Thermal decomposition of $\beta$-FeOOH

S. Musi´c, S. Krehula, S. Popovi´c

Division of Materials Chemistry, Rudjer Boskovic Institute, P.O. Box 180, Bijenička cesta 54, HR-10002 Zagreb, Croatia

Department of Physics, Faculty of Science, University of Zagreb, P.O. Box 331, HR-10002 Zagreb, Croatia

Received 1 June 2003; received in revised form 2 June 2003; accepted 6 June 2003

Abstract

$\beta$-FeOOH particles were prepared by a forced hydrolysis of the 0.1 M FeCl$_3$ + 5 $\times$ 10$^{-3}$ M HCl solution, whereas sulfated $\beta$-FeOOH particles were prepared by forced hydrolysis of the 0.1 M FeCl$_3$ solution containing 5 $\times$ 10$^{-3}$ M quinine hydrogen sulfate (QHS). $\beta$-FeOOH particles, as well as sulfated $\beta$-FeOOH particles, were thermally treated up to 600 °C. The samples were characterized using DTA, XRD, FT-IR and TEM. $\beta$-FeOOH particles showed a cigar-type morphology, whereas bundles of $\beta$-FeOOH needles were obtained in the presence of QHS. Heating of $\beta$-FeOOH particles at 300 °C and above yielded $\alpha$-Fe$_2$O$_3$ particles. Specific adsorption of sulfate groups showed a strong effect on the thermal decomposition of $\beta$-FeOOH particles. Upon heating of sulfated particles between 300 and 500 °C the formation of an amorphous phase and a small fraction of $\alpha$-Fe$_2$O$_3$ were observed. Needle-like morphology of amorphous particles in these samples was preserved. At 600 °C, $\alpha$-Fe$_2$O$_3$ particles were obtained; however, they were much smaller than those obtained by heating a pure $\beta$-FeOOH. © 2003 Elsevier B.V. All rights reserved.

Keywords: $\beta$-FeOOH, Sulfated $\beta$-FeOOH, $\alpha$-Fe$_2$O$_3$, Thermal decomposition

1. Introduction

$\beta$-FeOOH (akaganeite) powder undergoes decomposition at high temperature and $\alpha$-Fe$_2$O$_3$ (hematite) is the reaction end-product. In spite of the fact that many works were published on this subject in the past 35 years, the results of these works are in many cases inconsistent concerning the temperature of phase transition and the route by which the end-product is formed. It seems that this inconsistency in thermal behavior of $\beta$-FeOOH is a consequence of a different history of the samples.

Inouye et al. [1] prepared $\beta$-FeOOH particles by forced hydrolysis of 0.2 M FeCl$_3$ solutions containing up to 6% Cu relative to total Fe. A strong exothermic peak observed for $\beta$-FeOOH at $\sim$ 350 °C was shifted to $\sim$ 450 °C for the sample containing 6% Cu. This shift was explained by possible Cu–Cl interactions in the $\beta$-FeOOH structure. Nagai et al. [2] found that at a higher content of chlorides in $\beta$-FeOOH the direct transition to $\alpha$-Fe$_2$O$_3$ occurred at 300 °C, whereas at a lower content of chlorides this transition proceeded via the amorphous phase into crystalline $\alpha$-Fe$_2$O$_3$ at 400 °C. Cham-
precipitated by forced hydrolysis of the FeCl₃ solution to which quinine hydrogen sulfate (QHS) was added. Sulfated iron oxides are materials usable in organic catalysis [7–9].

