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Synthesis and characterization of new hydroxycarboxylate compounds obtained in the redox reaction between $Fe(NO_3)_3$ and diol

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ABSTRACT

The paper presents experimental studies and structural investigations of two new Fe(III) hydroxycarboxylate coordination compounds.

The homopolynuclear complex combinations of Fe(III) glyoxylate and succinate type were obtained in the redox reaction between $Fe(NO_3)_3$ and diols (1,2-ethanediol and 1,4-butanediol). The synthesized coordination compounds and the products formed during their thermal conversion were characterized by thermal analysis (in air and nitrogen), FT-IR and UV–VIS spectrometry, Mössbauer spectrometry, electron microscopy and XRD.

By thermal decomposition of the complex combinations, at 300 °C, the well crystallized pure phase γ-Fe_2O_3 as nanoparticles were formed.

1. Introduction

Combinations of transitional metals with anions of carboxylic acids are intensively used to obtain metal oxides at low temperatures [1–3]. The knowledge of the formation of thermal decomposition products from various precursors is very important in the materials synthesis.

The aliphatic monocarboxylates (formate, acetate, propionate), the dicarboxylates and poly(hydroxy)carboxylates (oxalates, maleates, tartrates and malonates) [4,5] are used as precursors for obtaining of metal oxides, with good results, through their thermal decomposition. At oxidative degradation of the carboxylate ligands of the coordination compounds, it is possible to isolate reaction intermediates as oxalates and maleates in tartrates complexes [6,7], malonates and acetates in maleates complexes [8,9], which by oxidative decomposition lead to metal oxides.

In the past few years, the interest has been focused on the synthesis of γ-Fe_2O_3 nanoparticles from organic precursors: $Fe(acac)_3$, $Fe(CO)_5$, Fe–urea complex ($[Fe(CON_2H_4)_6](NO_3)_3$) [10–13]. These synthesis methods are characterized by homogenous mixing of reactants at molecular or atomic level. Common for this type of synthesis are: low temperatures of thermal treatment, small particles size, high homogeneity and stoichiometry as compared to the conventional methods of syntheses [14].

In our previous papers, we have shown the preparation of mixed oxide systems like ferrites [15,16] and chromites [17] from polynunclear complex combinations of metal carboxylate, using a new synthesis method. The present study aims at synthesis and characterization of two coordination compounds of Fe(III) hydroxycarboxylate (i.e. glyoxylate and succinate) type using the method [18] based on the redox reaction between Fe(III) nitrate and diol (1,2-ethanediol and 1,4-butanediol).

By thermal decomposition of the synthesized compounds at ~300 °C, in air we obtained the single phase γ-Fe_2O_3, as nanoparticles.

2. Experimental

For the synthesis of the hydroxycarboxylate type combinations as iron(III) source: $Fe(NO_3)_3 9H_2O$ and the diols 1,2-ethanediol (EG) and 1,4-butanediol (1,4 BG), of purity >98% (Merck) were used.

The complex combinations were obtained according to the previous described method [18,19]. The synthesis method is based on the redox reaction between the anion $NO_3{}^-$ of $Fe(NO_3)_3{\cdot}9H_2O$ and the —OH groups of the diols. According to the stoichiometry of the redox reactions the molar ratios of the used reactants are: $NO_3{}^-$:EG = 2:1 (Eq. (1)) and $NO_3{}^-$:1,4 BG = 8:3 (Eq. (2)). For the synthesis a diol excess of 50% compared to the stoichiometric necessary $NO_3{}^-$ was used. Table 1 presents the composition of the mixtures $Fe(NO_3)_3{\cdot}9H_2O$–diol.

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Table 1
The compositions of the solutions $Fe(NO_3)_3 \cdot 9H_2O$–diol.

