SYNTHESIS AND CHARACTERIZATION OF Co(II) CARBOXYLATES RESULTED IN THE Co(NO$_3$)$_2$ – 1,3-PROPANEDIOL REDOX REACTION

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ABSTRACT

This paper presents the study of the redox reaction Co (NO$_3$)$_2$ – 1, 3 propanediol (HOCH$_2$CHCH$_2$OH) and the characterization of its product by means of thermal analysis, FTIR spectrometry and acidic – basic titrations. The study of the acidic – basic properties of the redox reaction product, correlated with the thermal analysis and FTIR spectrometry, highlights the formation of cobalt malonate (1.3 propane dicarboxilic acid). This product that thermally decomposes at 300°C was used as precursor for cobalt oxides.

As evidenced by XRD analysis of the annealing products at 400°C and 700°C, nanocrystallites Co$_3$O$_4$ is obtained at both temperatures.

INTRODUCTION

This method consists of two steps: the preparation of the precursors that contains the metallic ions in the desired molar ratio and the thermal decomposition of the precursors [1].

The method used in the paper for the preparation of cobalt oxides, use as oxide precursor the product of the redox reaction between cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O) and 1,3 propanediol (1,3PD) [2].

For the characterization of the precursors we can use thermal analysis,IR spectrometry and acidic-basic titrations. Titration techniques have the advantage of ease of implementation, cost-effectiveness and accuracy. Electrometric titrations have also the advantage of automation, increasing the analysis throughput and securing the consistent quality of the results. The study of acidic–basic properties of the precursor allows us to presume if we have a carboxylate compound [3]. The thermal analysis of the obtained precursor showed that it decomposes in the range of 200-300°C, leading to Co$_3$O$_4$ as nanocrystallites.

MATERIAL AND METHODS

The reagents used in synthesis were: Co (NO$_3$)$_2$.6H$_2$O and 1,3 propanediol (1,3PD), of purity p.a. (Merck).The method of synthesis consists in dissolving the cobalt nitrate in the appropriate amount of 1,3-propanediol, followed by controlled heating at temperatures above 100°C until the onset of redox reaction, visible through the release of nitrogen oxides.

The temperature of redox reaction initiation is around 140°C, this is an energic reaction, an important role here is played by the catalytic character of cobalt. Depending on the molar ratio (NO$_3^-$:1.3PG) the reaction may be more or less controlled, the reaction product is difficult to isolate (presents a high tendency for combustion). Reaction products were kept at a temperature of 140°C until the end of eliminating the brown gas (reaction completion).Oxidation of 1,3-PG takes place at the dicarboxylic anion, in the system is formed the cobalt malonate. The powder obtained at 140°C was washed with acetone for removing of reactant excess. The obtained products were characterized by thermal analysis, FT-IR spectrometry and conductometric/ pH-metric acidic-basic titrations. In order to obtain

cobalt oxides, the precursor was thermally decomposed at 300°C and annealed at 400°C and 700°C. The annealing products were studied by XRD.
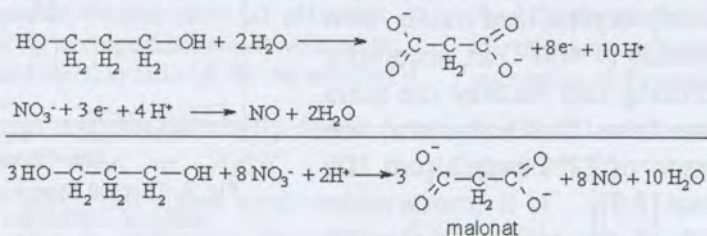
Thermal analysis was performed on a 1500D MOM Budapest Derivatograph. The heating was achieved in static air, until 500°C, with a heating rate of 5°C/min, on Pt plates using α-Al$_2$O$_3$ as inert material.

