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Dissolution and oriented aggregation: transformation from lepidorocite to goethite by the catalysis of aqueous Fe (II)

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Abstract

At a low temperature, lepidocrocite-to-goethite occurred in the presence of Fe(II) ions, whereas lepidocrocite was stable in the absence of Fe(II) ions. The results reveal that Fe(II) accelerate the dissolution of the lepidocrocite . The dissolved Fe(III) ions hydrolysed to form goethite . The mechanism of transformation included dissolution-reprepitation and oriented aggregation.

1.Introduction

The iron oxide family consists of iron oxides, iron hydroxides and iron oxyhydroxides, all of which exist in nature. Iron oxides have 16 established polymorphs. Numerous transformations occur

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between the iron oxides and iron oxyhydroxides[1-3]. Among iron oxyhydroxides, goethite is the most stable phase, because of its lower Gibbs free energy[4]. Other iron oxyhydroxides can transform to goethite under appropriate conditions. These transformations between iron oxyhydroxides and iron oxides occur in soil and iron corrosion and other natural phenomena.

Previous works by Liu et al[2,5] on the transformation of ferrihydrite and feroxyhyte to hematite showed that the introduction of trace Fe(II) resulted in a rapid transformation from ferrihydrite and feroxyhyte to hematite at high temperatures. In phase transformation, the Fe(II) ions in solutions play an important catalytic role[3,5-7]. The contact of unreacted Fe(II) ions with Fe(III)-bearing minerals can lead to Fe(III) mineral transformation or change in of grain size through the conversion of an adsorbed Fe(II) into an Fe(III) atom (electron transfer)[8-10]. Therefore, understanding the effect of ferrous ions and the mechanism of the transformation between iron oxyhydroxides and iron hydroxides is important to clarify iron cycling, rust layer formation and the applications of the varying properties of Fe (III) phases.

The previous work mainly researched phase transformation and the mechanisms from ferrihydrite to iron oxides or iron oxyhydroxides[3]. The objectives of this study are therefore to investigate the transform between iron oxyhydroxides at room temperature and the mechanism of transformation.

2.Experimental

All reagents were used as received without further purification. Exactly120 mL of 0.01 mol L^{-1} EDTA-Na solution was poured into 1200 mL of 0.1 mol L^{-1} $FeSO_4$ solution. Then, the solution was adjusted to within a pH range of 8.3-8.5 using 6.0 mol L^{-1} NaOH solution. Air was pumped into the prepared solution at room temperature by stirring for 2 h. The orange-yellow deposit was centrifuged and repeatedly washed using distilled water.

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The γ-FeOOH particles were again uniformly dispersed in distilled water with a concentration in 0.3 mol L^{-1}. An aqueous FeSO$_4$ solution was added into the γ-FeOOH suspension. The molar ratio of ferrous ions to the γ-FeOOH suspension (R = C$_{[Fe(II)]}$/C$_{[FeOOH]}$) ranged from 0 to 0.06. The suspension was adjusted to pH 7 by adding a diluted NaOH solution. The suspension was aged for different lengths of time at 30 °C. The experiments were carried out under nitrogen gas, and oxygen-free distilled water was used in all stages. The final products were centrifuged, repeatedly washed with distilled water, and dried at room temperature.

X-ray diffraction (XRD) data were collected from the dried samples on a Bruker D8 Advance diffractometer with Cu-Kα radiation. Infrared (IR) spectra were obtained over a range of 400–4000 cm^{-1} with a NICOLET IS 50 Fourier transform IR (FTIR) spectroscopy. The morphologies of the samples were characterised by transmission electron microscopy (TEM) using a Hitachi H-7650 microscope operated at 80 kV. X-ray photoelectron spectroscopy analyses were carried out by using Thermo Scientific Escalab 250Xi spectrometer with Al K-alpha X-rays and Theta Probe. High-resolution TEM HRTEM images were obtained with a JEM-2100 at 80-200 kV.