Sample	Diol	Quantity (moles)			Molar ratio NO_3^-:diol
		$Fe(NO_3)_3 \cdot 9H_2O$	NO_3^-	Diol	
B1	EG	0.0375	0.1125	0.0844	1:0.750
B2	1,4 BG	0.0375	0.1125	0.0633	1:0.563

$Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in diol resulting a homogenous, clear solution, which was heated in an oven up to ~60 °C, when the redox reaction (exothermal) was initiated with evolving of brown nitrogen oxides and temperature increase up to ~100 °C. The heating was continued at 130 °C, 3 h, when the reaction was ended. The resulted products were grinded and washed with acetone in order to remove the reactant excess.

The redox reaction deployment was studied by thermal analysis [19] and FT-IR spectrometry. The complex combinations synthesized at 130 °C were characterized by thermal analysis, in air and nitrogen, FT-IR, UV–VIS and Mössbauer spectrometry. The iron content in the synthesized samples was determined by atomic absorption spectrometry. The synthesized ferritic precursors were thermally treated in order to obtain the spinel, γ-Fe_2O_3, which was identified by FT-IR spectrometry and XRD.

2.1. Techniques

The thermal analysis curves (TG, DTA, DTG) in air and nitrogen were recorded on a Diamond Perkin Elmer thermobalance. All experiments were carried out under identical conditions maintaining the following instrumental parameters: heating rate 10 °C/min, mass of the sample ~20 mg, the reference material employed for DTA was Al_2O_3.

FT-IR spectra of the complex combinations and their decomposition products were recorded in the range 400–4000 cm^{-1} on a Shimadzu Prestige-21 FT-IR spectrophotometer using KBr pellets.

The powder XRD patterns of the decomposition products were recorded at room temperature with an Advanced-Bruker AXS diffractometer, using MoKα radiation (λ = 0.7093 Å).

Mössbauer spectra measurements were carried out in the transmission mode with ^{57}Co diffused into a Rh matrix as a source moving with constant acceleration. The spectrometer (Wissel) was calibrated by means of a standard α-Fe foil, and the isomer shift was expressed with respect to this standard at room temperature. The fitting of the spectra was performed using the NORMOS program.

The diffuse reflectance data were recorded with a Spekol 10 Carl Zeiss Jena spectrophotometer using MgO as reference material.

Atomic absorption measurements of iron (λ = 284.3 nm) were carried out using AA280FS Varian, with flame type: air/acetylene, air flow: 13.50 L/min, acetylene flow: 2.00 L/min and lamp current 5.0 mA and the analysis was performed according to Ref. [20].

The electron microscopy was performed on a JEOL JEM 3010 microscope.

3. Discussion

Literature studies [21] have established that in certain conditions, 1,2-ethanediol (EG) is oxidized according to Eq. (1) to the glyoxylate dianion ($C_2H_2O_4^{2-}$) while 1,4-butanediol (1,4 BG) is oxidized to the succinate anion ($C_4H_4O_4^{2-}$) according to Eq. (2), similar to the oxidation of 1,3-propanediol [22].

$$HO{-}CH_2{-}CH_2{-}OH + 2NO_3^- \rightarrow C_2H_2O_4^{2-} + 2NO + 2H_2O \quad (1)$$