The FT-IR spectra were registered on a Schimadzu Prestige-21 FT-IR spectrometer, in KBr pellets, in the range 4000-400°C. Phase analysis was achieved with a Bruker Advanced diffract meter (the samples obtained at 400°C) using Cu-K$_α$ radiation ($λ_{Cu}$= 1, 54056 Å)

The acidic-basic properties of the precursors were studied by conductometric/ pH-metric acid-basic titrations, on a Crison MM41 Multimeter.

RESULTS

The redox reactions between cobalt nitrate and 1,3 propanediol lead to formation of coordination compounds of Co(II) with the carboxylate anions, diols oxidation products [4]. These compounds can be used as precursors for the corresponding cobalt oxides [5].

$$HO-\underset{H_2}{C}-\underset{H_2}{C}-\underset{H_2}{C}-OH + 2H_2O \longrightarrow ^-O{>}C-\underset{H_2}{C}-C{<}^O_{O^-} +8e^- + 10H^+$$

$$NO_3^- + 3e^- + 4H^+ \longrightarrow NO + 2H_2O$$

$$3HO-\underset{H_2}{C}-\underset{H_2}{C}-\underset{H_2}{C}-OH + 8NO_3^- + 2H^+ \longrightarrow 3 ^-O{>}C-\underset{H_2}{C}-C{<}^O_{O^-} + 8NO + 10H_2O$$

malonat

The reaction is promoted by the formation of the coordination compounds between the resulted carboxylate ions and the Co (II) cations (the diol does not interact with HNO$_3$).

Samples were prepared which corresponds to the reactions with molar ratio NO3-: diol stoichiometric = 1: 0.375 (G1) and the excess diol NO3-: 1.3 pg = 1:0,75 (G2).

The redox reaction Co (NO$_3$)$_2$ – 1, 3 PG was studied by thermal analysis. For this purpose the solution of cobalt nitrate in 1, 3 propanediol was deposed in thin film on Pt plates and heated in air, until 500°C. Figure 1 presents the obtained TG and DTA curves.

The presented thermal curves show two exothermic processes. The first process that takes place in the temperature range 150-180°C, corresponds to the redox reaction Co (NO$_3$)$_2$ – 1, 3 PG (visually confirmed by the formation of the brown gas-nitrogen oxides). As a result, coordination compounds form between Co (II) and the diol oxidation product. The second exothermic process in the range 250-300°C, can by assigned to the oxidative decomposition of the formed complex [5]. Taking into account the results of thermal analysis, we have choose the value of 140°C for the synthesis of the carboxylate –Co(II) compounds, used as precursors for the cobalt oxides.
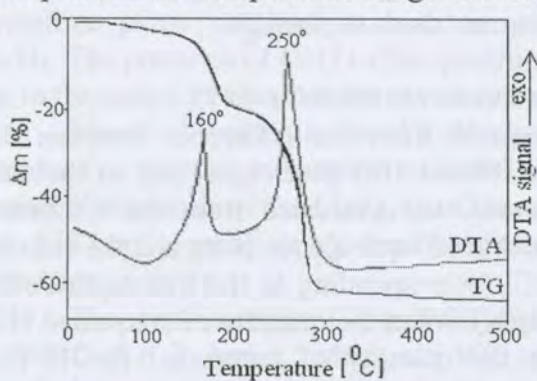

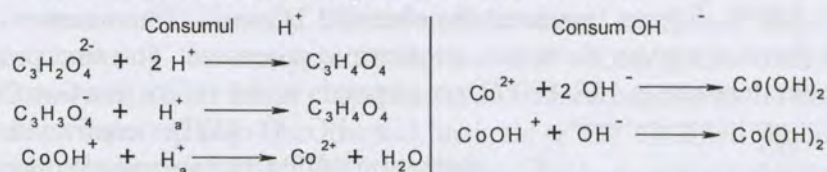
Fig 1. Thermal curves of the sol. Co (NO$_3$)$_2$-1,3PG

G1 spectrum (corresponding to the sample synthesized at the stoichiometric reports), from Figure 2 shows characteristic bands of carboxylate anions coordinate to metal ions: $ν_{as}$ (COO-) at 1646 cm^{-1}, $ν_s$(OCO) at 1360 cm^{-1}, and $ν_s$(CO) + δ (OCO) at ~ 1310 cm^{-1}, confirming the formation of this type of compound. The bands at 2974 cm^{-1} , 2940 cm^{-1} and 2870 cm^{-1} are characteristic to the stretching vibrations of the C-H bonds from-CH$_3$ [6,7].