3.Results and discussion

3.1 Synthesis of original γ-FeOOH aged in the absence of Fe(II) ions

The XRD and IR patterns of the original iron oxides and the samples aged for 120 h with R = 0 are shown in Figs. 1a and b. Fig. 1a indicates that the synthesised original γ-FeOOH particles were pure lepidocrocite with poor crystallisation. The IR spectra (Fig. 1b) confirmed that no other iron oxyhydroxide phases were present in detectable amounts in the samples, as specifically shown in the O–H bending (1154–1160, 1021, 744–755 cm^{-1})[11]modes of lepidocrocite. The XRD patterns and IR patterns in Fig. 1 indicate that no transformation into a new phase is observed. The TEM images

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in Fig. 1 c and d indicate no obvious difference between the original iron oxides and the samples

aged for 120 h with $R = 0$. Therefore, although lepidocrocite is a thermodynamically metastable

phase of iron oxyhydroxides, it was stable in our experiment.

Fig. 1

3.2. Synthesis of original γ-FeOOH aged in the presence of Fe(II) ions

The synthesis of the original γ-FeOOH aged in the presence of Fe (II) ions was characterised by

XRD, IR spectroscopy and TEM (Fig. 2). As shown in Fig. 2a, with $R = 0.004$, no goethite formed

when the samples were aged for 120 h. With $R = 0.02$, portions of the lepidocrocite particles

transformed into goethite. The FTIR spectra (Fig. 2b) exhibit in-plane and out-of-plane bending

mode vibrations of Fe_O_O_H at 791 and 890 cm^{-1}, respectively[12], thereby confirming that

goethite started to form in the samples. With $R = 0.04$ and $R = 0.06$, little magnetite formed (Fig. 2a).

The TEM image obtained from the lepidocrocite particles aged for 120 h with $R = 0.02$ (Fig. 2c)

indicates that an acicular and irregular-shaped morphology formed at the moment of aging for 120 h.

The results reveal that an appropriate amount of Fe (II) ions has obvious accelerating action in the

transformation of lepidocrociteeven even at room temperature.

Fig. 2

3.3. Mechanism of fast transformation in the presence of Fe(II)

The sample aged with $R = 0.02$ was monitored during the aging process to investigate the phase

transformation from lepidocrocite to goethite. The synthesis of the original γ-FeOOH aged with $R =$

0.02 for different lengths time was characterised by XRD and TEM (Figs. S1 and S2). In Fig. S1, the

diffraction peaks are assigned to lepidocrocite aged for 72 h. However, after aging for 73 h, peaks

caused by goethite appeared. The acicular goethite particles formed after aging for 73 h, as shown in

Fig. S2a. The number of goethite particles increased with aging time (Figs. S2b and c). The results

indicate that the transformation occurred between 72 and 73 h of aging. The sample aged with $R =$

0.02 for different length time were characterised by XPS (Fig. 3). Fig 3 displays the spectra of Fe 2p

in original sample and the original sample aged for 73 h. The peaks at Binding Energy of 711.59 and

725.4 eV in the original sample are attributed to Fe 2p3/2 and Fe 2p1/2 respectively, which is in

good agreement with γ-FeOOH[13]. When γ-FeOOH aged for 73 h with $R = 0.02$, the α-FeOOH has

a Fe (2p) spectrum similar, in many respects[13], so there were no obviously changes in Fe 2p

between the samples before and after aged with Fe(Ⅱ) ion for 73 h. Fe(III) compounds are always

high-spin, leading to complex multiplet-split Fe2p spectra. The satellite peaks around 719 eV of the

XPS spectra of Fe 2p is clearly distinguishable. The satellite peaks have been ascribed to shake-up or

charge transfer process[14]. The satellite peaks pertain to Fe(III)2p$_{3/2}$[14]. The existed satellite in Fig.