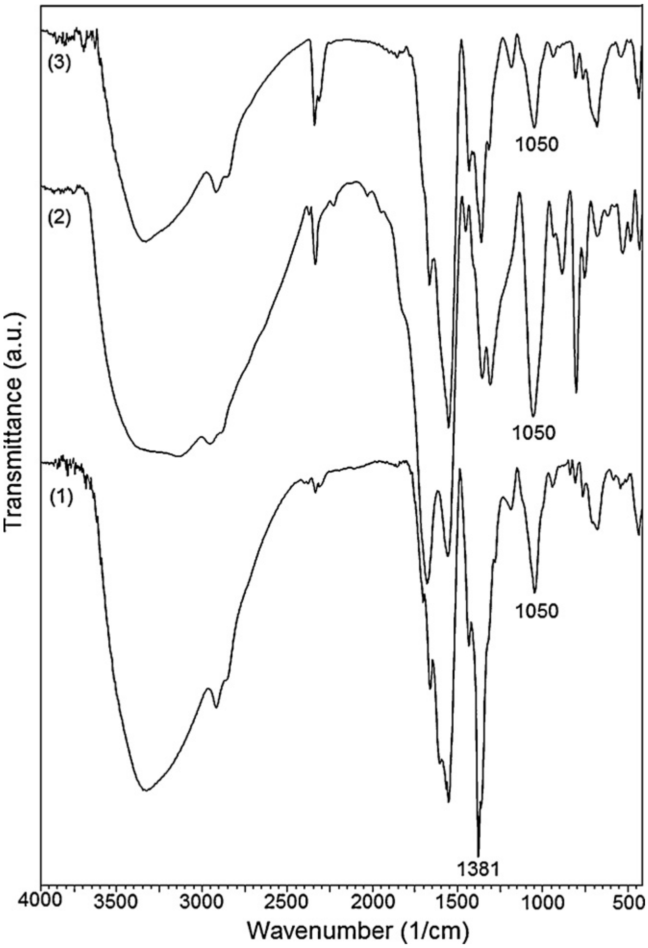


Fig. 1. FT-IR spectra of samples: B1 at 100 °C (1), B1 at 130 °C (2) and B2 at 130 °C (3).

$$3HO{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH + 8NO_3^- + 2H^+ \rightarrow 3C_4H_4O_4^{2-} + 8NO + 10H_2O \quad (2)$$

The oxidation of the diol develops simultaneous with the coordination of the oxidation product (glyoxylate, $C_2H_2O_4^{2-}$ or succinate, $C_4H_4O_4^{2-}$) at the complex generator (Fe^{3+}), which moves the equilibrium towards the formation of coordination compounds with the proposed formulae: $[Fe_2(C_2H_2O_4)_2(OH)_2(H_2O)_2]$ and $[Fe_2(C_4H_4O_4)(OH)_4(H_2O)_2]$.

3.1. Thermal analysis and FT-IR spectrometry

FT-IR spectrometry was used in order to follow the progress of the redox reaction between iron nitrate and diol and to obtain informations on the function of ligands coordinated to the bonds of the complex.

Fig. 1 presents the FT-IR spectrum (1) for sample B1 heated at 100 °C, when the redox reaction was not completed, showing the intense band at 1381 cm^{-1} characteristic for the free ion NO^{3-} (not totally reacted) together with bands corresponding to the complex combination, which starts to form at this temperature. The spectra (2) and (3) for the samples B1 and B2 heated at 130 °C, when the redox reaction was complete, present the bands characteristic for the carboxylate type complex combinations: $\nu_{as}(COO^-)$ in the range 1500–1700 cm^{-1} and $\nu_s(COO^-)$ in the range 1300–1400 cm^{-1}. The band at ~1050 cm^{-1} is attributed to the ν(OH) bridge [23,24].