2. Experimental

Analytical grade chemicals FeCl₃·6H₂O and HCl supplied by Kemika, and quinine hydrogen sulfate (C₂₀H₂₄O₂N₂·H₂SO₄·7H₂O) supplied by BDH were used. The solutions were prepared using doubly distilled water. β-FeOOH (sample A) was precipitated by the hydrolysis of the 0.1 M FeCl₃ solution, containing 5 × 10⁻³ M HCl, at 90 °C for 7 days. Sulfated β-FeOOH (sample SA) was precipitated by the hydrolysis of the 0.1 M FeCl₃ solution, containing 5 × 10⁻³ M QHS, at 90 °C for 24 h. After a proper aging time solid hydrolytic products were separated from the mother liquor using an ultraspeed centrifuge (Sorvall RC2-B, operational range up to 20 000 r.p.m.). The solid hydrolytic products were subsequently rinsed with doubly distilled water to remove the “neutral” electrolyte, then dried in vacuum. Thermal decomposition was performed in air ambient. The samples were characterized by X-ray powder diffraction (XRD), differential thermal analysis (DTA), Fourier transform infrared (FT-IR) spectroscopy, and transmission electron microscopy (TEM).

3. Results and discussion

Fig. 1 shows TEM photographs of β-FeOOH particles (samples A and SA), used in the thermal decomposition experiments. Well-defined, cigar-shaped particles were present in sample A. The addition of 5 × 10⁻³ M QHS to the hydrolyzing FeCl₃ solution strongly changed the morphology of these particles. XRD showed a β-FeOOH structure for both samples, A and SA, the latter exhibiting rather broad diffraction lines. The formation of the bundles of β-FeOOH needles (sample SA) could be ascribed to a possible complexing role of quinine at the very beginning of the hydrolysis of Fe³⁺ ions and a specific adsorption of sulfates on the crystal planes along the c-axis of β-FeOOH crystallites.

Samples A and SA were subjected to thermal treatment in air, and their DTA curves showed significant differences (Fig. 2). β-FeOOH (sample A) showed an endothermic peak at 230 °C and a shoulder at 260 °C, a sharp and strong endothermic peak centered at 275 °C, and an exothermic peak at 455 °C.
peak of smaller intensity at 455 °C. The endothermic peaks at 230, 260 and 275 °C can be ascribed to dehydroxylation of \( \beta \)-FeOOH. It seems that dehydroxylation of \( \beta \)-FeOOH is not a continuous process. The exothermic peak at 455 °C can be ascribed to the recrystallization of a less crystalline to a better crystallized \( \alpha \)-Fe\(_2\)O\(_3\), not to an intermediate phase [2].

Table 1
X-ray powder diffraction analysis of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase composition</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \beta )-FeOOH</td>
<td>SDL</td>
</tr>
<tr>
<td>A-300</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>SDL</td>
</tr>
<tr>
<td>A-600</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>SDL</td>
</tr>
<tr>
<td>SA</td>
<td>( \beta )-FeOOH</td>
<td>BDL</td>
</tr>
<tr>
<td>SA-300</td>
<td>amorphous + ( \alpha )-Fe(_2)O(_3)</td>
<td>BDL</td>
</tr>
<tr>
<td>SA-400</td>
<td>amorphous + ( \alpha )-Fe(_2)O(_3)</td>
<td>BDL</td>
</tr>
<tr>
<td>SA-500</td>
<td>amorphous + ( \alpha )-Fe(_2)O(_3)</td>
<td>BDL</td>
</tr>
<tr>
<td>SA-600</td>
<td>( \alpha )-Fe(_2)O(_3)</td>
<td>SDL</td>
</tr>
</tbody>
</table>

SDL = sharp diffraction lines; BDL = broad diffraction lines.

The fraction of \( \alpha \)-Fe\(_2\)O\(_3\) in samples SA-300 to SA-500 is of the order of 0.05, whereas the crystallite size of \( \alpha \)-Fe\(_2\)O\(_3\) in these samples is of the order of several nanometers.

This conclusion is confirmed by XRD measurements, as shown in Table 1. \( \alpha \)-Fe\(_2\)O\(_3\) as a single phase was obtained upon heating the sample A at 300 °C or higher.

