Synthesis of acicular α-FeOOH particles at a very high pH

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Abstract

The acicular α-FeOOH particles were synthesized from $FeCl_3$ solutions at a very high pH using tetramethylammonium hydroxide as a precipitating agent. Samples were characterized by X-ray powder diffraction, FT-IR spectroscopy and transmission electron microscopy. α-FeOOH precipitated as a single phase from room temperature to 160 °C in a broad aging time interval. The ratio of the length to the width of α-FeOOH particles depended on the temperature and concentration of the starting $FeCl_3$ solution. Multidomainic character of α-FeOOH particles gradually decreased with an increase in the temperature and time of aging. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Goethite (α-FeOOH) is a major constituent of many soils, sediments and iron ores. It also appears as the weathering product of various rocks containing iron. Goethite ores are used for the production of raw iron. Natural goethite was used as a pigment in paintings for many centuries. Today, the synthetic α-FeOOH pigment is widely used in various compositions of house paints or fine colors for painting. The color of goethite can vary from dark brown to lemon yellow, as observed with the naked eye. Synthetic α-FeOOH particles are utilized as a starting material in the production of acicular maghemite (γ-Fe_2O_3) particles for use as the magnetic recording medium. Generally, α-FeOOH is also very important from the academic standpoint. In colloid and surface chemistry, the synthetic α-FeOOH particles are often used as a model adsorbent in fundamental studies of the adsorption/desorption phenomena.

The simplest way to produce α-FeOOH particles is to subject the diluted $Fe(NO_3)_3$ aqueous solutions to hydrolysis for a longer time at room temperature (slow hydrolysis). The hydrolysis of Fe^{3+} ions is much accelerated with the increase in temperature (forced hydrolysis). With prolonged time of hydrolysis α-FeOOH undergoes transformation to α-Fe_2O_3 (hematite) via dissolution/reprecipitation mechanism [1,2]. α-FeOOH particles also precipitate by forced hydrolysis of diluted aqueous solutions of $Fe_2(SO_4)_3$ [3] or $NH_4Fe(SO_4)_2$ salts [4,5]. At higher concentrations of these salts, the jarosites $H_3OFe_3(OH)_6(SO_4)_2$ or $NH_4Fe_3(OH)_6(SO_4)_2$ are precipitated. The yield of α-FeOOH is small in all these hydrolytic reactions, and α-FeOOH may also undergo a phase transformation

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during these precipitation processes. The yield of α-FeOOH is significantly higher in the precipitation processes from $FeSO_4$ solutions [6,7]. However, the formation of α-FeOOH by this method is highly sensitive to experimental parameters such as pH, temperature, reaction time and oxygenation. α-FeOOH can be also produced by crystallization from ferrihydrite in a highly alkaline pH medium. Synthetic α-FeOOH particles show different morphologies such as acicular-, star-, X- and K-shapes. More details can be found in a book by Cornell and Schwertmann [8].

In a previous publication [9], we reported on the formation of α-Fe_2O_3 particles from $FeCl_3$ aqueous solutions with varying additions of TMAH (tetramethylammonium hydroxide). TMAH is a strong organic alkali and in many inorganic syntheses, it also plays the role of a structural template. In the present work, we focused on the synthesis of α-FeOOH at a very high pH using TMAH.

2. Experimental

Analytical reagent $FeCl_3 \cdot 6H_2O$ supplied by Kemika and 25% w/w electronic grade (99.9999%) aqueous solution of tetramethylammonium hydroxide supplied by Alfa Aesar were used. Twice distilled water was used in all experiments. The experimental conditions for preparation of samples are given in Table 1. A predetermined volume of TMAH solution was added to the $FeCl_3$ solution. The suspension formed was vigorously shaken for approximately 30 min, then left to age in plastic bottles for use in highly alkaline medium. Autoclaving at 100 and 160 °C was performed using a

general-purpose bomb by Parr (model 4744). After the proper time of aging, the precipitates were subsequently washed with twice distilled water using an ultra-speed centrifuge Sorvall RC2-B (up to 20 000 rpm). The precipitates were dried and then characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM).