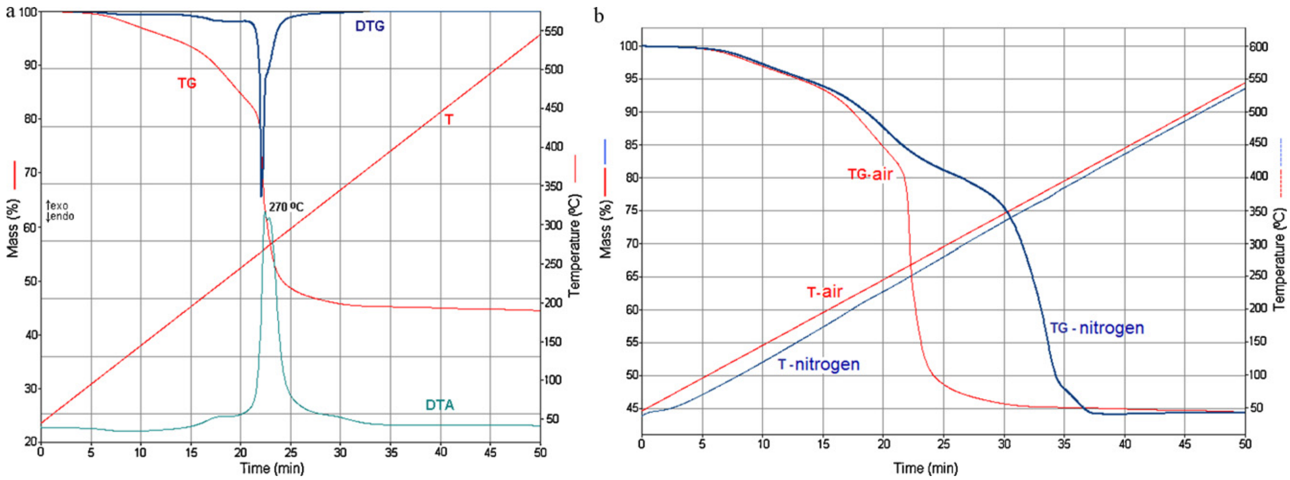


Fig. 2. Thermal curves of the complex combination B1 obtained at 130 °C: (a) in air; (b) TG curves in air and nitrogen.

From the FT-IR data, the synthesis temperature of the Fe(III) hydroxycarboxylate type complex combinations was established at 130 °C.

In order to establish the composition formulae of the Fe(III) complex combinations, the compounds B1 and B2, synthesized at 130 °C, were thermally analyzed, in air and nitrogen atmosphere.

Fig. 2a presents the TG, DTG and DTA curves, in air, of the complex combination B1 heated at 130 °C. The evolution of the thermal curves evidences a mass loss of 9.5% up to 210 °C, attributed to the elimination of coordinated water. In the temperature range 210–350 °C takes place the mass loss of 45.5% corresponding to the oxidative decomposition of the organic ligand (burning), with an exothermic effect on DTA at 270 °C. Up to 500 °C, the mass remains constant, and the residue corresponds to iron oxide (45 wt% Fe_2O_3).

Fig. 2b presents the TG curves recorded at decomposition of the complex combination B1 in air and nitrogen atmosphere. The thermal curves indicate a similar mass loss up to 220 °C, which corresponds to the elimination of the coordinated water. In the second stage, corresponding to the decomposition of the complex combination (nitrogen) and to the oxidative decomposition in air, the processes develop with different rates, in different temperature ranges, resulting in the same residual mass (45 wt% Fe_2O_3).

The oxidative decomposition in air may take place according to Eq. (3):

$$[Fe_2(C_2H_2O_4)_2(OH)_2(H_2O_2)]\xrightarrow[-2\,H_2O]{20-220\,^{\circ}C}$$

$$[Fe_2(C_2H_2O_4)_2(OH)_2]\xrightarrow[-3\,H_2O]{+2\,O_2/220-350\,^{\circ}C}Fe_2O_3+4CO_2 \qquad (3)$$

The evolution of the TG, DTG and DTA curves, in air, for the complex combination B2 (Fig. 3a) is similar to the one for the complex combination B1. The first mass loss of ∼10% up to 200 °C on the TG curve, corresponds to the elimination of the coordinated water. The second stage, with a high rate mass loss of 38%, in a narrow temperature range 200–220 °C, is attributed to the oxidative decomposition of the ligand, with a strong exothermic effect at 230 °C on DTA. This behavior may be attributed to the nature of the diol (ligand) with lower thermal stability.

The oxidative decomposition of precursor B2 at lower temperature leads to residual carbon, which burns in the temperature range 300–400 °C, with a large exothermic effect at 330 °C on DTA and mass loss on TG (6%). Up to 500 °C, the mass remains constant and corresponds to Fe_2O_3 (46 wt%).