The DTA curve of sulfated \( \beta \)-FeOOH (sample SA) showed a different feature in relation to sample A. Two broad endothermic peaks at 275 and 350 °C and a much stronger exothermic peak at 550 °C were visible. XRD measurements of the samples, produced by heating the sample SA at 300, 400, and 500 °C, showed that they were dominantly amorphous and containing a little fraction (~0.05) of \( \alpha \)-Fe\(_2\)O\(_3\). The crystallite size of the \( \alpha \)-Fe\(_2\)O\(_3\) fraction in these samples is of the order of several nm, as estimated from the broadening of XRD lines. XRD patterns of sulfated \( \beta \)-FeOOH and its thermal decomposition products from 300 to 600 °C are shown in Fig. 3. Indices of diffraction lines are given in terms of hexagonal axes for hematite (space group \( R3c \), \( a = 5.035 \) Å, \( c = 13.74 \) Å), and in terms of tetragonal axes of akaganeite (space group \( I4/m \), \( a = 10.50 \) Å, \( c = 3.030 \) Å). The phases were identified according to the data contained in Powder Diffraction File (International Centre for Diffraction Data), e.g. cards nos. 33-664 and 89-599 for hematite, and cards nos. 34-1266 and 75-1594 for akaganeite.

Thermal decomposition products of samples A and SA were also analysed by FT-IR spectroscopy and the results of these measurements are shown in Fig. 4. The characteristic

![Fig. 3. Characteristic parts of XRD patterns of sulfated \( \beta \)-FeOOH (sample SA) and its thermal decomposition products at 300 °C (SA-300), 400 °C (SA-400), 500 °C (SA-500) and 600 °C (SA-600). \( \alpha \)= akaganeite, \( \beta \)= hematite.](image1)

![Fig. 4. FT-IR spectra of \( \beta \)-FeOOH (sample A) and its thermal decomposition products at 300 °C (A-300) and 600 °C (A-600); sulfated \( \beta \)-FeOOH (sample SA) and its thermal decomposition products at 300 °C (SA-300), 400 °C (SA-400), 500 °C (SA-500) and 600 °C (SA-600).](image2)
parts of the FT-IR spectra of samples obtained by heating the sample A (pure \(\beta\)-FeOOH) indicate a complete transformation of \(\beta\)-FeOOH into \(\alpha\)-Fe\(_2\)O\(_3\) at 300 and 600 °C. On the other hand, the FT-IR spectra of samples obtained by heating the sample SA (sulfated \(\beta\)-FeOOH) showed a different path in the formation of \(\alpha\)-Fe\(_2\)O\(_3\) by thermal decomposition. Sulfated \(\beta\)-FeOOH, as prepared, shows IR bands at 1200, 1129, 1075 and 979 cm\(^{-1}\), which can be assigned to a sulfate group. Harrison and Berkheiser [10] reported IR bands at 1215, 1125, 1040 and 970 cm\(^{-1}\) for sulfate adsorbed on freeze-dried hydrous iron oxide, which conforms with our measurements. These IR bands were smaller and smaller in the spectra of the thermal decomposition products of sulfated \(\beta\)-FeOOH; however the bands of small intensity corresponding to a sulfate group were still present in the spectrum of the sample produced at 600 °C. The FT-IR spectra of the samples heated from 300 to 500 °C are difficult to ascribe to some of the specific iron oxide or oxyhydroxide forms. It is evident that the sulfated \(\beta\)-FeOOH decomposes under a strong influence of adsorbed sulfate groups. Also, in our thermal decomposition experiments with the sulfated \(\beta\)-FeOOH we did not observe the formation of \(\beta\)-Fe\(_2\)O\(_3\). It was reported that \(\beta\)-Fe\(_2\)O\(_3\) may be formed by thermal decomposition of some iron compounds containing a sulfate group [11]. A strong influence of the sulfate group was also observed [12] in the case of the thermal decomposition of basic iron(III)-sulfates formed by forced hydrolysis of \(\text{NH}_4\text{Fe(SO}_4\text{)}_2\) and \(\text{Fe}_2\text{(SO}_4\text{)}_3\) solutions. \(^{57}\text{Fe}\) Mössbauer spectra obtained for thermally treated basic iron(III)-sulfates at 320 and 400 °C showed the presence of Fe\(_2\)O(SO\(_4\))\(_2\), whereas thermal treatment at 500 °C produced Fe\(_2\)(SO\(_4\))\(_3\) as well. \(\alpha\)-Fe\(_2\)O\(_3\) was produced as a single phase upon heating at 600 °C.