3. Results and discussion

α-FeOOH crystallizes in the orthorhombic space group *Pbnm* (62) with the unit-cell parameters at RT [10]: $a = 0.4608$, $b = 0.9956$ and $c = 0.3022$ nm. Four formula units are present in a unit cell of α-FeOOH. The crystal structure of α-FeOOH is discussed in a paper by Mathieu and Rousset [11].

Fig. 1 shows characteristic parts of XRD patterns of samples G1, G2, G6 and G7. XRD analysis showed that in all prepared samples α-FeOOH is formed as a single phase (Table 1). The crystallite sizes and shape were estimated from the broadening of diffraction lines. Because of small crystallite sizes and overlapping of adjacent diffraction lines and due to the absence of diffraction lines of type *h*00, 0*k*0 and 00*l*, one can only estimate the approximate crystallite shape. The width of diffraction lines *hk*0 decreases with the increasing of the index *k*. Diffraction lines of type 0*kl* (e.g. 021) are narrower than the *hk*0 lines. From the widths of diffraction lines, one can estimate the crystallite shape as follows: the smallest size along the *a*-axis, the medium along the *b*-axis and the biggest along the *c*-axis. Table 2

Table 1
Experimental conditions for preparation of samples and the results of their XRD analysis

Sample	2 M $FeCl_3$ (ml)	25% w/w TMAH (ml)	H_2O (ml)	Temperature (°C)	Aging time	Phase composition of the precipitate[a]
G1	5	25	70	RT	1 day	α-FeOOH
G2	5	25	70	RT	21 days	α-FeOOH
G3	5	25	70	60	1 day	α-FeOOH
G4	5	25	70	60	21 days	α-FeOOH
G5	15	75	10	60	7 days	α-FeOOH
G6	2	10	28	160	2 h	α-FeOOH
G7	2	10	28	160	3 days	α-FeOOH

[a] Samples G1–G6 showed broadened diffraction lines, whereas sample G7 showed little broadened diffraction lines.
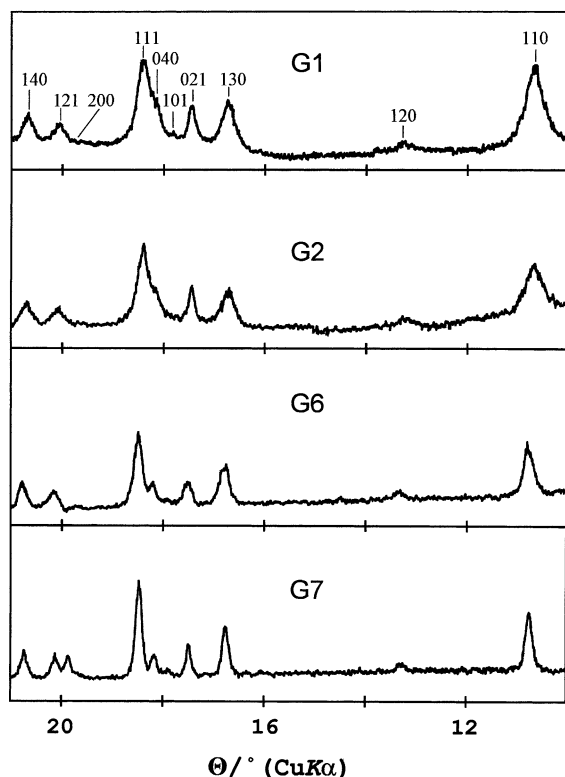
Fig. 1. Characteristic parts of XRD patterns of samples G1, G2, G6 and G7. XRD patterns were measured at room temperature.

shows the crystallite sizes of selected samples as estimated by using the Scherrer method and diffraction lines 130 and 110. The data indicate that the sizes of α-FeOOH crystallites are in nanosize range (upper limit). These crystallites form acicular α-FeOOH particles, as will be mentioned later in the discussion on the TEM results. The α-FeOOH crys-

Table 2
Crystallite sizes of selected α-FeOOH samples, as estimated by using the Scherrer method

