was then followed by the addition of Fe(II) ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) solution ($n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$) to the above mixture. The pH of the system was again adjusted to 7 by adding a dilute NaOH solution (1.0 mol/L). The total volume of the system was also 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 was aged in closed polypropylene bottles at 25 °C for two days. The products were confirmed as goethite by XRD.

Subsequently, the pH of the prepared akaganeite or goethite suspension was again adjusted to 7 using a dilute NaOH solution (1.0 mol/L), followed by the addition of Fe(II) solution ($n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$) to the suspension. This suspension was then heated, with nitrogen flowing within the vessel until it boiled. The suspension was allowed to boil and reflux for a certain time, varying from 1 to 12 h, under vigorous stirring. The product was centrifuged and washed thoroughly with distilled water and then dried at about 70–80 °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 products consist of a mixture of akaganeite and hematite, the proportion of each compound was estimated by EVA software installed on X-ray diffractometer according to (104) peak of hematite and (110) peak of akaganeite.

Transmission electron micrographs (TEM) were obtained with a Hitachi H-7500. The samples were dispersed in ethanol using an ultrasonic treatment.

3. Results and discussion

3.1. Effect of trace Fe(II) on the transformation of $\beta\text{-FeOOH}$

Fig. 1 shows the XRD patterns of the product obtained in the presence or absence of trace Fe(II). The sample without Fe(II) showed no noticeable change even after 8 h (Fig. 1a). However, in the presence of trace Fe(II), a small amount of hematite was formed after 1 h. At this time, the proportion of hematite in the product was about 27.6% (Fig. 1b). The amount of hematite gradually increased as the transformation proceeded, with the proportion of hematite in the product reaching about 80.6% after 8 h (Fig. 1c). This result indicates that the presence of trace Fe(II) can accelerate the transformation of akaganeite.

Figs. 2 and 3 present the XRD patterns and the TEM images of the samples, respectively, obtained at different times in the transformation of akaganeite. Fig. 4 presents the curve of the proportion of both hematite and akaganeite in the reaction system in relation to the reaction time. Fig. 2a shows the XRD pattern of the precursor akaganeite and Fig. 3a indicates that such akaganeite are needle-like or plate-like particles. When the suspension of akaganeite was refluxed for 1 h, hematite was detected by XRD (Fig. 2b). At this time, only 27.6% of akaganeite was transformed to hematite and the obtained hematite particles are spherical (Fig. 3b). Hereafter, the amount of hematite in the system increased gradually and that of akaganeite decreased as the transformation proceeded (Figs. 2c–e, 3c–e, and 4). When akaganeite was refluxed for 8 h, about 80.6% of akaganeite was transformed. A complete transformation was observed at 12 h (Figs. 2f and 3f). The particle size distribution of the obtained hematite is in the range of 50–180 nm, indicating that second nucleation probably happens during the transformation from akaganeite to hematite.

In the presence of trace Fe(II), the transformation from akaganeite to hematite accelerated significantly. In order to

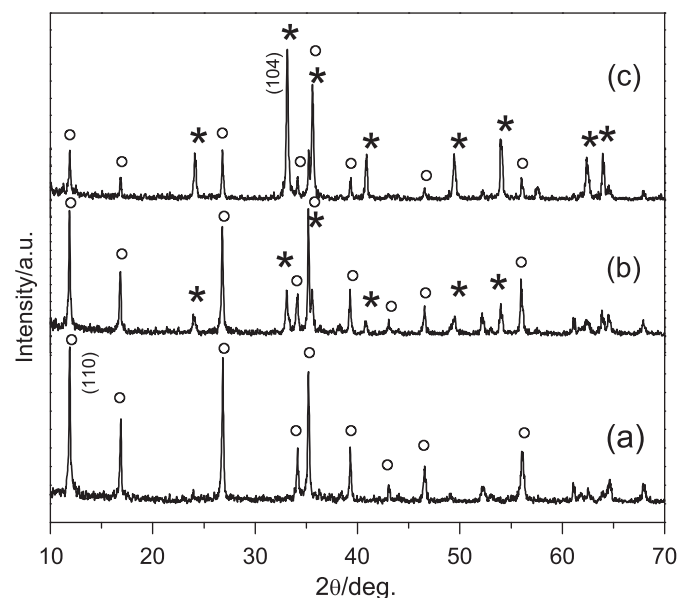


Fig. 1. XRD patterns of products obtained in the presence or absence of Fe(II). $c_{\text{Fe(III)}}=0.3\text{ mol/L}$; pH = 7; (a) $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0$, $t=8\text{ h}$, (b) $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$, $t=1\text{ h}$, (c) $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$, $t=8\text{ h}$; ○: Akaganeite, *: Hematite.