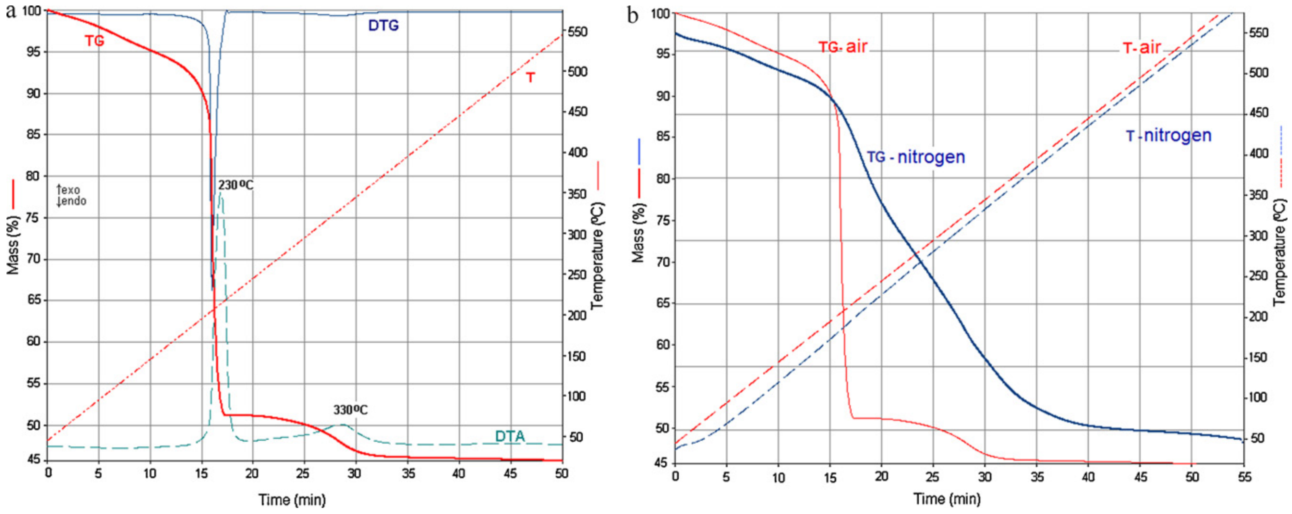


Fig. 3. Thermal curves of the complex combination B2 obtained at 130 °C: (a) in air; (b) TG curves in air and nitrogen.

Table 2
The residues corresponding to the proposed formulae.

Sample	Composition formula	*M* (g/mol)	$m_{res.}$ (%) 500 °C		
			calc.	exp. air	exp. nitrogen
B1	$[Fe_2(C_2H_2O_4)_2(OH)_2(H_2O)_2]$	362	44.2	45.0	45.0
B2	$[Fe_2(C_4H_4O_4)(OH)_4(H_2O)_2]$	332	48.2	46.0	52.5

Table 3
Diffuse reflectance spectral data of the investigated compounds.

Wavenumber (cm^{-1})		Assignments
B1	B2	
11110	11720	$^6A_1 \rightarrow {}^4T_1$
21370	21280	$^6A_1 \rightarrow {}^4T_2$
26810	29240	$^6A_1 \rightarrow {}^4A_1, {}^4E$

The evolution of the TG curves in air and nitrogen (Fig. 3b), sustains the fact that during the decomposition process, the mass at 500 °C is higher in nitrogen than in air due to the presence of residual carbon (Table 2).

According to the evolution of the thermal curves, we can propose the following scheme for the progress of the thermal processes in air (Eq. (4)):

$$[Fe_2(C_4H_4O_4)(OH)_4(H_2O_2)] \xrightarrow[-2\,H_2O]{20-220^\circ C} [Fe_2(C_4H_4O_4)(OH)_4] \xrightarrow[-4\,H_2O]{+7/2\,O_2/200-400^\circ C} Fe_2O_3 + 4\,CO_2 \qquad (4)$$

From the thermal behavior of the two complex combinations, B1 and B2, we can notice that Fe(III) glyoxylate presents a higher stability (exothermic effect at 270 °C) compared to Fe(III) succinate (exothermic effect at 230 °C).