3a indicates that there was not Fe(II) in it. To further explore the change of the sample before and

after aged with Fe(Ⅱ) ion, the O 1s region was also characterized (shown in Fig. 3b). As shown in

Fig. 3b, the O 1s signal is multicomponent and was fitted with three curves[15]centered at 529.95,

531.27 and 532.56 eV, which corresponds to O^{2-}, OH^- and adsorbed H_2O. However, the O^{2-} peak, the

OH^- peak and the adsorbed H_2O peak in the sample aged for 73 h shift 0.15, 0.23, 0.49 eV,

respectively. Such a shift may suggest a change in chemical environment of the elements. Though

there were no changes of element, lepidocrocite was built with $FeO_4(OH)_2$ octahedral and goethite

was built with $FeO_3(OH)_3$ octahedra[16]. The change of the binding energy indicated that the ratio of

the chemical bond between Fe^{3+} and OH^- and chemical bond between Fe^{3+} and O^{2-} changed[17].

Fig. 3

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The pH and $C_{[Fe(III)]}$ values were monitored during the aging process for a more in-depth exploration of the phase transformation mechanism and the results are shown in Fig. S3. Fig. S3a) show that, in the absence of Fe(II), the concentration of Fe(III) in the supernatant liquor of the suspension was almost zero, whereas in the presence of Fe (II) ions, the concentration of Fe (III) in the supernatant liquor of the suspension distinctly increased. These results indicates that adding Fe(II) accelerated the dissolution of lepidocrocite. The obvious increasing of Fe (III) ions in the supernatant liquor of suspension maybe caused by an electron transfer taking place within the lepidocrocite and Fe (II) ions[18,19]. Firstly, the added Fe (II) ion was adsorbed on the surface of the particles of lepidocrocite. Secondly, the adsorbed Fe (II) ion lost the electron to form a new Fe (III) ion, and it hydrolyzed to form new polymer[12]. Meanwhile, the Fe (III) ion in lepidocrocite captured the electron from the adsorbed Fe (II) ion and changed into a new-born Fe (II) ion. And the new-born Fe (II) ion could obtain electron from the adjacent Fe (III). The electron transfer process conducted continuously. Therefore, the concentration in the supernatant liquor of the suspension increased obviously. Due to the very low activation energy, electron transfer is very quick [20,21]. So the Fe(III) ion rate of hydrolysis is slower than electron transfer and the concentration of the Fe(III) ion in the supernatant liquor of the suspension increased rapidly. In Fig. S3b, the pH value decreased from 7 to 6.14 with $R = 0$, whereas the value of pH decreased from 7 to 3.71 with $R = 0.02$ when lepidocrocite was aged for 120 h. The reasons for the decrease in the pH value are as follows: the dissolved Fe(III) ions hydrolysed to form a new polymer[12] and released protons. The HRTEM images (Fig. 4) were obtained to illustrate crystal growth. The morphology of the original lepidocrocite particles showed bullet-headed tails (Fig. 4a). Fig. 4a shows that the lattice fringe spacing of 0.209 nm corresponded to the (060) plane of lepidocrocite mineral and synthetic alike

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[22]. The HRTEM images in Fig. 4b and c indicate that the lattice fringe spacings of 0.256 and 0.269

nm corresponded to the (021) and (130) planes of goethite, respectively. The HRTEM images in Fig.

4b and c show that some small particles formed acicular shapes. The lepidocrocite particles were

assumed to have been initially dissolved by the catalysis of Fe(II) ions, and then Fe (III) ions

hydrolysed to form $Fe(OH)^{2+}$ and/or $Fe(OH)^{2+}$ and/or Fe^{3+} [12]. The absolute quantity of Fe(III) ions

increased with aging time, and the primary nanoparticles produced by hydrolysed Fe(III) ions in

number. Fig. 4b shows that the lattice fringe spacing of 0.256 nm corresponded to a (021) plane. The

acicular shapes of goethite particles have a closing form of {021} at the end [23]. Goethite particles

seemed to have nucleated first before a few primary nanoparticles approached each other with

crystallographic alignment[24]. Burleson and Penn [25] also proved that the transformation of

ferrihydrite to goethite preceded the formation of oriented aggregate. The isolated nanoparticles and

relatively dense nanoclusters formed the primary nanoparticles. Then, the aggregates of primary

nanoparticles increased separately. Long, thin assemblies composed of primary particles

subsequently began to appear, with their number concentrations increasing with time [24-26].