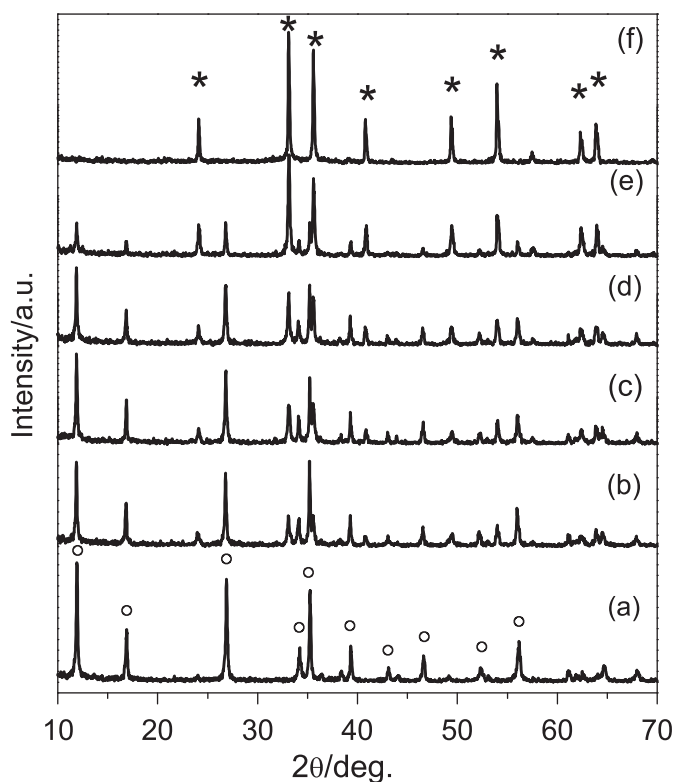


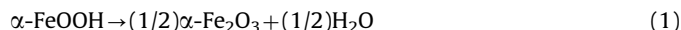
Fig. 2. XRD patterns of products obtained at different reaction times: (a) $t=0$ h, (b) $t=1$ h, (c) $t=3$ h, (d) $t=5$ h, (e) $t=8$ h, (f) $t=12$ h, and $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$; \circ : Akaganeite, $*$: Hematite.

understand the transformation mechanism from akaganeite to hematite, a special experiment was designed. The akaganeite suspension was centrifuged and washed thoroughly with distilled water after its preparation. It was then again dispersed into distilled water, followed by the addition of trace Fe(II) and the adjustment of the pH of the reaction system to pH 7. When the above reaction system was refluxed for a certain time (e.g., 3 h), the formation of hematite was detected. The formation of hematite from the akaganeite washed by distilled water was much slower than that from the akaganeite not washed by distilled water. This result indicates that the nucleation for akaganeite and hematite occurs simultaneously in the preparation process of akaganeite [16]. The action of Fe(II) is to accelerate the transformation from akaganeite to hematite even under the absence of the nuclei of hematite. It has been confirmed that the transformation from akaganeite to hematite in liquid phase was completed by a dissolution re-precipitation [12]. According to the literature data and our results, it is concluded that the action of Fe(II) lies in its capacity to accelerate the dissolution of akaganeite. No similarity in the structure between akaganeite and hematite also supplies a circumstantial evidence.

3.2. Transformation of goethite in the presence of Fe(II)

Figs. 5 and 6 present the XRD patterns and TEM images of the samples, respectively, obtained at different times in the transformation of goethite. When the suspension of goethite was refluxed for half an hour, only a little diffraction peak of hematite was detected by XRD (Fig. 5b) and some spherical hematite particles can be observed in Fig. 6b. It was also found that goethite particles grow. The amounts of hematite and goethite in the system remained almost constant (Fig. 5c–e). Flynn [17] posited

that the stability of goethite relative to hematite and water is uncertain. The ΔG_{298}^0 for reaction (1) is 0 ± 1 kJ/mol.



