

THERMAL DECOMPOSITION OF SOME METAL-ORGANIC PRECURSORS

Fe₂O₃ nanoparticles

M. Ștefănescu^{1*}, O. Ștefănescu¹, M. Stoia¹ and C. Lazau²

¹Faculty of Industrial Chemistry and Environmental Engineering, University 'Politehnica' of Timisoara, P-ta Victoriei nr. 2. 300006, Timisoara, Romania

²National Institute of Condensed Materials Research, Str. C. Drănescu No. 1, Timisoara, Romania

In this paper we present a study on the synthesis of Fe(III) oxide, by thermal decomposition of some complex combinations of Fe(III) with carboxylate type ligands, obtained in the redox reaction between some polyols (ethylene glycol (EG), 1,2-propane diol (1,2PG), 1,3-propane diol (1,3PG) and glycerol (GL)) and NO₃⁻ ions (from ferric nitrate). Fe₂O₃ was obtained by thermal decomposition of the synthesized metal-organic precursors at low temperatures. γ-Fe₂O₃ was obtained as nanoparticles at 300°C, while at higher temperatures α-Fe₂O₃ starts to crystallize and becomes single phase at ~500°C.

The formation of the metal-organic precursors and their thermal decomposition were studied by thermal analysis and FTIR spectroscopy.

The evolution of Fe₂O₃ crystalline phases with the thermal treatment of iron complexes was followed by RX diffractometry. The size of γ-Fe₂O₃ nanoparticles was estimated by transmission electron microscopy (TEM).

Keywords: carboxylate, γ-Fe₂O₃, nanoparticles, thermal analysis, XRD

Introduction

Fe₂O₃ represents one of the most studied materials due to the multiple applications of this oxidic system: catalysts, pigments, magnetic and optical materials, ferrofluids etc. [1, 2].

The diversity of the characteristic crystalline Fe₂O₃ forms (α-, β-, γ- and ε-) and their applications in different domains, makes this oxidic system to be intensively studied [1–5].

Fe₂O₃ as nanoparticles has significantly different properties compared to the properties of the bulk material. For example, magnetic iron oxide nanoparticles exhibit enhanced surface effects, superparamagnetic behavior and changes in saturation magnetization and coercitive fields [6]. This is the reason why the studies on Fe₂O₃ nanoparticles and their synthesis methods have always been on the researcher attention [7–9].

One of the most used methods for the synthesis of Fe(III) oxides nanoparticles, is the thermal conversion of its complex combinations [10–13]. Thermal analysis is the most suitable method to study the thermal decomposition of complexes [14–16], in order to establish the optimal conditions for the thermal conversion to iron oxides.

In our studies we have obtained oxidic systems by thermal decomposition of some polynuclear complex combinations, with ligands which are oxidation products of the diols [17, 18].

The synthesis method is based on the redox reaction between polyols and the nitrate ions, which progresses during the heating of the metal nitrates and polyols solutions. The carboxylate ions resulted from the redox reaction form with the existing metallic ions, polynuclear complex combinations. These carboxylate type complexes decompose in the range 250–350°C, forming simple or mixed oxide systems [19, 20].

In this paper we present a study on the obtaining of γ-Fe₂O₃ and α-Fe₂O₃ as nanoparticles by thermal decomposition of some complex combinations of carboxylate type resulted in the redox reaction of Fe(NO₃)₃ with different polyols (EG, 1,2 PG, 1,3 PG, GL).

Experimental

The reagents used in synthesis of Fe₂O₃ were: Fe(NO₃)₃·9H₂O as iron source, the polyols: ethylene glycol (EG), 1,2-propylene glycol (1,2 PG), 1,3-pro-

* Author for correspondence: mircea.stefanescu@chim.upt.ro

ylene glycol (1,3 PG), glycerol (GL), all of purity >98%, Merck.

The synthesis involves two stages: obtaining of precursors and obtaining of Fe₂O₃ by corresponding thermal treatment of the precursors.

Synthesis

The synthesis of the precursors is based on the redox reaction of iron(III) nitrate with polyol, which takes place at heating, with formation of an iron(III) complex combination of carboxylate type (depending on the polyol).

