FT-IR and $^{57}$Fe Mössbauer spectroscopic investigation of oxide phases precipitated from Fe(NO$_3$)$_3$ solutions

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Abstract

Iron oxides (group name) were precipitated by the hydrolysis of Fe(NO$_3$)$_3$ solutions in the presence of urotropin (hexamethylenetetramine). In an acidic medium at elevated temperature, urotropin undergoes hydrolysis with a gradual release of OH$^-$ ions. The precipitation time varied between 5 h and 21 days. The typical IR bands of the iron oxide phases were identified and used, together with XRD, to monitor phase changes in the precipitates. At the beginning of the precipitation process an amorphous phase was dominant and with prolonged time of Fe$^{3+}$ hydrolysis $\alpha$-FeOOH was formed. $\alpha$-FeOOH transformed to $\alpha$-Fe$_2$O$_3$ by the dissolution/reprecipitation mechanism. The concentration effect of urotropin on the phase composition of the precipitates after 7 days of aging was observed with XRD, FT-IR and $^{57}$Fe Mössbauer spectroscopies. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The synthesis and properties of iron oxides (group name) were extensively investigated in the past, because these compounds have important applications as pigments, anticorrosion coatings, catalysts, magnetic recording media, gas sensors etc. The forced hydrolysis of acidic Fe(III)—salt solutions is a very simple way to produce iron oxides. The phase composition of solid hydrolytic products of Fe$^{3+}$ ions depends on the concentration of Fe(III)—salt, type of anion, temperature and time of hydrolysis. Music et al. [1] proposed a mechanism for the precipitation by forced hydrolysis of acidic Fe(III)—salt solutions containing Cl$^-$, NO$_3^-$, or SO$_4^{2-}$ anions. The Fe$^{3+}$ hydrolysis results in the release of H$^+$ ions, and consequently, a decrease in pH takes place. In previous works [2,3], the process of forced FeCl$_3$ hydrolysis was modified by the addition of urotropin (hexamethylenetetramine) at the beginning of the precipitation process. Urotropin generates OH$^-$ ions in an acidic medium at elevated temperatures in accordance with the chemical reactions:

$$(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 6\text{HCHO} \quad (1)$$

and

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (2)$$

In the present work we focus on the formation of iron oxide phases from Fe(NO$_3$)$_3$ solutions with decomposing urotropin. Mössbauer and vibrational spectroscopies have important applications in the investigation of iron oxides.
2. Experimental

Fe(NO₃)₃·9H₂O and urotropin of analytical grade purity and doubly distilled water were used for the preparation of the samples. The chemical composition of the solutions and the experimental conditions for the preparation of samples are given in Table 1. Precipitation systems were kept in glass autoclaves at 90°C for varying times. For different times of aging, the solid hydrolytic products were separated from the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Urotropin (M)</th>
<th>Time of aging</th>
<th>pH (final)</th>
<th>Phase composition</th>
<th>Diffraction lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>0.025</td>
<td>5 h</td>
<td>1.72</td>
<td>AM + GO</td>
<td>GO:VB</td>
</tr>
<tr>
<td>N2</td>
<td>0.025</td>
<td>24 h</td>
<td>1.09</td>
<td>AM + GO + HE</td>
<td>GO: VB, HE: B</td>
</tr>
<tr>
<td>N3</td>
<td>0.025</td>
<td>3 d</td>
<td>1.04</td>
<td>HE + GO ( + AM)</td>
<td>HE: LB, GO: B</td>
</tr>
<tr>
<td>N4</td>
<td>0.025</td>
<td>7 d</td>
<td>2.02</td>
<td>HE ( + AM)</td>
<td>HE: LB</td>
</tr>
<tr>
<td>N5</td>
<td>0.025</td>
<td>21 d</td>
<td>1.27</td>
<td>HE ( + AM)</td>
<td>HE: LB</td>
</tr>
<tr>
<td>N6</td>
<td>0.0125</td>
<td>7 d</td>
<td>1.26</td>
<td>HE + GO ( + AM)</td>
<td>HE: LB, GO: B</td>
</tr>
<tr>
<td>N7</td>
<td>0.0175</td>
<td>7 d</td>
<td>1.20</td>
<td>HE</td>
<td>HE: LB</td>
</tr>
<tr>
<td>N8</td>
<td>0.02</td>
<td>7 d</td>
<td>1.30</td>
<td>HE</td>
<td>HE: LB</td>
</tr>
<tr>
<td>N9</td>
<td>0.05</td>
<td>7 d</td>
<td>1.95</td>
<td>HE + GO ( + AM)</td>
<td>HE: LB, GO: B</td>
</tr>
</tbody>
</table>

*The sequence of phases corresponds to their fractions; AM = amorphous, HE = hematite, GO = goethite, ( + AM) means that an amorphous fraction may be present.