Fig. 4

Conclusions

Phase transformation from lepidocrocite to goethite in the presence of Fe(II) ions at a low

temperature was investigated in this paper. Results show that the mechanism of the phase

transformation from lepidocrocite to goethite with trace Fe(II) ions at room temperature is not only

dissolution re-precipitation mechanism but also including oriented aggregation mechanism**.** The

dissolution of lepidocrocite with Fe(II) ions is a precondition. Then, new Fe(III) ions hydrolysed into

primary nanoparticles. The primary nanoparticles aggregated with each other to form mesocrystals.

Finally, mesocrystals recrystallised to form goethite crystals.

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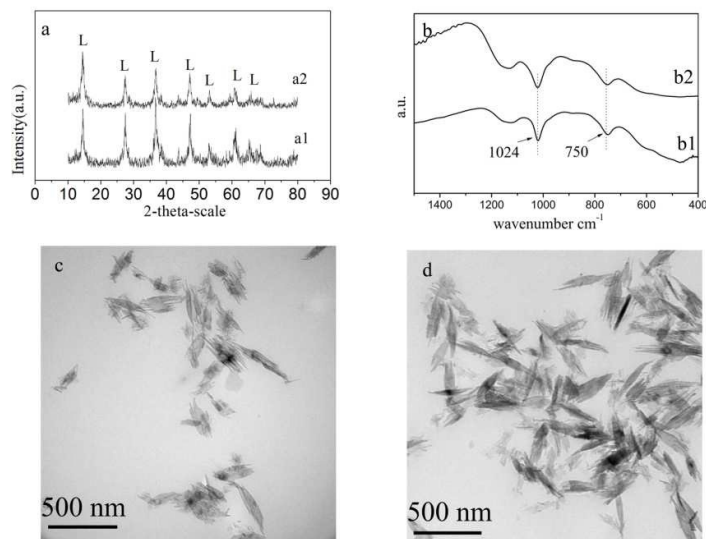
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Fig.1 (a) XRD patterns of the samples, (a1) the original iron oxides, and (a2) the sample aged for 120 h with $R = 0$; L: lepidocrocite; (b) IR spectra of the samples, (b1) the original iron oxides and (b2) the sample aged for 120 h with $R = 0$; (c) TEM image of the original iron oxides;(d) TEM image of the sample aged for 120 h with $R = 0$
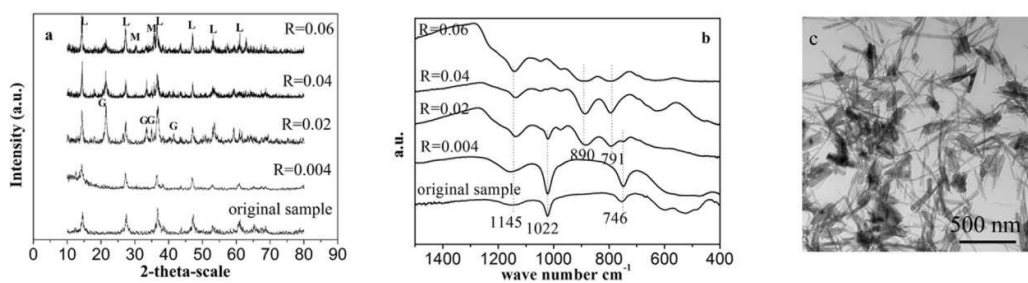