There were synthesized four samples with different polyols, according to Table 1:

- Fe(NO₃)₃·9H₂O-EG (sample O1)
- Fe(NO₃)₃·9H₂O-1, 2 PG (sample O2)
- Fe(NO₃)₃·9H₂O-1, 3 PG (sample O3)
- Fe(NO₃)₃·9H₂O-GL (sample O4)

The corresponding Fe(NO₃)₃·9H₂O amount was dissolved in polyol (using an excess of polyol compared to the stoichiometric necessary). The obtained solution is heated, on water bath, until the release of the redox reaction between the polyol and the nitrate ions. The heating is continued until the reaction is over, when no gas (NO₂) emission was observed. The reaction product was thermally treated at 130°C, for 3 h, when we obtain the complex combination of carboxylate type.

The obtained precursors, as powders, were thermally treated at different temperatures, in order to obtain iron(III) oxide.

The compositions and some characteristics of the synthesized samples are presented in Table 1.

Experimental techniques

The progress of the redox reactions between iron(III) nitrate and polyols and the decomposition of the formed complexes, were achieved by thermal analysis using a 1500 D MOM Budapest derivatograph. The experiments have been done with platinum plates, in air, in the temperature range 20–500°C, with a heating rate of 5°C min⁻¹, using as reference α-Al₂O₃.

The synthesized samples were also characterized by FTIR spectrometry with a JASCO 430 FTIR spectrometer, in KBr pellets, in the range 400–4000°C.

The phases analysis of the thermally treated samples was achieved on a D8 Advanced-Bruker AXS diffractometer, using CuK_α radiation (λ_{Cu}=1.54056 Å).

The transmission electron microscopy was performed with a JEOL JEM 1010 Microscop.

Results and discussions

Studies on the redox reaction between NO₃⁻ and different polyols have shown that in this reaction participate only the –OH groups from the primary C atom. Thus, depending on the work conditions, the polyols may oxidize to aldehydes, carboxylic acids or compounds with joint functions [21]. For example, EG may oxidize to glycolic aldehyde, glycolic acid, glyoxilic acid or oxalic acid [22, 23].

In case of 1,2 propane diol, the oxidation with nitrate ions takes place at the primary –OH group, when the lactate anion (CH₃–CH₂(OH)–COO⁻) forms [24, 25]. In case of 1,3 propane diol, depending on the conditions (temperature, acidity, molar ratio diol/metallic nitrate), oxidation may take place only at one of the primary –OH groups, when the anion 3-hydroxy-propionate (HO–CH₂–CH₂–COO⁻) forms, or at both primary –OH groups, when the malonate anion forms (OOC–CH₂–COO⁻) [25, 26].

In case of glycerol, due to the three adjacent –OH groups, the oxidation process is much more complex, leading to different products (glyceric acid, glyceric aldehyde, dihydroxy acetone, hydroxy malonic acid, etc.). Generally, it is difficult to obtain a unitary oxidation product of glycerol [27].

The oxidation products of the polyols (carboxylate, hydroxycarboxylate or dicarboxylate anions) resulted in the redox reaction with Fe(III) nitrate, form with Fe³⁺ ions, coordinative compounds used at forerunners of the Fe₂O₃ oxidic system as nanoparticles.

Thermal analysis

In order to establish the synthesis conditions of Fe₂O₃, starting from Fe(III) nitrate and polyols (EG, 1,2PG,

Table 1 Characteristics of the synthesized samples

Sample	Polyol	Quantity/mole			Molar ratio NO ₃ ⁻ :Pol
		Fe(NO ₃) ₃ ·9H ₂ O	NO ₃ ⁻	Polyol	
O1	EG	0.0626	0.1878	0.1878	1:1
O2	12PG	0.0626	0.1878	0.1878	1:1
O3	13PG	0.0626	0.1878	0.1878	1:1
O4	GL	0.0626	0.1878	0.1878	1:1

1,3PG, GL) we have followed by thermal analysis the redox reaction NO_3^- -polyol with the formation of the carboxylic compounds and their thermal decomposition, also.

Figures 1, 2, 3 and 4 present the TG and DTA curves obtained at thermal analysis until 500°C , in air, of the $\text{Fe}(\text{NO}_3)_3$ -polyol solutions, deposited in film on platinum plates. In all the four cases, the DTA curves show two exothermic effects in the same temperature ranges. The first exothermic effect, weak, in the range 60 – 100°C , corresponds to the redox reaction between the nitrate ions and the polyol when the complex combination is formed. The mass loss registered in this interval, on the TG curve is due to the waters evaporation, to the elimination of the resulted NO in the redox reaction and to the evaporation of the polyol excess.

The second exothermic effect, stronger, localized in the interval 250 – 300°C , accompanied by a mass loss on the TG curve, corresponds to the oxidative thermal decomposition of the complex.