G2 spectrum (corresponding to the sample synthesized with diol excess) present in addition to bands characteristic of cobalt carboxylate, the characteristic bands of excess diols: bands at 3000-2800 cm^{-1} are characteristic C-H bonds from $-CH_3$ şi $-CH_2-$ groups, bands at 1200-900 cm^{-1} are characteristic $\equiv C-OH$ groups.

Figure 3 shows the thermal behavior of compound G2 which is approximately similar. The thermal analysis of the precursor (fig.3) has evidenced that the thermal decomposition takes place in the range of 250-300°C with a pronounced exothermic effect, corresponds to oxidative decomposition of complex combinations formed (Malonic). Decomposition occurs with the generation in situu of a reducing atmosphere which leads to the reduction of Co (II) until Co metal, with its reoxidation to a poorly crystallized oxide, with increased reactivity. The residue at 400°C is, according to the XRD is the Co_3O_4. Taking into account the mass of the residue at 400°C we have thus calculated the content of Co in the precursor, of 29% (wt). Up to 500 °C, the mass remains constant [8,9].
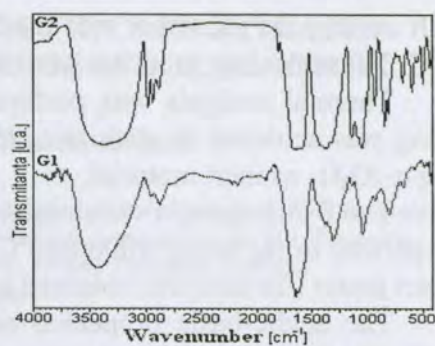

Fig 2. FTIR spectrum of the G1 and G2 precursors obtained at 140°C
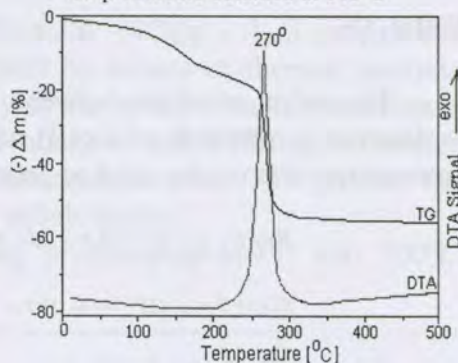
Fig. 3. Thermal behaviour of the G2 precursor synthesized at 140°C

In order to establish if the precursor Co (II) hydroxylactate, we have studied the acidic-basic properties, by using conductometric and pH-metric titrations.

In this purpose a corresponding mass of precursor that contains 2.10^{-4} moles of Co (II) was solved in 10 cm^3 of 0.1 mol/l HCl solution. The solution was then titrated with 0.1 mol/L NaOH solution. The processes that may take place when the precursor is treated with HCl solution and with NaOH solution are presented in scheme 1.

Consumul H$^+$

$$C_3H_2O_4^{2-} + 2 H^+ \longrightarrow C_3H_4O_4$$
$$C_3H_3O_4^- + H_a^+ \longrightarrow C_3H_4O_4$$
$$CoOH^+ + H_a^+ \longrightarrow Co^{2+} + H_2O$$

Consum OH$^-$

$$Co^{2+} + 2 OH^- \longrightarrow Co(OH)_2$$
$$CoOH^+ + OH^- \longrightarrow Co(OH)_2$$

Scheme 1. The processes that take place when the precursor is treated with HCl (left) and with

The quantity of consumed acid was calculated from the difference between the quantity of HCl introduced and the quantity of unreacted HCl (corresponding to the first equivalence point). The quantity of NaOH consumed was evaluated from the difference between the quantity of NaOH corresponding to the second equivalence point and the amount of introduced HCl and the amount of unreacted HCl (corresponding to the first equivalence point). The precursor is a Co (II) malonate ($CoC_3H_2O_4$), when the quantity of consumed HCl (for protonation of malonate ion) is equal with the quantity of consumed NaOH (for precipitation Co(II) as $Co(OH)_2$). The results obtained from the conductometric and pH-metric titrations are presented in table 1.