Table 2 presents the residual masses, in air and nitrogen, at 500 °C (Figs. 2b and 3b) and the calculated masses corresponding to the proposed formulae for the synthesized compounds, B1 and B2.

The results of the atomic absorption measurements showed the following iron content for the complex combinations synthesized at 130 °C:

- Fe(III) glyoxylate type complex combination (B1): calculated = 30.9 wt% Fe, experimental = 30.5 wt% Fe;
- Fe(III) succinate type complex combination (B2): calculated = 33.7 wt% Fe, experimental = 32.4 wt% Fe.

3.2. Diffuse reflectance measurements and Mössbauer spectrometry

Table 3 shows the wavenumbers, which correspond to the diffuse reflectance spectral bands with tentative assignments. The values of the wavenumbers indicate an octahedral stereochemistry with a chromophore $[Fe(III)O_6]$, for the complex combinations B1 and B2 [25].

Fig. 4 presents the Mössbauer spectrum of the complex B2 of Fe(III) succinate type. The Mössbauer spectrum presents a doublet at room temperature, characterized by an isomer shift of 0.39 mm/s and a quadrupole splitting of 0.75 mm/s. The Mössbauer parameters indicate the compounds to be high spin iron(III) with octahedral geometries [26]. The Mössbauer spectrum of the complex B1 of Fe(III) glyoxylate type, is similar.

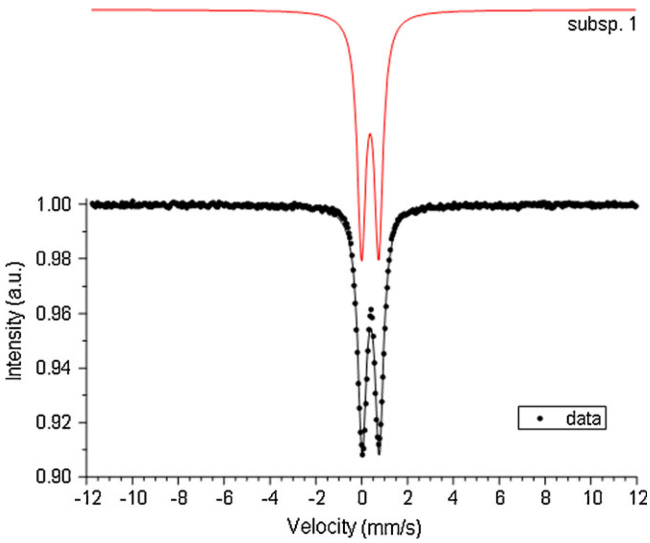
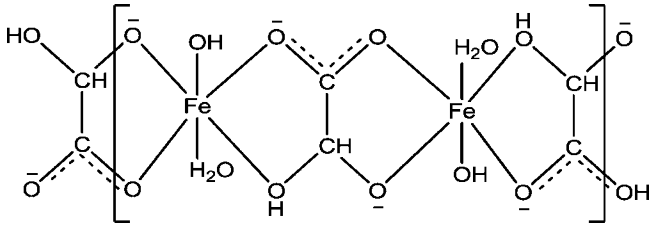
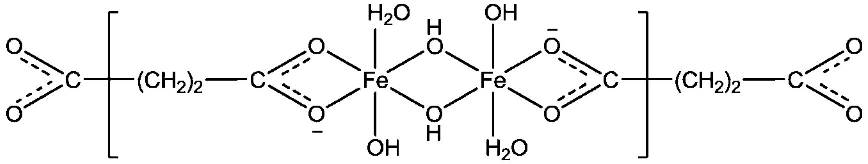


Fig. 4. Mössbauer spectrum of the complex B2 heated at 130 °C.