From this study we have established the temperature 130°C as optimal for the synthesis of the carboxylate complexes.

The complex combinations synthesized at 130°C (O1, O2, O3, O4), were studied by FTIR spectrometry

and thermal analysis in air, until 500°C on platinum plates (Figs 5–8).

FTIR analysis

To evidence the formation of complex combinations between Fe^{3+} and the carboxylate anions, FTIR spectrometry was used.

Figure 5 presents the FTIR spectra of the precursors O1, O2, O3, O4 synthesized at 130°C from

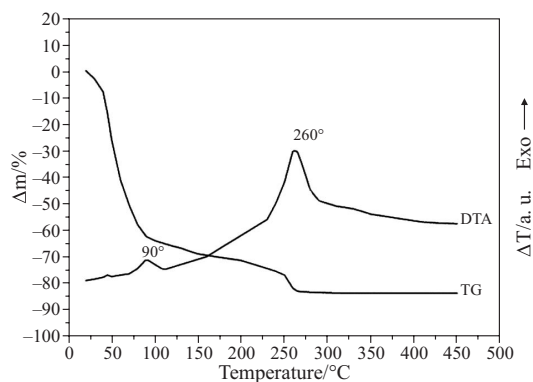


Fig. 3 TG and DTA thermal curves of the solution $\text{Fe}(\text{NO}_3)_3$ -13PG

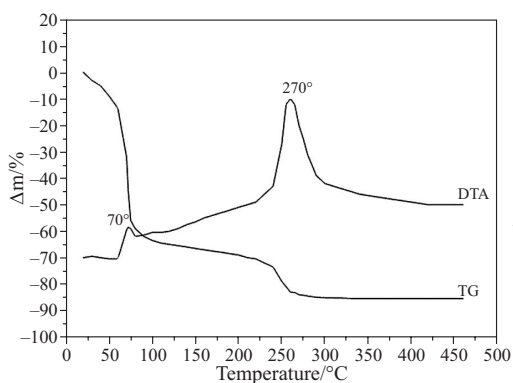


Fig. 1 TG and DTA thermal curves of the solution $\text{Fe}(\text{NO}_3)_3$ -EG

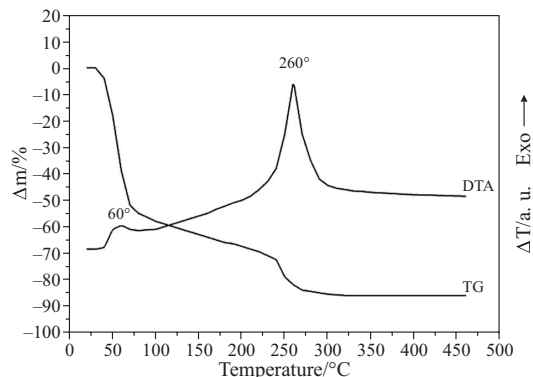


Fig. 4 TG and DTA thermal curves of the solution $\text{Fe}(\text{NO}_3)_3$ -GL

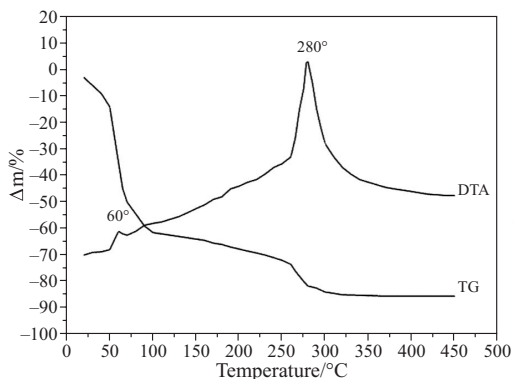


Fig. 2 TG and DTA thermal curves of the solution $\text{Fe}(\text{NO}_3)_3$ -12PG

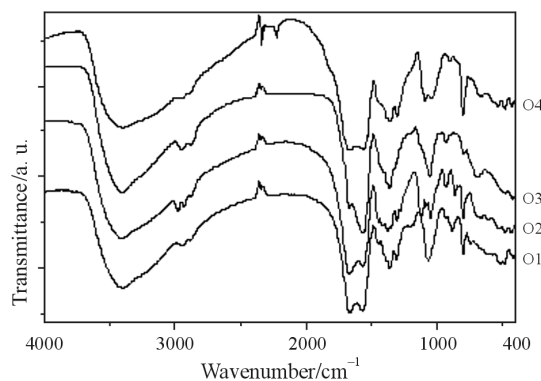


Fig. 5 The FTIR spectra of the complexes obtained at 130°C in the reaction of $\text{Fe}(\text{NO}_3)_3$ with: EG (O1), 1,2PG (O2), 1,3PG (O3), GL (O4)

$\text{Fe}(\text{NO}_3)_3$ and EG (sample O1), 1,2PG (sample O2), 1,3PG (sample O3) and GL (sample O4), respectively.