After analyzing the dependence of ΔG of reaction (1) on the particle size, Langmuir [18] concluded that the effect of particle size on ΔG becomes significant (exceeding 5 kJ/mol) for particle size $< 10^{-1}$ μm . Based on the above viewpoint, the results in Fig. 5 can be explained as follows. With the catalytic action of trace Fe(II), the very small goethite particles can dissolve to form Fe(III) ions. On the one hand, the dissolved Fe(III) ions can form hematite particles. On the other hand, these Fe(III) ions can cause goethite particles to grow. Interestingly, some hematite particles are embedded within the crystal of goethite (Fig. 6c and d). Repeat experiments revealed that this phenomenon is not occasional. We deduced that the separate hematite particles were probably formed by the little crystals of goethite through a dissolution re-precipitate mechanism, whereas the hematite particles embedded within the crystal of goethite were probably formed by topotactic transformation. The reason is discussed in Section 3.3.

3.3. Transformation mechanism of different iron oxyhydroxides in the presence of Fe(II)

We have reported the transformation of ferrihydrite, ferroxhyte, and lepidocrocite in the presence of trace Fe(II) [9,10,13]. The results indicate that the introduction of trace Fe(II) results in a rapid transformation from ferrihydrite or ferroxhyte to hematite [9,13]. It has been reported that Fe(II) can accelerate the dissolution of lepidocrocite [1]. Our results indicate that the velocity of the transformation of lepidocrocite in the presence of Fe(II) depends on its crystalline. A low-crystalline lepidocrocite can rapidly transform to spherical hematite particles in the presence of trace Fe(II) [10]. However, with the increase in the crystalline degree of lepidocrocite, its transformation rate becomes slow. Compared with the transformation of ferrihydrite, ferroxhyte, and lepidocrocite, the transformation rate of akaganeite in the presence of trace Fe(II) is much slower (Figs. 2–4). The transformation of goethite is also related to its crystalline. According to data from the literature and our results, very small goethite particles can transform to hematite. Once the crystal particles of goethite grow, its transformation becomes more difficult even in the presence of Fe(II) (Figs. 5 and 6).

According to our earlier and present results, although trace Fe(II) can accelerate the transformation from ferrihydrite, ferroxhyte, lepidocrocite, akaganeite, and goethite to hematite, there are great differences in their transformation time. The transformation time follows the order $t_{\text{ferrihydrite}} \leq t_{\text{ferroxhyte}} < t_{\text{lepidocrocite}} < t_{\text{akaganeite}} \ll t_{\text{goethite}}$. The thermodynamic stability of these iron oxyhydroxides follows the same order as well. For instance, a species with poor thermodynamic stability can easily transform to a stable one. In addition to the thermodynamic stability of the precursor, its crystal structure is also an important factor to influence the transformation. It is probable that the former concerns the driving force of transformation while the later is influencing the kinetic. Table 2 presents the structure parameters of different iron oxyhydroxides and the transformation mechanism to hematite [1,19]. Comparing the structure of the five iron oxyhydroxides with that of hematite, it was found that ferrihydrite, ferroxhyte, and hematite all belong to the hexagonal crystallographic system and share a similar hexagonal close-packed anion sublattice. The similar crystal structure between them allows the possibility of solid-state transformation. Therefore, the transformation from ferrihydrite and ferroxhyte to hematite can be carried out not only by dissolution re-precipitation