The qualitative and quantitative results obtained by the used investigation methods, and the literature data [21,27], can sustain the composition formulae proposed for the Fe(III) hydroxycarboxylate type complex combinations.

The synthesized complex combinations, B1 and B2, are practically insoluble in water. The proposed structure formulae (Schemes 5 and 6) could suggest a polymer structure of the synthesized combinations. The complex combination synthesized with 1,2-ethanediol is formed by the coordination of two Fe(III) ions to the double bridged glyoxylate dianion ($C_2H_2O_4^{2-}$) (Scheme 5) [21]. In case of the synthesis with 1,4-butanediol, the Fe(III) complex combination is formed by hydroxyl bridges (—OH) between two Fe(III) ions coordinated at the succinate anion ($C_4H_4O_4^{2-}$) (Scheme 6).





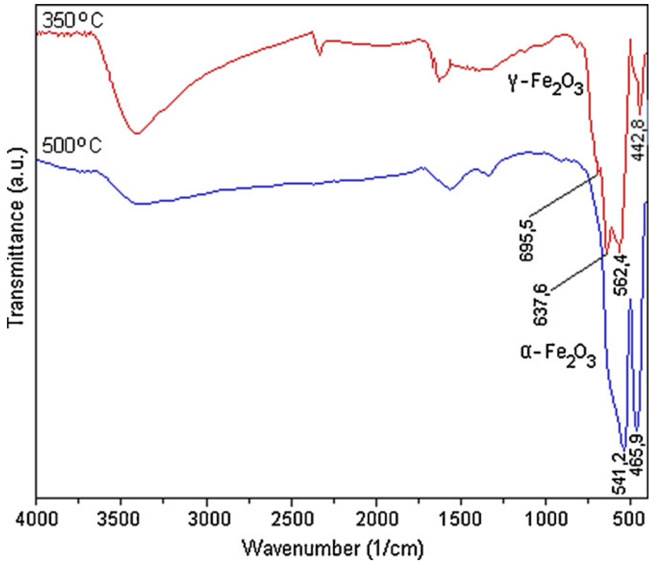


Fig. 5. FT-IR spectra of the complex B2 annealed at 300 and 500 °C.

3.3. XRD analysis

The new synthesized Fe(III) hydroxycarboxylate compounds, are potential precursors for the obtaining of iron oxides. From previous studies [19] results the particularity of these types of compounds, which by low temperature decomposition (250–300 °C), lead directly to the single crystallized phase γ-Fe_2O_3. At higher temperatures, γ-Fe_2O_3 turns to the more stable α-Fe_2O_3. Fig. 5 presents the FT-IR spectra of the precursor B2 annealed at 300 and 500 °C, 3 h. The spectrum from 300 °C presents the bands (695.5, 637.6, 562.4 and 442.8 cm^{-1}) attributed to the phase γ-Fe_2O_3 [28]. The spectrum from 500 °C presents the clear bands of the phase α-Fe_2O_3 [29].