Table 1 The results from the titrimetric analysis

	Experimental molar ratio H$^+$/OH$^-$		Compound
Nr	Conductometric	pH-metric	
G1	4.0± 0.2	4,2 ± 0.3	n(CoOH)$_2$ .CoC$_3$H$_2$O$_4$
G2	4.0 ± 0.2	4,0 ± 0.3	

In the Figures 4 and 5 are presented the curves of conductometric titration and pH-metric of acid solutions G1 and G2 samples (1.3 PG) and of the HCl solution (volume of solution used to dissolve the precursor and processing experimental results.
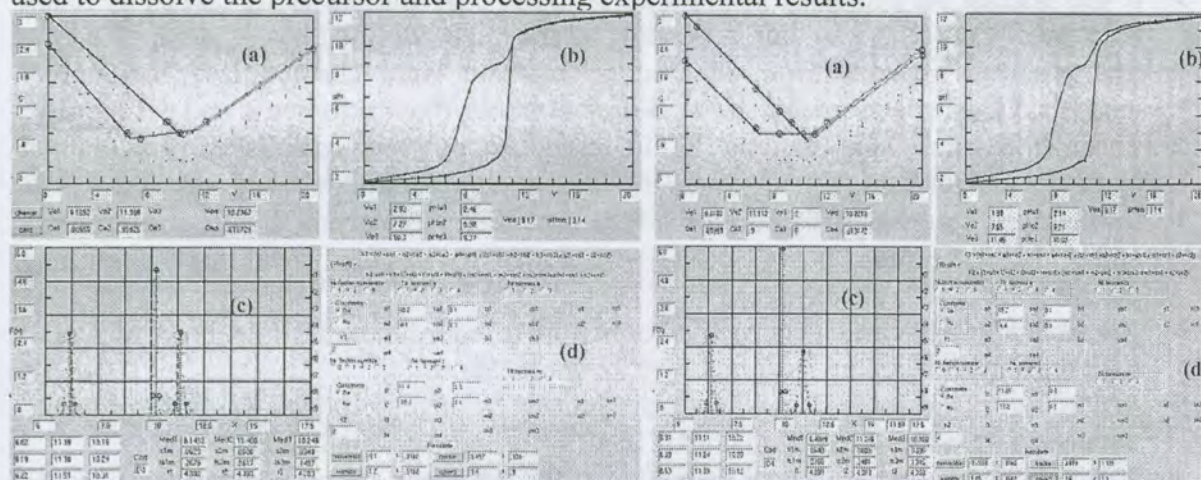

Fig 4. Conductometric titration curve (a), pH metric (b), calculation of the average equivalence volume (c), calculation of the reaction ratio (d) for the sample G1

Fig 5 Conductometric titration curve (a), pH metric (b), calculation of the average equivalence volume (c), calculation of the reaction ratio (d) for the sample G2

The precursor was thermally decomposed at 300°C for 6 hours and then annealed for 3 hours at 400°C and at 700°C. At the thermal decomposition of carboxylates type combinations, it is generated in situ a reducing atmosphere (C, CO) depending on the nature of the hypothetic complex combination. Reducing atmosphere may be influenced by the nature and diol excess which can be found next to the synthesized compounds, as well as by the means (conditions) in which the decomposition is performed (heat treatment), it was studied the way by which it can be obtained as unique crystalline phase Co_3O_4 and CoO respectively. The annealing products were studied by XRD analysis (fig.6). According to XRD data the only crystalline phase obtained at both temperatures was Co_3O_4. The presence of CoO in the spectrum (1) may be due to the nature of the precursor synthesized.
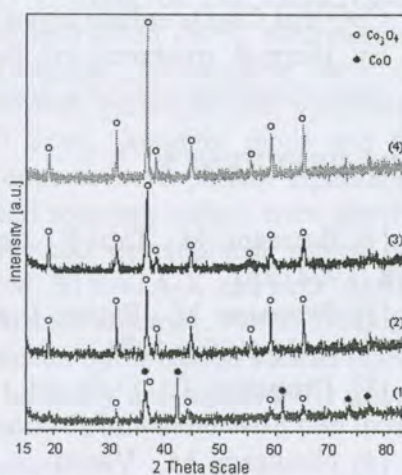