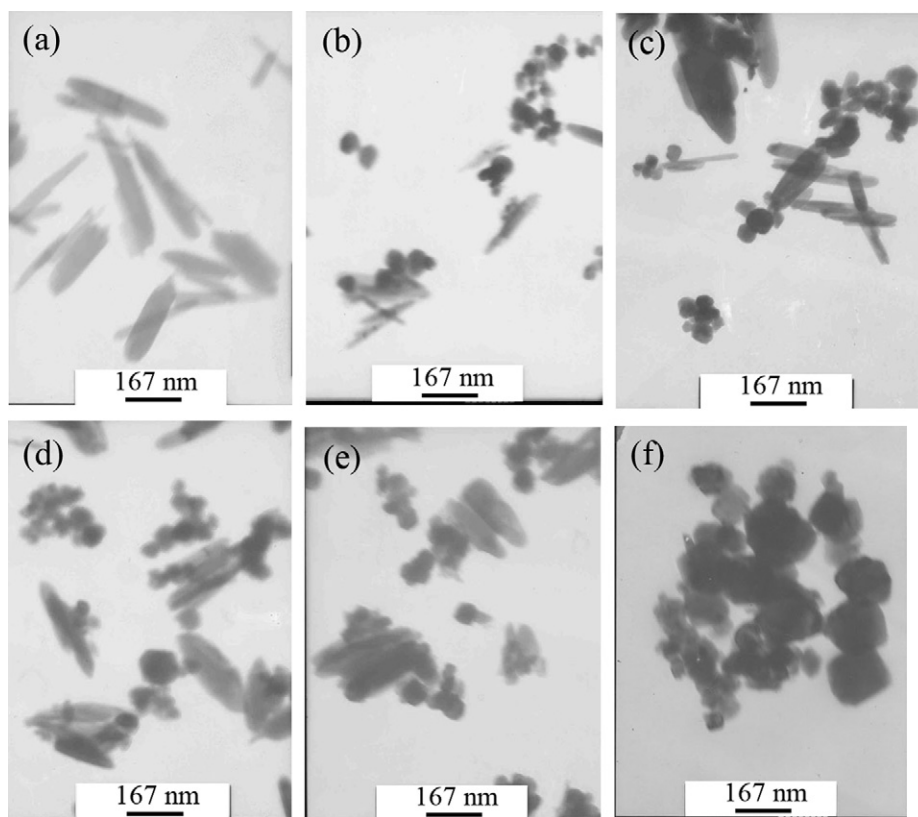


Fig. 3. TEM images of products obtained at different reaction times: (a) $t=0$ h, (b) $t=1$ h, (c) $t=3$ h, (d) $t=5$ h, (e) $t=8$ h, (f) $t=12$ h, and $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$.

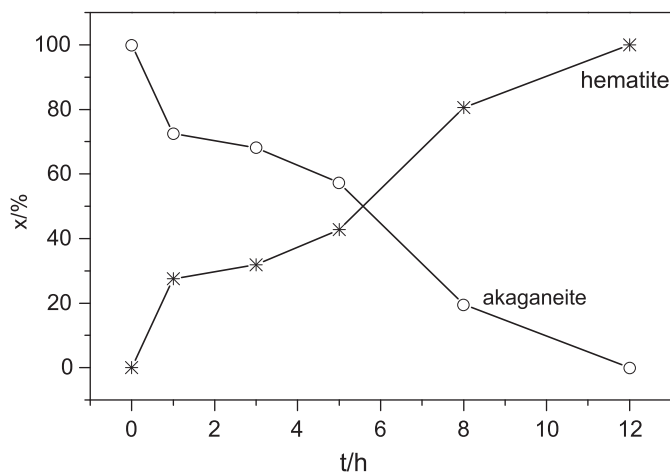


Fig. 4. The proportion of hematite and akaganeite in the reaction system versus the reaction time. $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.02$, $c_{\text{Fe(III)}}=0.3$ mol/L, pH=7.

mechanism but also by solid-state transformation. Moreover, the transformation velocity by solid-state transformation is much larger than that by dissolution re-precipitation transformation [13]. Hence, the coexistence of the two mechanisms shortened the completion of the transformation from ferrihydrite and ferroxhyte to hematite.

Compared with hematite, lepidocrocite and akaganeite belong to different crystallographic systems. Moreover, they share different stacking of close-packed anions. The transformation from lepidocrocite and akaganeite to hematite in solution was carried out only by the dissolution re-precipitate mechanism. The dissolution process of iron oxyhydroxides usually proceeds slowly, especially for a well-crystalline species. Thus, longer time to complete the transformation from lepidocrocite and akaganeite to hematite is needed. Compared

