MÖSSBAUER SPECTROSCOPIC AND X-RAY DIFFRACTION STUDY OF THE THERMAL DECOMPOSITION OF Fe(CH₃ COO)₂ AND FeOH(CH₃ COO)₂

S. MUSIĆ, M. RISTIĆ, S. POPOVIĆ

Rudjer Bošković Institute, P.O.Box 1016, 41001 Zagreb (Yugoslavia)

Department of Physics, Faculty of Sciences, University of Zagreb, P.O.Box 162, 41001 Zagreb (Yugoslavia)

(Received September 4, 1987)

Thermal decomposition of iron(II) acetate, Fe(CH₃ COO)₂, and iron(III) acetate hydroxide, FeOH(CH₃ COO)₂, has been studied using ⁵⁷Fe Mössbauer spectroscopy and X-ray diffraction. Samples were thermally treated in air atmosphere between 150 °C and 1000 °C. The formation of maghemite, γ-Fe₂O₃, and hematite, α-Fe₂O₃, is discussed. Hematite appears as the final decomposition product.

Introduction

Iron oxides have great technical importance (catalysts, pigments, gas sensors, electronic components, etc.). For this reason, their chemical and structural properties have been the subject of numerous studies. Also, the experimental conditions for the preparation of various Fe-oxides have been extensively investigated.

The dehydration of Fe(III) oxyhydroxide, α-FeOOH, is a basic method for the preparation of α-Fe₂O₃ (hematite) or γ-Fe₂O₃ (maghemite) with a high dispersity and a high chemical reactivity. For instance, synthetic acicular microcrystals of α-FeOOH are an important raw material for the preparation of γ-Fe₂O₃ particles, which have application in the production of magnetic recording devices. α-FeOOH can be transformed into γ-Fe₂O₃ by the following reactions:

\[ 2 \alpha-\text{FeOOH} \rightarrow \alpha-\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}, \quad (\sim 250 \, ^\circ\text{C}) \]

\[ 3 \alpha-\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}, \quad (\sim 300 \, ^\circ\text{C}) \]

and \[ 4 \text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6 \gamma-\text{Fe}_2\text{O}_3. \quad (\sim 250 \, ^\circ\text{C}) \]
The thermal decomposition of some Fe-organic complexes can be an alternative route for the preparation of good quality Fe-oxides.

Synthetic and natural α-FeOOH transforms to α-Fe₂O₃ at elevated temperatures (>200 °C).¹⁻⁶ A poly-domain material with an imperfect α-Fe₂O₃ structure is produced⁴ by heating α-FeOOH at temperatures below 600 °C. MUSIĆ and POPOVIĆ showed that α-Fe₂O₃ crystallites formed at lower temperatures (200–300 °C) are small and contain stacking faults.⁶

INOUGE and coworkers⁷ found the formation of ferromagnetic Fe-oxides during the thermal decomposition of synthetic β-FeOOH (akaganeite) in vacuum.

On heating in air, synthetic γ-FeOOH (lepidocrocite) transforms to γ-Fe₂O₃ and α-Fe₂O₃:

\[
\gamma\text{-FeOOH} \rightarrow \gamma\text{-Fe₂O₃} \rightarrow \alpha\text{-Fe₂O₃}
\]

The transition temperatures T₁ and T₂ are very dependent on the method⁸ of sample preparation.

The structure of δ-FeOOH is closely related to that of α-Fe₂O₃, and because of this similarity δ-FeOOH easily transforms to α-Fe₂O₃ at elevated temperatures.⁹

MUSIĆ, SIMMONS and LEIDHEISER¹⁰ studied thermal decomposition of Fe(IO₃)₃ using Mössbauer spectroscopy. A magnetic splitting component of small intensity was observed after 42 hour heating at 370 °C. Iron(III) iodate was completely decomposed after 1 hour heating at 470 °C.

Thermal decomposition of basic iron(III) sulfate was studied¹¹ also by using Mössbauer spectroscopy.⁵⁷ Fe Mössbauer spectra recorded for thermally treated basic iron(III) sulfate at 320 and 400 °C showed the presence of Fe₂O(SO₄)₂. Thermal treatment at 500 °C produced Fe₂(SO₄)₃ as well. Pure α-Fe₂O₃ phase was formed at 600 °C.

RANDHAWA and coworkers¹² investigated the thermal decomposition of Na₃[Fe(RCOO)₆] · xH₂O, (R=H, CH₃, C₂H₅). The particle size of α-Fe₂O₃ formed during thermolysis increased with increasing temperature. At high temperature (700 °C), α-NaFeO₂ is formed as the end product from all the complexes.

VENKATARAMAN and coworkers¹³ investigated the synthesis of α-Fe₂O₃ by the thermal decomposition of ferrous succinate tetrahydrate (FeC₄H₄O₄ · 4H₂O). They found that in the first step FeC₄H₄O₄ is formed, which then oxidatively decomposes to α-Fe₂O₃ with probable intermediates such as FeO, Fe₃O₄ and γ-Fe₂O₃.

The preparation of γ-Fe₂O₃ in a single step by the thermal decomposition of N₂H₅Fe(N₂H₅COO)₃ · H₂O and Fe(N₂H₅COO)₂(N₂H₅)₂ was reported.¹⁴ The thermal decomposition of these iron-organic complexes yielded very fine particles of γ-Fe₂O₃.