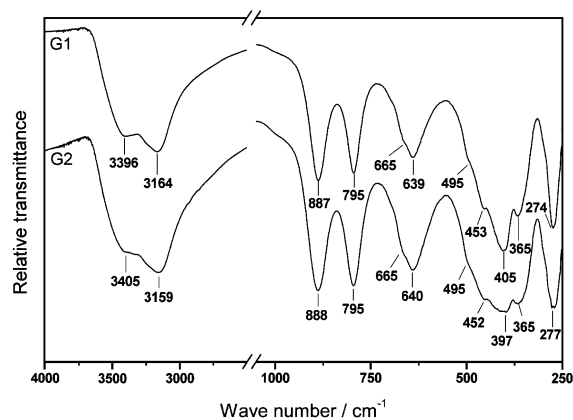| Sample	Crystallite size (nm)	
	D_{130}	D_{110}
G1	14 (3)	11 (3)
G2	15 (3)	12 (3)
G5	13 (4)	7 (2)
G6	25 (6)	22 (6)
G7	44 (10)	29 (8)

Fig. 2. Fourier transform infrared spectra of samples G1 and G2 recorded at room temperature. Aqueous suspensions of these samples were aged at room temperature for 1 and 21 days, respectively.

tallite sizes increase with an increase in the temperature and time of aging.

In the investigated precipitation systems, very high pH values $\sim 13.5-13.8$ were obtained by using TMAH. The main difference between NaOH (or KOH) and TMAH as a precipitating agent lies in the fact that in the case of TMAH, the initially formed precipitate is completely dissolved on strong shaking, as observed by the naked eye. In this way, a homogenous precipitation conditions for the synthesis of α-FeOOH in highly alkaline medium were achieved with the prolonged time of aging.
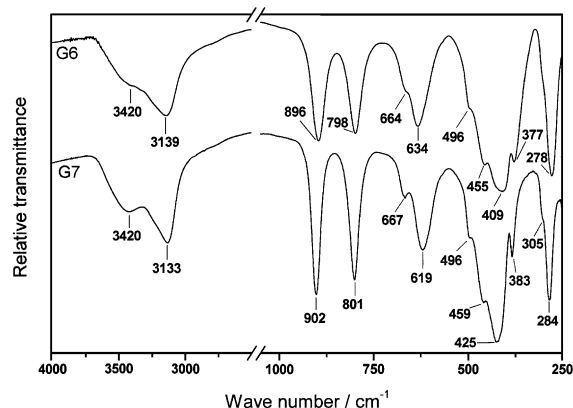

Fig. 3. Fourier transform infrared spectra of samples G6 and G7 recorded at room temperature. Aqueous suspensions of these samples were aged at 160 °C for 2 h and 3 days, respectively.

Lewis and Schwertmann [12] observed the effect of OH$^-$ ions on the crystallization of α-FeOOH from ferrihydrite under alkaline conditions. A change in the concentration of OH$^-$ ions during the crystallization process influenced the crystallinity and reactivity of α-FeOOH particles. Formation of α-FeOOH and α-Fe$_2$O$_3$ from ferrihydrite in an alkaline medium was explained with two competitive mechanisms [13]. According to these mechanisms, α-FeOOH particles form by the dissolution/reprecipitation mechanism, whereas α-Fe$_2$O$_3$ particles form through dehydration and rearrangement within the ferrihydrite aggregates. Cornell and Giovanoli [14] found that the formation of multidomainic α-FeOOH was favored at pH $\geq$ 13 and at low pH values with the addition of NaNO$_3$ to the system. A decrease in the temperature of α-FeOOH synthesis from 70 to 20 °C also enhanced multidomainic microstructure. In a highly alkaline medium (pH 12–13), the addition of Na$_2$SiO$_3$ retarded the crystallization of α-FeOOH [15]. At these pH values, much larger crystals of α-FeOOH (several hundreds of nanometers) were obtained in relation to low pH values where the crystal size was about 20 nm.