Comparing these spectra with the ones of the corresponding polyols, we have noticed, in all the four cases, the appearance of some characteristic bands of the carboxylate anions: an intense band at 1670 cm^{-1} , attributed to the vibration $\nu_{\text{as}}(\text{COO}^-)$, prove of the corresponding carboxylic ligands formation [24]. In the range $1300\text{--}1450\text{ cm}^{-1}$ are evidenced characteristic bands of the group (COO^-) at 1320 and 1380 cm^{-1} attributed to the vibrations $\nu_{\text{s}}(\text{CO})+\delta(\text{OCO})$, respectively at 1450 cm^{-1} attributed to the vibrations $\nu_{\text{s}}(\text{COO}^-)$ [28, 29]. The characteristic bands of the $(-\text{OH})$ group vibrations are also presented in the range $1300\text{--}1400\text{ cm}^{-1}$, which overlap with the ones corresponding to the carboxylic groups.

The FTIR analysis confirms the fact that in the redox reaction between ferric nitrate and polyols, complex combinations with ligands of carboxylate type, are formed.

Thermal analysis of precursors

Figures 6–9 presents the thermal curves (TG, DTA) registered at the heating in air, until 500°C of the precursors: O1, O2, O3, O4.

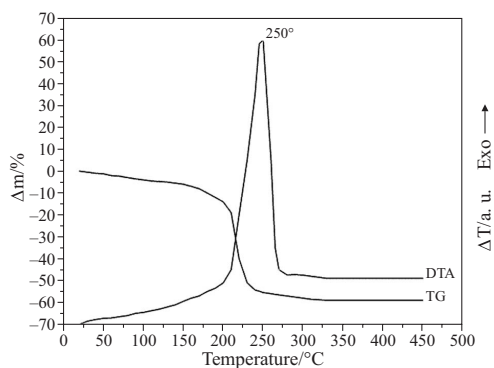


Fig. 6 TG and DTA thermal curves obtained at thermal analysis of the precursor O1 (from $\text{Fe}(\text{NO}_3)_3$ and EG)

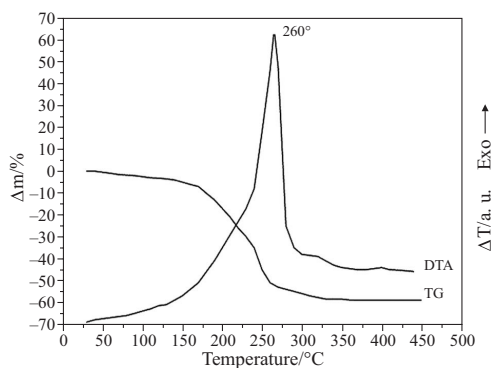


Fig. 7 TG and DTA thermal curves obtained at thermal analysis of the precursor O2 (from $\text{Fe}(\text{NO}_3)_3$ and 12PG)

TG curves evolution shows that the decomposition of $\text{Fe}(\text{III})$ complexes with carboxylate ligands, takes place in the range $150\text{--}300^\circ\text{C}$, independently on the ligands nature. The thermal decomposition processes are accompanied on the DTA curve, by strong exothermic effects. In the range $150\text{--}250^\circ\text{C}$, the high mass loss is due to the decomposition of the organic ligand of the complex, which creates in situ a reducing atmosphere (CO). In this conditions take place the partial reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$, followed by the reoxidation at Fe_2O_3 . Until 500°C , the mass of the samples maintains practically constant.

Considering the mass losses registered at thermal analysis of the complex combinations (Figs 6–9) and the oxidation possibilities of the polyols [22–28], we presume, for the synthesized compounds in the specified conditions, the composition formula presented in Table 2.