**VB** = very broadened, crystallite size of several nanometers, **B** = broadened, crystallite sizes of the order of 10 nm, **LB** = little broadened, crystallite size of the order of several tens of nanometers.

Fig. 1. FT-IR spectra of samples N1–N5, recorded at room temperature.

Fig. 2. FT-IR spectra of samples from 0.1 M Fe(NO₃)₃ at 90°C, with varying initial concentrations of urotropin from a) 0.0125 M; b) 0.015 M; c) 0.0175 M; d) 0.02 M; e) 0.0225 M; to f) 0.05 M, recorded at room temperature (aging time = 7 days).
mother liquor and washed with doubly distilled water several times. Separation of phases was performed using an ultra-speed centrifuge (operational range up to 20 000 rpm). Iron oxide powders were investigated by X-ray powder diffraction, FT-IR and $^{57}$Fe Mössbauer spectroscopies.

3. Results and discussion

The results of X-ray powder diffraction analysis are given in Table 1. Fig. 1 shows FT-IR spectra of the precipitates formed between 5 h and 21 days, for the urotropin concentration of 0.025 M. The spectrum of the precipitate formed after 5 h can be ascribed to $\alpha$-FeOOH (goethite). After 1 day of aging, the precipitate showed IR bands at 886 and 798 cm$^{-1}$ typical for $\alpha$-FeOOH, and also the appearance of a broad band at 563 cm$^{-1}$ which can be ascribed to $\alpha$-Fe$_2$O$_3$ (hematite). After 3 days of aging, the fraction of $\alpha$-Fe$_2$O$_3$ was significantly increased and the corresponding bands at 567 and 472 cm$^{-1}$ are very visible. In the precipitates, formed between 7 and 21 days, only a small amount of $\alpha$-FeOOH (bands at 892 and 800 cm$^{-1}$) remained. The bands at 892 and 800 cm$^{-1}$ can be assigned to Fe–O–H bending vibrations in $\alpha$-FeOOH [4]. Verdonck et al. [5] compared observed IR spectra of $\alpha$-FeOOH and deuterated $\alpha$-FeOOD with calculated spectra. The bands at 630, 495 and 270 cm$^{-1}$ were ascribed to Fe–O stretching vibrations. Cambier [6] observed in $\alpha$-FeOOH a band at 3150 cm$^{-1}$, owing to the OH stretching mode and bands at 892 and 795 cm$^{-1}$ because of the OH bending mode. The IR spectrum of $\alpha$-Fe$_2$O$_3$ was discussed by Serna et al. [7].

Fig. 2 shows FT-IR spectra of the precipitates
obtained with varying initial concentrations of urotropin from 0.0125 to 0.05 M, for an aging time of 7 days. The pH of the mother liquor varied between 1.20 and 1.95. In spite of the fact that the change in pH was small, the fraction of $\alpha$-FeOOH at first decreased (to a value not detectable by XRD) and then increased, as the concentration of urotropin increased. This effect, visible by XRD, is shown in Fig. 3. Atkinson et al. [8] investigated crystal nucleation and growth in hydrolysing FeCl$_3$ solutions and observed that in the pH range between 1 and 2 the phase composition of precipitates may vary depending on the experimental conditions.

Mössbauer spectra of the precipitates obtained for 0.0125, 0.0175, 0.02 and 0.05 M urotropin are shown in Fig. 4. The outer sextet (dominant) with varying HMF (hyperfine magnetic field) from 505 to 511 kOe can be ascribed to $\alpha$-Fe$_2$O$_3$. The inner sextet of small relative intensity, corresponding to $\alpha$-FeOOH, could not be fitted satisfactorily using HMF $\sim$ 390 kOe. For the precipitates obtained in 0.0125 to 0.05 M urotropin the fits were performed with HMF values varying from 283 to 295 kOe. Also, the precipitates showed a central quadrupole doublet of small intensity with $\Delta = 0.95$ mm s$^{-1}$ which could be ascribed to the amorphous fraction. The value $\Delta = 1.61$ mm s$^{-1}$ calculated for the precipitate obtained in 0.050 M urotropin represents only the optimization of the fit, and paramagnetic doublet is actually of the same origin as previous doublets. In acidic medium at elevated temperature, the Fe$^{3+}$ ions undergo hydrolysis, producing various hydroxy complexes, and this process is continued with their polymerization and formation of oxo-bridges (oxolation). The present work showed that at the beginning of the precipitation process $\alpha$-FeOOH was formed as a single phase. With prolonged time of aging, $\alpha$-FeOOH transformed to $\alpha$-Fe$_2$O$_3$ by the dissolution/reprecipitation mechanism. The addition of urotropin increases pH and thus modifies the hydrolysis of Fe(NO$_3$)$_3$ solutions.

References