Transmission electron microscopy showed significant differences in size and morphology of the particles produced by thermal treatment of \(\beta\)-FeOOH, as well as sulfated \(\beta\)-FeOOH. Fig. 5 shows TEM photographs of thermal decomposition products of \(\beta\)-FeOOH at 300 and 600 °C, and the particles shown correspond to \(\alpha\)-Fe\(_2\)O\(_3\). A TEM photograph of sample A-300 showed a few residual \(\beta\)-FeOOH particles with great holes, due to their dehydration.

Fig. 6 shows TEM photographs of thermal decomposition products of sulfated \(\beta\)-FeOOH at 300, 500 and 600 °C. The needle-like morphology of sulfated \(\beta\)-FeOOH particles was preserved between 300 and 500 °C. In Fig. 6a the formation of stars from the bundles of needles was observed. In Fig. 6c there were only \(\alpha\)-Fe\(_2\)O\(_3\) particles and their aggregates. \(\alpha\)-Fe\(_2\)O\(_3\) particles produced from a sulfated \(\beta\)-FeOOH are much smaller than those produced from a pure \(\beta\)-FeOOH.

For comparison, heating of sulfated \(\alpha\)-FeOOH (goethite) at 350 °C [13] yielded \(\alpha\)-Fe\(_2\)O\(_3\) particles with small holes.
These particles preserved the acicular morphology of α-FeOOH precursor. In the present case the α-Fe₂O₃ particles produced by thermal decomposition of a sulfated β-FeOOH at 600 °C did not show the needle-like morphology of its precursor.

4. Conclusions

β-FeOOH and sulfated β-FeOOH particles precipitated by forced hydrolysis of the Fe³⁺ ions showed different morphologies, as well as a different thermal behavior. Upon heating of β-FeOOH particles at 300 °C and above, α-Fe₂O₃ particles were produced. The formation of great holes was observed inside β-FeOOH particles with the increase in temperature, due to their dehydration. Upon heating of sulfated β-FeOOH particles between 300 and 500 °C an amorphous phase was formed, preserving the needle-like morphology. A small fraction of α-Fe₂O₃ was also found in the samples produced between 300 and 500 °C. α-Fe₂O₃ was produced as a single phase at 600 °C; it was contaminated, however, with residual sulfate groups. Evidently, the sulfates specifically adsorbed onto β-FeOOH needles formed strong chemical bonds with terminal iron ions, and therefore thermally behaved in a way similar to as many iron-sulfate compounds. Due to the stability of the sulfate group in the temperature range between 300 and 500 °C, the formation of α-Fe₂O₃ in this temperature range was strongly suppressed, whereas the morphology of precursor particles was preserved. Yu et al. [14] observed a release of SO₃ from the SO₄ group in schwertmannite around 600 °C. Upon heating of sulfated β-FeOOH between 300 and 500 °C, formation of porous internal microstructure, as well as of solid fractals inside the needles, occurred. As a result of these processes an amorphous-like phase was observed by XRD. This process of amorphization of sulfated β-FeOOH is progressing under the preserved morphology of the starting compound.

Acknowledgements

The authors wish to thank Professor N. Ljubešić for his valuable assistance in the electron microscopic work.

References