XRD analysis

Thermal analysis experiments have shown that the four synthesized precursors, totally decompose until 300°C , forming the oxidic system $\text{Fe}(\text{III})\text{--O}$. To follow the evolution of the characteristic phases of the system $\text{Fe}(\text{III})\text{--O}$, the precursors were thermally

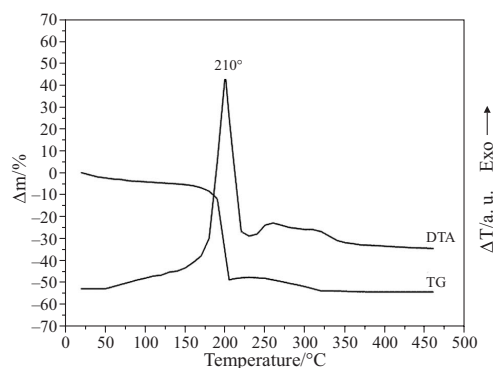


Fig. 8 TG and DTA thermal curves obtained at thermal analysis of the precursor O3 (from $\text{Fe}(\text{NO}_3)_3$ and 13PG)

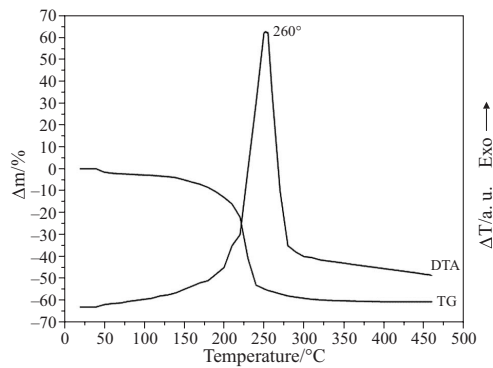


Fig. 9 TG and DTA thermal curves obtained at thermal analysis of the precursor O4 (from $\text{Fe}(\text{NO}_3)_3$ and GL)

Table 2 Composition formula of the synthesized precursors

Sample	Composition formula of the precursors	$M/g\ mol^{-1}$	$m_{res}\%/calculated$	$m_{res}\%/experimental$
O1	$[Fe_2(OH)_2(C_2H_2O_4)_2(OH_2)_2]_n \cdot nH_2O$	$n^*379.7$	42.1	42.5
O2	$[Fe_2(OH)_4(C_3H_5O_3)_2(OH_2)_2]_n \cdot nH_2O$	n^*412	38.8	41.0
O3	$[Fe_2(OH)_4(C_3H_2O_4)(OH_2)_2]_n \cdot nH_2O$	n^*335	47.6	45.0
O4	$[Fe_2(OH)_4(C_3H_2O_5)(OH_2)_2]_n \cdot 2nH_2O$	$n^*369.7$	43.3	41.0

treated at different temperatures, and the obtained powders were characterized by XRD.

Figures 10–12 present the XRD spectra of the samples O1, O2, O3, O4, heated at 300, 350 and at 400°C, for 3 h.

The XRD spectra presented in Fig. 10, for the precursors O1, O2, O3, O4, heated at 300°C, show the presence of $\gamma\text{-Fe}_2\text{O}_3$ (JPCDS-24-0081) as unique phase. Formation of $\gamma\text{-Fe}_2\text{O}_3$ is promoted by the reduction – reoxidation process: $Fe(III) \leftrightarrow Fe(II) \leftrightarrow Fe(III)$, during the thermal decomposition of the precursors, in agreement with those presented in the specialist literature [3].

The XRD spectra of the samples O1, O2, O3, O4 heated at 350°C, evidence the appearance of the

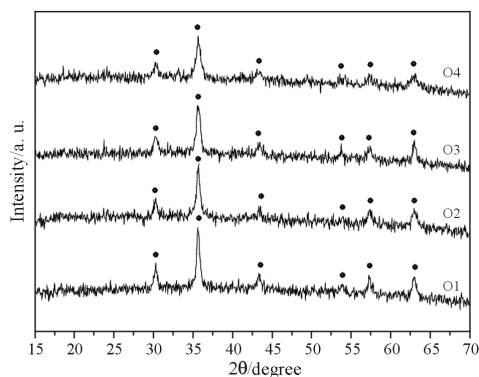


Fig. 10 XRD spectra of the samples obtained by the calcinations of the precursors O1, O2, O3, O4 at 300°C
● – $\gamma\text{-Fe}_2\text{O}_3$

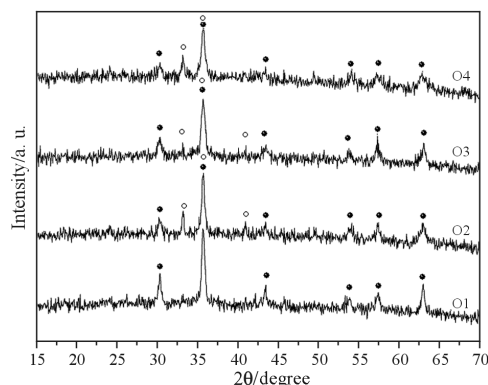


Fig. 11 XRD spectra of the samples obtained by the calcinations of the precursors O1, O2, O3, O4 at 350°C
● – $\gamma\text{-Fe}_2\text{O}_3$, ○ – $\alpha\text{-Fe}_2\text{O}_3$