The conditions for the preparation of α-FeOOH from partially reduced Fe(OH)$_3$ [16] and from Fe(OH)$_2$ with addition of Na$_2$CO$_3$ [17] were also investigated. Template-assisted preparation of superparamagnetic α-FeOOH was reported [18]. All these works showed a strong influence of experimental conditions on synthesis of α-FeOOH as a single phase, much more than in the case of application of TMAH as a precipitating agent.

All FT-IR spectra of the samples prepared in the present work showed features typical of α-FeOOH. Figs. 2 and 3 show the FT-IR spectra of samples G1, G2, G6 and G7. The best pronounced IR bands were observed for sample G7 prepared by autoclaving at 160 °C for 3 days. A very strong IR band at 3133 cm^{-1} is due to the presence of the OH stretching mode in α-FeOOH, whereas the IR band at 3420 cm^{-1} can be ascribed to stretching modes of surface H$_2$O molecules or to the envelope of hydrogen-bonded surface OH groups [19]. Two typical bands of goethite at 902 and 801 cm^{-1} can be ascribed to Fe–O–H bending vibrations in α-FeOOH.

Verdonck et al. [20] applied a method of normal coordinate analysis in the study of the IR spectrum of α-FeOOH. For α-FeOOH and deuterated α-FeOOD, the experimental and calculated vibrational frequencies were compared. The IR bands recorded at 630, 495 and 270 cm^{-1} were rather insensitive to deuteration, and on the basis of this finding, they were ascribed to Fe–O stretching vibrations [20]. Cambier [21] also investigated the IR spectrum of goethite and in that work, a band at 3150 cm^{-1} was ascribed to the OH stretching mode, whereas the bands at 892 and 795 cm^{-1} were ascribed to the OH bending modes in α-FeOOH. The interpretation of bands below 650 cm^{-1} was similar to that of Verdonck et al. [20]. It was suggested that an intense IR band around 630 cm^{-1} was affected by the shape of the α-FeOOH particles.

In the present work, the positions of IR bands and their sharpness depend on the temperature and time of aging of α-FeOOH suspensions. For example, the IR
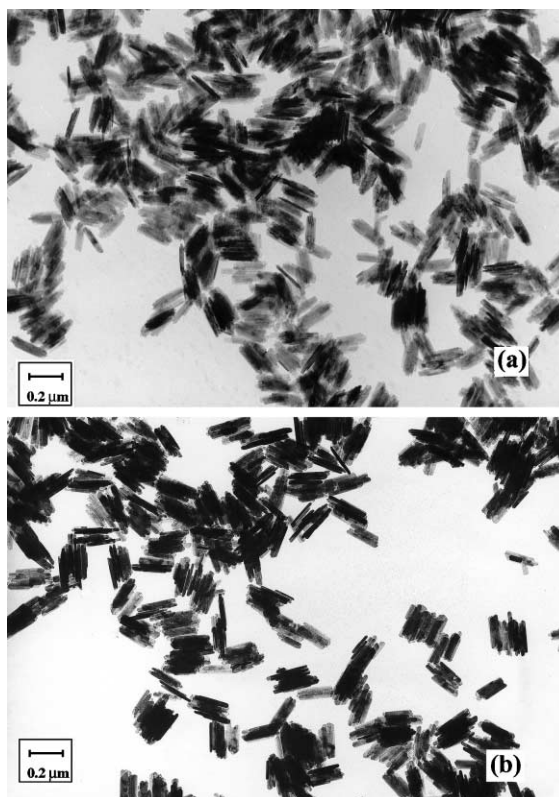

Fig. 4. TEM photographs of α-FeOOH particles: samples (a) G3 and (b) G4. Aqueous suspensions of these samples were aged at 60 °C for 1 and 21 days, respectively.

bands at 887 and 795 cm^{-1} observed for sample G1 were shifted to 902 and 801 cm^{-1} for sample G7. The shoulder at 665 cm^{-1} observed for sample G1 transformed to a separate IR band at 667 cm^{-1} for sample G7. Significant shifts of the band at 405 cm^{-1} and the shoulder at 365 cm^{-1} for sample G1 to positions at 425 and 383 cm^{-1} for sample G7 were observed. A shoulder at 305 cm^{-1} was additionally visible for sample G7. This shoulder at 305 cm^{-1} in the FT-IR spectrum of α-FeOOH was also observed by Weckler and Lutz [22].