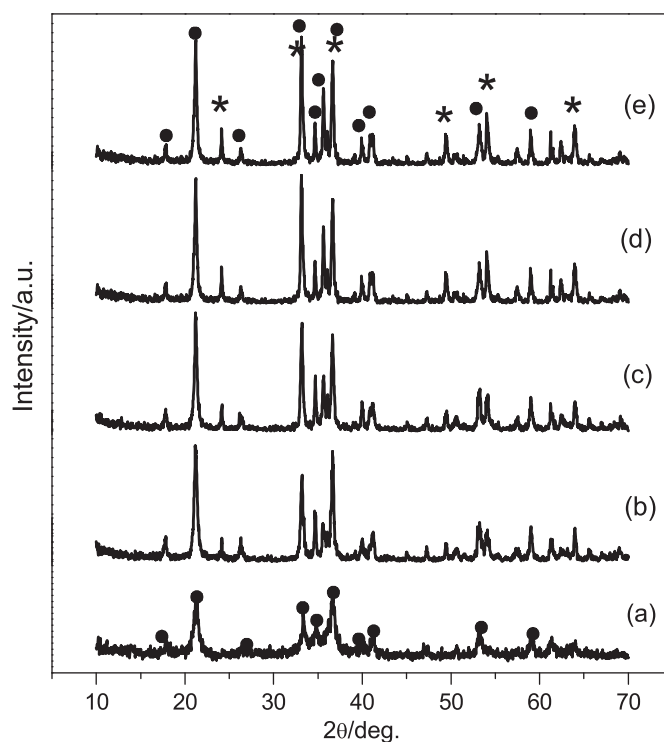


Fig. 5. XRD patterns of products obtained at different reaction times: (a) $t=0$ h, (b) $t=0.5$ h, (c) $t=1$ h, (d) $t=2$ h, (e) $t=5$ h, and $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.04$; ●: Goethite, *: Hematite.

with the transformation without Fe(II), the introduction of Fe(II) can accelerate the dissolution of lepidocrocite and akaganeite, which leads to rapid transformation to hematite.

