SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE POWDERS

M.N. Batin, V. Popescu

Abstract
Iron oxide powders (α-Fe₂O₃) were obtained via a chemical process. A homogenous mixture prepared from iron (II) chloride tetrahydrate and urea of analytical purity and water was heated at 90°C for a few hours in order to obtain the precursor powders. The obtained precipitates were filtered, washed and dried at room temperature, finally forming the precursor powders. Then the powders were heated in an oven at different temperatures. It was observed that the thermal treatment plays an important role in the size and the structure of the final product. The iron oxide powders were characterized by X-Ray Diffraction and UV-VIS spectroscopy. We also determined the grain size from XRD analysis.

Keywords: iron oxide, hematite α-Fe₂O₃, thermal treatment, XRD

INTRODUCTION
Iron oxide particles with controlled size and shape have attracted great attention in the last years. Because of their unique properties, the iron oxides are used in a wide range of applications as gas sensors [1, 2], catalysts [3] or pigments [4]. Due to their notable properties such as biocompatibility and magnetism, iron oxides (α-Fe₂O₃, γ-Fe₂O₃ and Fe₃O₄) are used in biomedicine as Magnetic Resonance Imaging contrast agents, vectors for drug delivery or agents for hyperthermia therapy [5,6]. Iron oxides are also used as a material for magnetic storage media [7] and in lithium-ion batteries [8,9].

Among the iron oxides, hematite (α-Fe₂O₃) is the most common iron oxide in nature. α-Fe₂O₃ is an n-type semiconductor, having a small band gap (2.1 eV) [10] and is the most stable iron oxide under ambient conditions. Because of its small band gap, hematite can absorb about 40% of the sunlight [11] which is an important advantage for its use in solar energy conversion.

In the last years many efforts have been focused on the obtaining methods of iron oxides. At present, iron oxide particles are synthesized by different methods such as the sonochemical route [12], coprecipitation [11], solid state chemical reaction [13], hydrothermal methods [10, 14], wood template [15], sol-gel [16] and mechanical methods [17,18].

In this work, we obtained iron oxide particles from homogenous precipitation of FeCl₂·4H₂O in the presence of NH₂CONH₂. The aim of this paper is to study the effect of the concentration of reactants, precipitation time, and thermal treatment on the formed iron oxide.
MATERIALS AND METHODS

The starting chemicals used were iron (II) chloride tetrahydrate (FeCl₂) and urea (NH₂CONH₂). Distilled water was used as solvent. All the reactants were analytically pure and used without further purification.

Precursor powders were synthesized by homogenous precipitation of iron (II) chloride in an aqueous solution that contained urea.

A fresh aqueous solution of FeCl₂·H₂O was prepared and mixed with an aqueous solution of NH₂CONH₂. Experimental conditions for the preparation of precipitates are given in Table 1. The experiments were performed in a thermostatic bath (Raypa Trade) at 90 °C. After a proper heating time, the solutions were filtered; the precipitates were washed several times with distilled water and then dried at room temperature.

α-Fe₂O₃ powders were obtained by thermal treatment of precursor powders prepared by the mentioned method, in an oven in presence of air for 4 hours at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FeCl₂ [M]</th>
<th>NH₂CONH₂ [M]</th>
<th>Precipitation time [hours]</th>
<th>Temperature of thermal treatment [ºC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>500</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>500</td>
</tr>
<tr>
<td>S3</td>
<td>0.9</td>
<td>0.7</td>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>S4</td>
<td>0.9</td>
<td>0.7</td>
<td>3</td>
<td>400</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns of samples were carried out on a Shimadzu XRD 6000 diffractometer with Cu Kα radiation, wavelength of 1.5405 Å. Scans were recorded in the 2θ ranging from 10° to 60°, with a scan rate of 2°/min. Optical properties of the samples were studied using a Perkin Elmer Lambda 35 spectrophotometer.