Table 3 Average diameter of the $\gamma\text{-Fe}_2\text{O}_3$ crystallites (at 300°C) and $\alpha\text{-Fe}_2\text{O}_3$ crystallites (at 400°C)

Sample	d/nm			
	O1	O2	O3	O4
$\gamma\text{-Fe}_2\text{O}_3$ (300°C)	34	30	27	22
$\alpha\text{-Fe}_2\text{O}_3$ (400°C)	50	50	42	41

$\alpha\text{-Fe}_2\text{O}_3$ phase (JPCDS-24-0072), weakly crystallized (Fig. 11).

The spectra presented in Fig. 12, for the samples obtained by calcinations at 400°C, show as crystallized phase $\alpha\text{-Fe}_2\text{O}_3$ in all cases.

Table 3 presents the values of the average diameter (d) of the crystallites estimated from the diffraction maximum (311) for $\gamma\text{-Fe}_2\text{O}_3$ (Fig. 10) and from

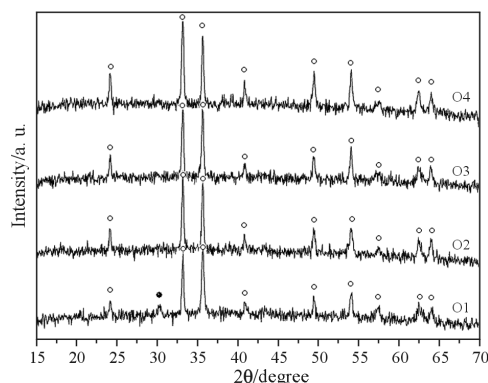


Fig. 12 XRD spectra of the samples obtained by the calcinations of the precursors O1, O2, O3, O4 at 400°C
● – $\gamma\text{-Fe}_2\text{O}_3$, ○ – $\alpha\text{-Fe}_2\text{O}_3$

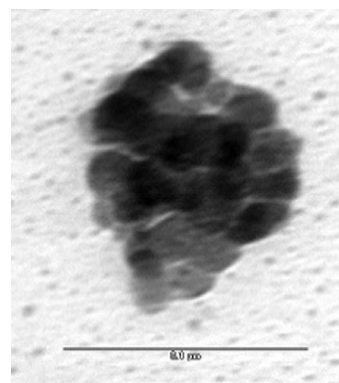


Fig. 13 TEM image of the $\gamma\text{-Fe}_2\text{O}_3$ powder obtained by calcinations at 300°C of the precursor O1

the diffraction maximum (104) for α -Fe₂O₃ (Fig. 12) using the Scherrer formula [30].

From Table 3 results that we obtained nanocrystallites of Fe₂O₃ (γ , α), with dimensions under 50 nm, depending on the nature of the used precursor and on the temperature of thermal treatment.

Obtaining γ -Fe₂O₃ as nanoparticles, was also confirmed by transmission electron microscopy (TEM). Figure 13 presents the TEM image of the sample obtained by calcinations of the precursor O1 at 300°C. This image shows that γ -Fe₂O₃ is obtained as spherical nanoparticles with size in the range 20–30 nm.

From the performed studies results that, depending on the precursor nature and on the thermal treatment, we can obtain different Fe₂O₃ phases as nanoparticles, depending on the followed purpose (magnetic, catalytic, optical properties).

Conclusions

The presented study has followed the synthesis of Fe₂O₃ by thermal decomposition of the carboxylate type complex combinations resulted from the redox reaction between some polyols (EG, 1,2PG, 1,3PG and GL) and Fe(III) nitrates. The decomposition of the synthesized precursors takes place at low temperatures (250–300°C) with the in situ reduction of Fe(III) at Fe(II), followed by reoxidation of Fe(II), when γ -Fe₂O₃ is obtained at 300°C, as unique phase. At higher temperatures (400, 500°C) α -Fe₂O₃ is obtained, for all the studied precursors.

The obtaining of these phases is not significantly influenced by the polyols nature used in synthesis, but small differences appear in nanoparticles size.

The advantage of this method is that these carboxylate compounds of Fe(III) lead, through thermal decomposition, to γ -Fe₂O₃ nanoparticles.

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