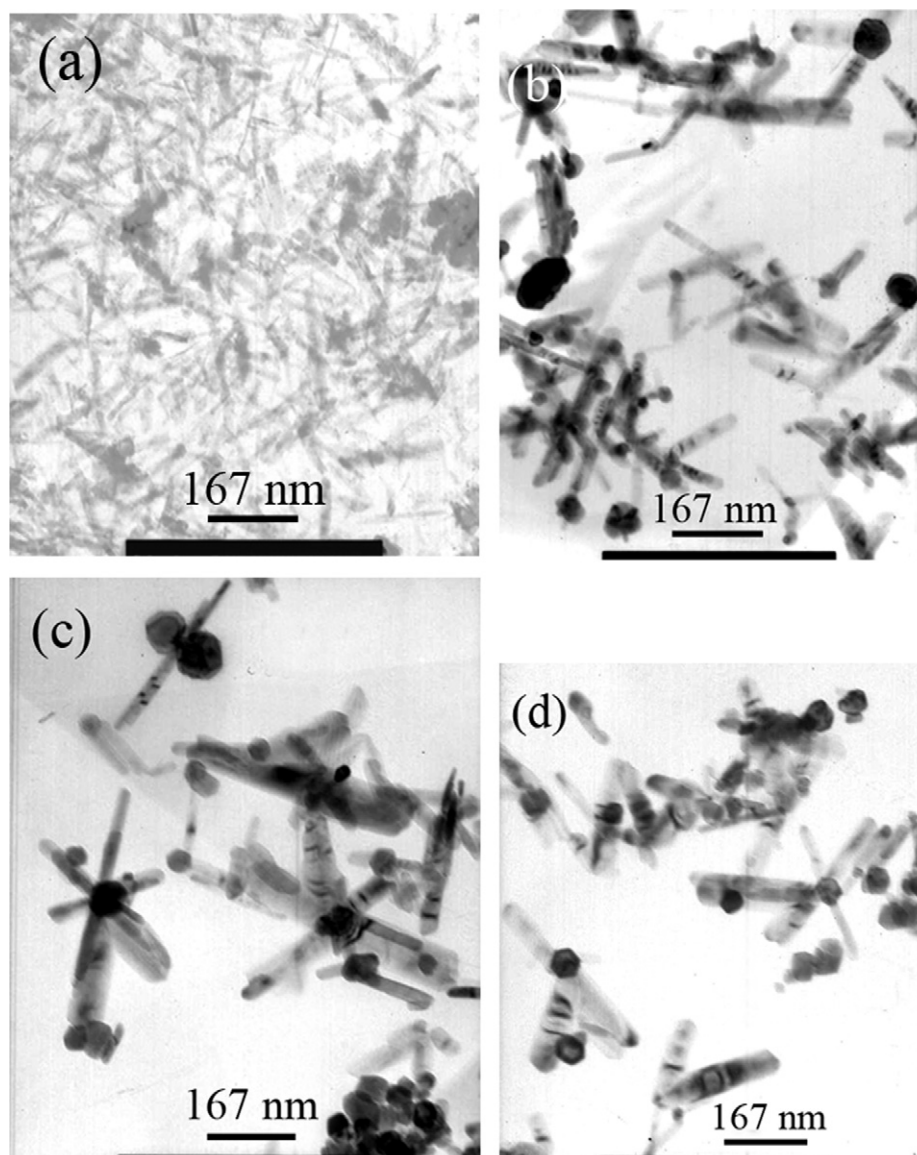


Fig. 6. TEM images of products obtained at different reaction times: (a) $t=0$ h, (b) $t=0.5$ h, (c) $t=1$ h, (d) $t=2$ h, and $n_{\text{Fe(II)}}/n_{\text{Fe(III)}}=0.04$.

Table 2

The crystal data of iron (hydro)oxides.

Mineral name	Composition	Crystallographic system	Space group	Stacking of close packed anions	Transformation mechanism to hematite
Ferrihydrite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	Hexagonal	$P3_1c$	ABAB[001]	Dissolution-re-precipitation Solid state transformation
Feroxyhyte	$\delta\text{-FeOOH}$	Hexagonal	$P3m1$	ABAB[001]	Dissolution-re-precipitation Solid state transformation
Lepidocrocite	$\gamma\text{-FeOOH}$	Orthorhombic	$Bbmm$	ABCABC[105]	Dissolution-re-precipitation
Akaganeite	$\beta\text{-FeOOH}$	Monoclinic	$I2/m$	bcc	Dissolution-re-precipitation
Goethite	$\alpha\text{-FeOOH}$	Orthorhombic	$Pnma$	ABAB[001]	Dissolution-re-precipitation topotactic transformation
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Hexagonal	$R\bar{3}c$	ABAB[001]	

Of the five iron oxyhydroxides, the transformation of goethite is the slowest. Even in the presence of Fe(II), a complete transformation from goethite to hematite was not observed. Thermodynamically, on the one hand, goethite is considered to be one of the most stable iron oxyhydroxides. Kinetically, on the other hand, the dissolution rate of synthetic goethite depends on its crystal morphology, size, and crystallinity. The lowest dissolution rate/unit area was observed for acicular crystals [1]. Thus, with the catalytic action of trace Fe(II),

only very small goethite particles can dissolve to form hematite. Interestingly, goethite and hematite share similar stacking of close-packed anions even if they belong to different crystallographic systems. Cudennec and Lecerf [7] posited that goethite can transform to hematite through topotactic transformation. Usually, the topotactic transformation from goethite to hematite is carried out by a thermal transformation in the dry state. In Fig. 6c and d, it can be seen that some of the hematite particles formed were embedded

within the crystal of goethite. We deduced that these hematite particles were probably formed by a topotactic transformation of goethite. A complete transformation from goethite to hematite was not observed due to the lower reaction temperature.

4. Conclusions

In this paper, the transformation from akaganeite and goethite to hematite in the presence of trace Fe(II) was investigated. The transformation of various iron oxyhydroxides in the presence of trace Fe(II) was compared based on experimental results, thermodynamic stability, crystalline structure, and transformation mechanism. The results indicate that Fe(II) can clearly accelerate the transformation of akaganeite. Goethite cannot completely transform to hematite even in the presence of Fe(II). The transformation time of the five iron oxyhydroxides follows the order ferrihydrite \leq ferrosulfate $<$ lepidocrocite $<$ akaganeite \ll goethite, which is consistent with the order of their thermodynamic stability. In the presence of Fe(II), all the five iron oxyhydroxides can transform to hematite by a catalytic dissolution re-precipitation mechanism. Moreover, ferrihydrite and ferrosulfate can transform to hematite by a catalytic solid-state transformation mechanism due to the similarity in the crystal structure between the precursor and the product, leading to a very rapid transformation rate. Goethite and hematite share similar stacking of close-packed anions even if they belong to different crystallographic systems, causing the transformation from goethite to hematite by topotactic transformation. Under boiling and refluxing condition, a complete topotactic transformation from goethite to hematite was not observed.

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