Fig 6. RX spectra of samples G1(1), G2(2) at 400°C, G1(3),G2(4) at 700°C

Figure 7 presents the FT-IR spectra of the samples G1 and G2, calcinated at 400°C. It is notable characteristic bands of the Co_3O_4 Co-O bonds (660 cm^{-1} and 570 cm^{-1}), confirming results obtained by RX diffraction analysis.
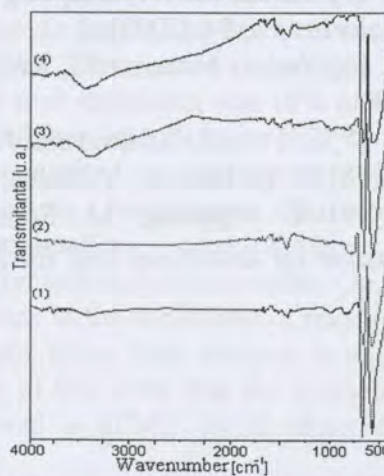
The same samples G1 and G2 were calcinated at 700°C for 2 hours, when all RX spectra were recorded as single phase well crystallized Co_3O_4 (Fig. 6). The corresponding FTIR spectra presents the same characteristic bands of Co_3O_4 Co-O bonds (660 cm^{-1} and 570 cm^{-1}) (Fig. 7). From the XRD data we have estimated the average diameter of the Co_3O_4 crystallites, using Scherrer formula. It resulted that Co_3O_4 is obtained as nanocrystallites with diameters of ~ 20 nm at 400°C and ~30 nm at 700°C.

Fig 7. FT-IR spectra of samples G1 (1), G2 (2) at 400°C, G1 (3), G2 (4) at 700°C

CONCLUSIONS

> ➢ It was studied the formation of some carboxylate type complexes of Co (II) by redox reaction of $Co(NO_3)_2$ and diol, depending on the molar mixing ratio of them;
>
> ➢ The products obtained from the redox reaction were characterized by thermal analysis, FT-IR spectrometry and acid-base titrations (conductometric and pH-metric);
>
> ➢ Through thermal analysis and FT-IR spectroscopy was established the optimal synthesis temperature (140°C) of the products obtained from the redox reaction;
>
> ➢ In the given conditions, based on the results of thermal analysis, FT-IR spectrometry and acid-base titrations in the $Co(NO_3)_2$: diol system, was confirmed that the resulting products are carboxylate type;
>
> ➢ All techniques have evidenced the formation of coordination compounds of Co(II) with the malonate anions, resulted by 1,3 PG oxidation.
>
> ➢ According to the study of acidic –basic properties of the product, we have probably obtained a mixture of Co(II) malonate and Co(II) hydroxyl malonate.
>
> ➢ It was shown that regardless of the nature of the precursor, decomposition occurs up to $\approx 300^{\circ}C$, with the generation of a reducing atmosphere, depending on its nature;
>
> ➢ It was found that during thermal decomposition of precursors, reducing atmosphere can lead to partial reduction of Co (II) to Co metallic;
>
> ➢ It was set the temperatures of heat treatment and nature of precursors leading to the CoO that Co_3O_4 unique crystalline phase.
>
> ➢ By thermal treatment of this product at 400°C and 700°C we have obtained nanocrystallites of Co_3O_4 having a dimension of 20nm at 400°C and 30 nm at 700 °C.

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