Fig. 2. (a) XRD patterns of the samples aged for 120 h; (b) IR spectra of the samples aged for 120 h; (c) TEM image of the sample aged for 120 h with $R = 0.02$.
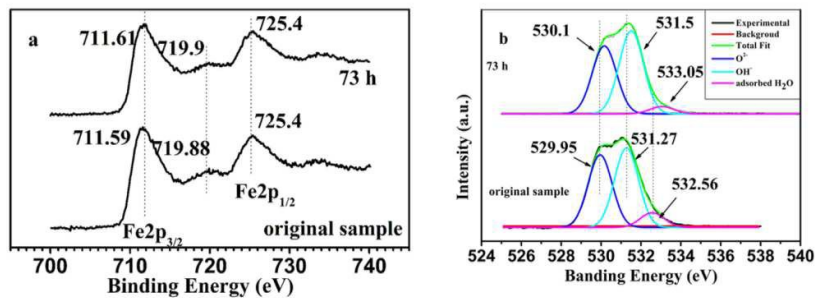
Fig. 3. The high resolution XPS spectra of (a) Fe 2p (b) O 1s collected from the original sample and
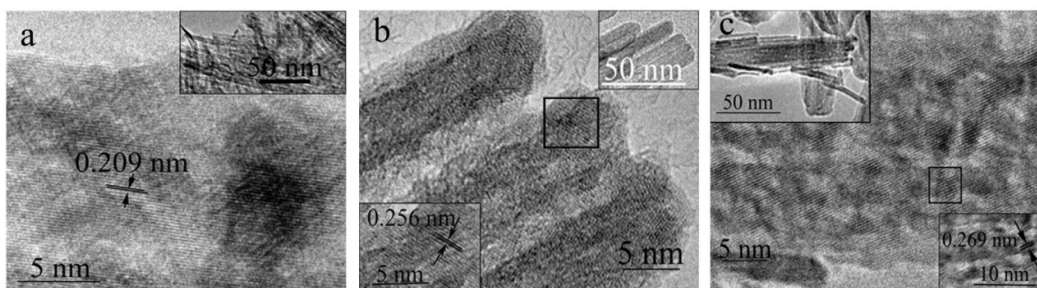
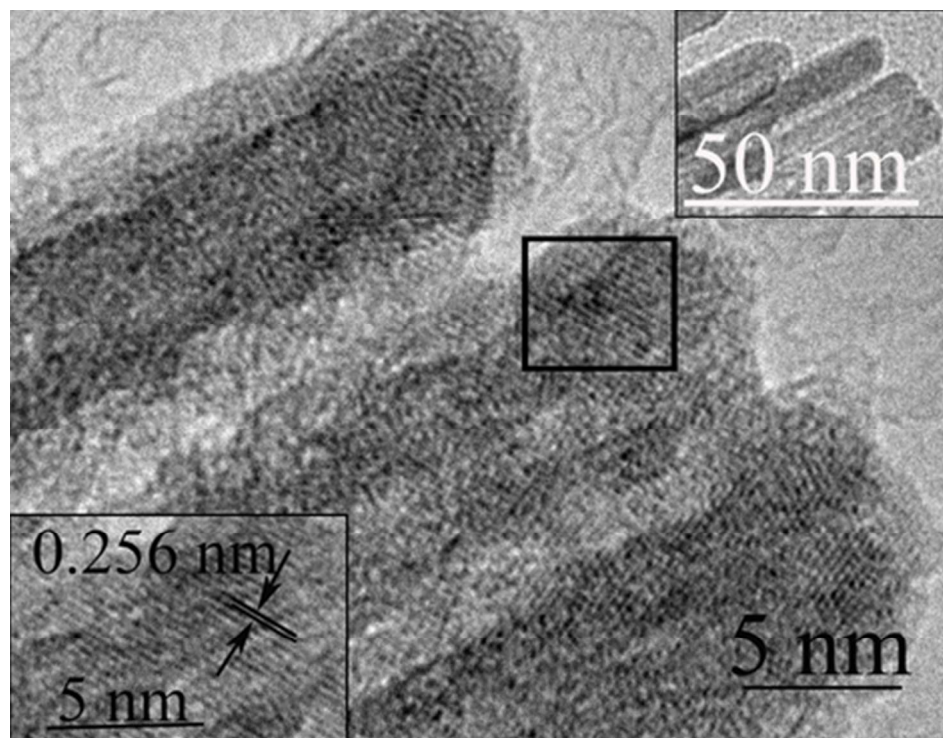the sample aged in Fe(Ⅱ) ion for 73 h.

Fig. 4. HRTEM images obtained from the rectangular area in each inset(a) original samples; (b , c)

lepidocrocite aged for 73 h with *R* =0.02.

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39x30mm (300 x 300 DPI)