RESULTS AND DISCUSSION

The crystal structure and the phase composition of samples were identified by X-ray diffraction powder. X-ray diffraction patterns of precursor powders obtained at different precipitation times are presented in Fig.1. The diffraction peaks of the precursor powders can be indexed to the tetragonal FeO(OH) - akaganeite (PDF Number 34-1266).

We observed that the precipitation time of the reactants concentration has not influenced the phase composition or the structure of the formed powders. For all samples (S1, S2, S3, S4) the XRD analysis confirmed the formation of FeO(OH) phase.

Presence of diffraction peaks in XRD spectra of the treated samples at 2θ = 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°, 57.5° (57.4° for sample S4T) were in good agreement with the corresponding (012), (104), (110), (113), (024), (116) and (018) ((122) for S4) diffraction planes of hematite α-Fe₂O₃ (PDF Number 33-0664). It can be observed from XRD patterns of the treated samples (Fig.2) that after the thermal treatment the sample S4T represents low crystallinity from among the rest of the samples.
Fig. 1. Diffraction patterns of the precursor powders.

Figure 2. presents the diffraction patterns for the treated samples (S1T and S2T treated at 500 °C, S3T and S4T treated at 400 °C).

Fig.2. XRD patterns of treated samples - \(\alpha\)-Fe\(_2\)O\(_3\).

Crystallite size of the treated samples was estimated using the William-Hall [19] method which is given in equation (1):

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + 4\varepsilon \frac{\sin \theta}{\lambda}
\]

where: \(\beta\) – is the full width at half maximum of the broadened diffraction line on the 2\(\theta\) radius, \(D\) - the crystallite size, \(\lambda\) - the wavelength of the X-radiation, \(\varepsilon\) - the lattice strain in percentage.
One can see that the crystallite size of hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) has been influenced by the thermal treatment. The powders treated at 500°C (S1T, S2T) presented an increased grain size dimension from powders treated at 400°C (S3T, S4T). The sample S4T obtained by precipitation at 3 hours exhibits a very small grain size dimension in comparison with the sample S2T obtained at the same precipitation time but at a lower concentration of reactants. The crystallite size of the hematite samples are presented in Table 2.

**Tab.2. Crystallite size of the $\alpha$-$\text{Fe}_2\text{O}_3$ powders.**

<table>
<thead>
<tr>
<th>Crystallite size (nm)</th>
<th>Lattice strain, $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1T</td>
<td>109</td>
</tr>
<tr>
<td>S2T</td>
<td>153</td>
</tr>
<tr>
<td>S3T</td>
<td>80</td>
</tr>
<tr>
<td>S4T</td>
<td>32</td>
</tr>
</tbody>
</table>

Optical investigation of the $\alpha$-$\text{Fe}_2\text{O}_3$ powders was performed using a Perkin Elmer Lambda 35 spectrophotometer. The optical absorption spectrums were recorded over wavelengths ranged from 350-900 nm. In Fig.3 are presented the optical absorption spectra of hematite samples visibly.

Fig.3. Absorption spectres of $\alpha$-$\text{Fe}_2\text{O}_3$ powders: S1T (T = 500°C), S2T (T = 500°C), S3T (T = 400°C), S4T (T = 500°C).

It can be seen that for all samples there is an absorption decrease with an increase of wavelength. We observed that $\alpha$-$\text{Fe}_2\text{O}_3$ powders obtained at 500°C show a narrow maximum absorption, while the $\alpha$-$\text{Fe}_2\text{O}_3$ powders obtained at 400°C show a large maximum absorption. We can conclude that thermal treatment influenced the optical absorption of the powders. However, the maximum absorption visibly ranged between 560 -572 nm for all samples, results which are in good agreement with the literature data [20].
CONCLUSIONS

Iron oxide particles were obtained by chemical precipitation. The thermal treatment of the powders leads to a phase conversion from FeO(OH) to $\alpha$-Fe$_2$O$_3$. We observed that the powders treated at 400°C presented smaller grain size than the powders treated at 500°C. Also the absorption peaks were influenced by the thermal treatment, the samples treated at higher temperature showed a narrow absorption maximum.

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REFERENCES