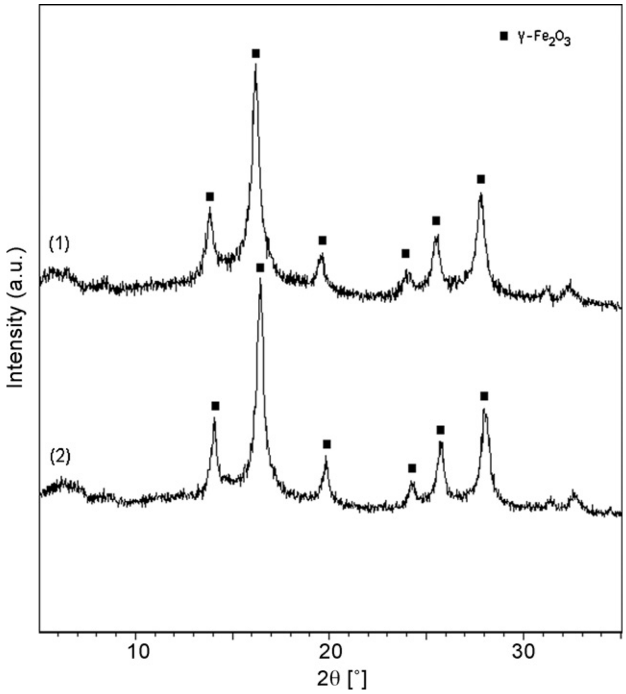


Fig. 6. XRD patterns of the complexes B1 (1) and B2 (2) annealed at 300 °C.

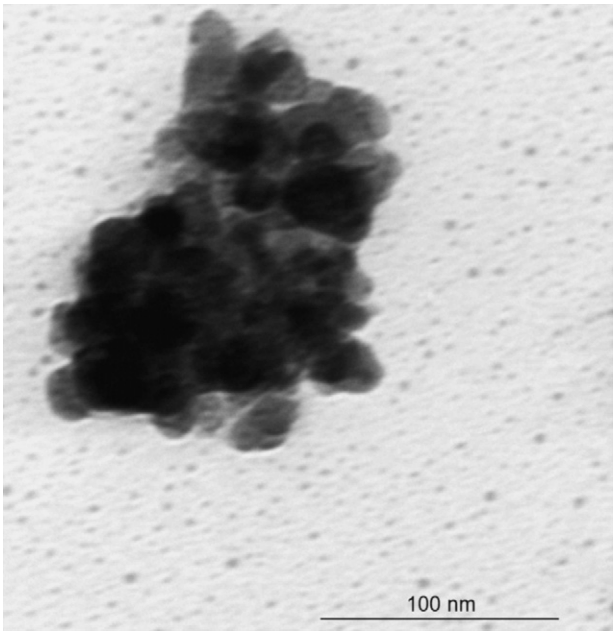


Fig. 7. TEM image of sample B2 annealed at 300 °C.

Fig. 6 presents the XRD patterns of the precursors B1 and B2 annealed at 300 °C, 3 h. In both spectra (1) and (2) appears the well crystallized, single phase γ-Fe_2O_3.

The reducing environment generated at burning of the ligand (Fe(III) glyoxylate or succinate) can influence the crystallization of the oxidic phase (γ-Fe_2O_3) and the particle size.

The average diameter of the crystallites was estimated from the diffraction patterns (Fig. 6) using the Scherrer equation [30] and the obtained values were in the range 11–16 nm. The TEM image Fig. 7 of sample B2, annealed at 300 °C, shows particles with diameters <20 nm, of almost spherical shape, well crystallized, with well defined margins. A pronounced agglomeration tendency is observed, due to the small particle size.

4. Conclusions

Fe(III) hydroxycarboxylate compounds were obtained by the proposed method based on the redox reaction between $Fe(NO_3)$ and diols (1,2-ethanediol and 1,4-butanediol).

Thermal analysis (in air and nitrogen) and FT-IR technique were successfully used for the investigation of the formation and decomposition mechanism of the Fe(III) complex combinations. FT-IR analysis has very well evidenced the evolution of the hydroxycarboxylate complexes formation by the presence of the band at 1381 cm^{-1} corresponding to the free NO^{3-} at ~100 °C, when the redox reaction did not take place, and the disappearance of this band with formation of the complex combination.

The results obtained by the used investigation methods allow to suggest composition and structure formulae for the two synthesized Fe(III) hydroxycarboxylate coordination compounds.

The evolution of the thermal curves has evidenced the thermal processes characteristic for this type of compounds and the final residue Fe_2O_3, at 500 °C, corresponds to the theoretic quantity according to the composition formulae. By controlled thermal treatment, at 300 °C, γ-Fe_2O_3 was formed.

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