The IR band at 634 cm^{-1} observed for sample G6 shifted to 619 cm^{-1} for sample G7. This can be related to the increased crystallinity of sample G7. On the other hand, the same band was observed at 639– 640 cm^{-1} for samples G1 and G2, i.e. it was not affected by aging between 1 and 21 days at RT. The multidomainic character of these particles was present at RT and it was not changed (or very slowly) for the given times of aging at this temperature. At 160 $^\circ$C, reactions were more accelerated.

Fig. 4 shows TEM photographs of samples G3 and G4 prepared at 60 $^\circ$C. The particles of sample G3 show a substructure, as visible from their irregular ends. With an aging time of aqueous suspensions prolonged up to 21 days (sample G4), the particles became more regular. Acicular α-FeOOH particles were also observed for sample G5 precipitated from 0.3 M FeCl$_3$ solution in a highly alkaline medium at 60 $^\circ$C, as shown in Fig. 5. The average length–width ratio of G5 particles is 9. Autoclaving of the starting precipitation system at 160 $^\circ$C after 3 days of aging yielded α-FeOOH particles closer to a monodomain

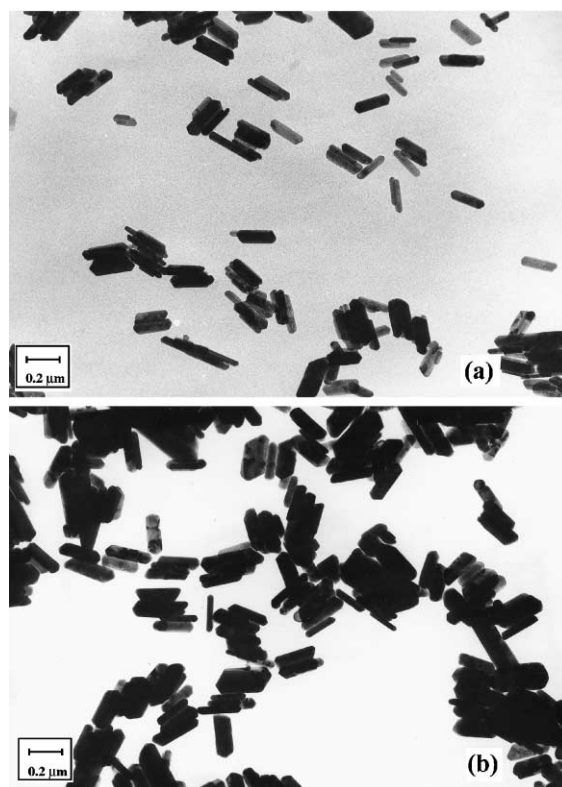Fig. 5. TEM photograph of α-FeOOH particles of sample G5.

Fig. 6. TEM photographs of α-FeOOH particles: samples (a) G6 and (b) G7. Aqueous suspensions of these samples were aged at 160 $^\circ$C for 2 h and 3 days, respectively.

microstructure (Fig. 6). However, the average length– width ratio of these particles is less than 5. This system produced α-FeOOH particles with a narrow size distribution, due to the homogenous precipitation conditions achieved with the TMAH as a precipitating agent. The tendency of the formation of lateral arrays (rafts) of α-FeOOH particles is visible.

4. Conclusions

- Tetramethylammonium hydroxide is a suitable precipitating agent for the synthesis of α-FeOOH at a very high pH.
- α-FeOOH precipitated as a single phase from RT to 160 $^\circ$C in a broad aging time interval. For the given experimental conditions transformation of α-FeOOH to α-Fe$_2$O$_3$ was not observed.

- The acicular α-FeOOH particles were produced. The length–width ratio of α-FeOOH particles depended on the temperature and concentration of the starting FeCl$_3$ solution.
- Multidomainic character of α-FeOOH particles was more pronounced at lower temperatures and for shorter aging times of aqueous suspensions.

Acknowledgements

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