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THE EFFECT OF POSITIONAL ISOMERISM OF PROPANEDIOL ON THE FORMATION OF COBALT OXIDES

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ABSTRACT. This paper focuses on a comparative analysis between the carboxylate precursors obtained through the redox reaction between cobalt nitrate and 1,2-propanediol, and cobalt nitrate with 1,3-propanediol, respectively. The formation of the lactate and malonate precursors was followed with thermal analysis, FTIR spectrometry and acido-basic analysis (conductometric/ potentiometric titrimetry). The decomposition of the carboxylate precursors and the formation rate of cobalt oxides were observed by X-ray diffractometry and FTIR spectrometry, following advanced thermal treatments at 500°C, 800°C and 1000°C, with a pretreatment at 300°C. The differences between the two positional diol isomers are comparatively discussed.

Keywords: lactate, malonate, Co_3O_4, electrometric titrimetry, thermal treatment

INTRODUCTION

Transitional metal oxides include a large spectrum of inorganic materials with distinctive compositions and morphologies, leading to a wide variety of characteristics [1,2].

Cobalt oxides have drawn increasing attention due to their unique size, shape dependent properties [3] and diverse spectrum of applications such as, ethylene oxidation [1], energy storage and conversion, glucose detection, water spitting [4], catalytic oxidation [5], lithium ion batteries [6], as a contrasting agent for magnetic resonance, in biomedical sensors [3] and targeted drug delivery [3,4,7].

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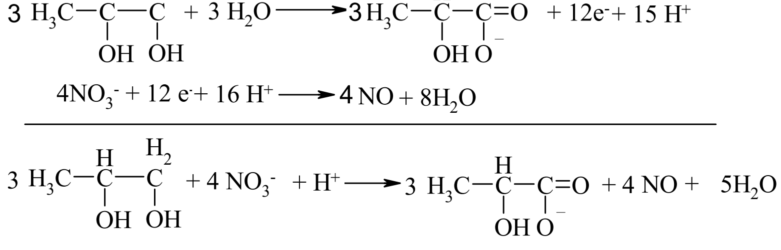
When falling in the nanosized range, cobalt oxides have been proven to exhibit even more attractive applications [8-9]. Up until now, cobalt oxide in the form of nanoparticles has been obtained through a number of methods, namely, thermal decomposition [4,10], sol-gel [2], hydrothermal [11], solvothermal [11], co-precipitation [12], photochemical synthesis, reversed micelles [13], microwave heating [9] etc. All these systems, comprising cobalt oxides of various compositions and stoechiometry, rely on the thermodinamic stability of Co^{2+}/Co^{3+} oxidation states.

In solution-phase synthesis, the main cobalt oxide crystal phase is Co_3O_4, followed by the less common CoO [1], both states being the most stable [8]. The greater thermodinamic stability of Co_2O_3 followed by the instant reducibility of CoO to Co, makes the synthesis of CoO in pure phase difficult. Relevant literature [14-15] studies the synthesis of single cobalt oxides and compound oxide nanoparticles through the redox reaction of metal salts with various diols, in different molar ratios.

This paper presents the synthesis of cobalt oxide precursors by the redox reaction between cobalt nitrate and 1,2-propandiol respectively 1,3-propandiol and the characterization of the precursors by Thermal analysis, FTIR and study of acido-basic properties, using conductometric and pH-metric titrations. Titration techniques have the advantage of ease of implementation, cost-effectiveness and accuracy. Electrometric titrations also have the advantage of automation, increasing the analysis throughput and securing the consistent quality of the results.

RESULTS AND DISCUSSION

Previous studies have shown the redox reactions between cobalt nitrate and diols (ethylene glycol, 1,2 propanediol, 1,3 propanediol) leads to the formation of coordination compounds of Co(II) with the carboxylate anions, diols' oxidation product, where only the primary C – OH groups participate. The secondary C –OH groups are not involved in the redox reactions. Thus, the oxidation of 1,2 propanediol leads, in particular working conditions, to the formation of lactate anions, according to the following equations (Scheme 1)



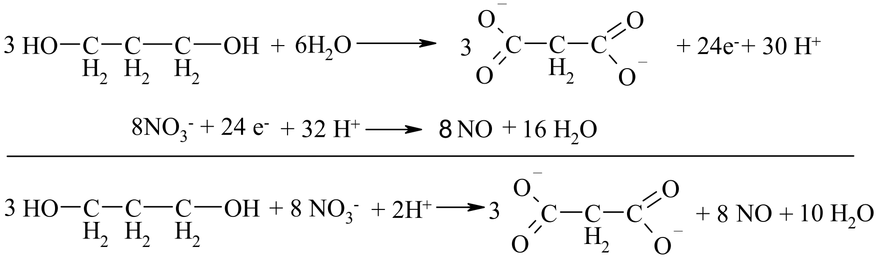
$$3\ H_3C-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H_2}{C}} + 3\ H_2O \longrightarrow 3\ H_3C-\underset{OH}{\overset{H}{C}}-\underset{O^-}{C}=O + 12e^- + 15\ H^+$$

$$4NO_3^- + 12\ e^- + 16\ H^+ \longrightarrow 4\ NO + 8H_2O$$

$$3\ H_3C-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H_2}{C}} + 4\ NO_3^- + H^+ \longrightarrow 3\ H_3C-\underset{OH}{\overset{H}{C}}-\underset{O^-}{C}=O + 4\ NO + 5H_2O$$

Scheme 1. The redox reaction leading to the formation of the lactate precursor

Similarly, the redox reaction between nitrate and 1,3-propanediol leads to the formation of malonate anions (Scheme 2).



Scheme 2. The redox reaction leading to the formation of the malonate precursor

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 only interact with HNO_3).

The redox reaction between $Co(NO_3)_2$ şi 1,2-PG, and $Co(NO_3)_2$ and 1,3-PG, respectively, was studied by thermal analysis. This entails the thin layer deposition of cobalt nitrate-diol solutions onto Pt pans, followed by an air heating up to 500°C. Figure 1 presents the thermal curves for the 1,2 propanediol, and 1,3 propanediol containing mixtures.

The presented DTA thermal curves show two exothermic processes. The first exothermic process, around 170°C, is attributed to the development of the $Co(NO_3)_2$-1,2PG redox reaction. The reaction unfolds integraly with the formation of a single oxidation product, respectively, of Co (II) combinations (visualy confirmed by the evolving of the brown gas-nitrogen oxides). The second effect, around 280°C, corresponds to the oxidative decomposition of cobalt lactate into cobalt oxide.

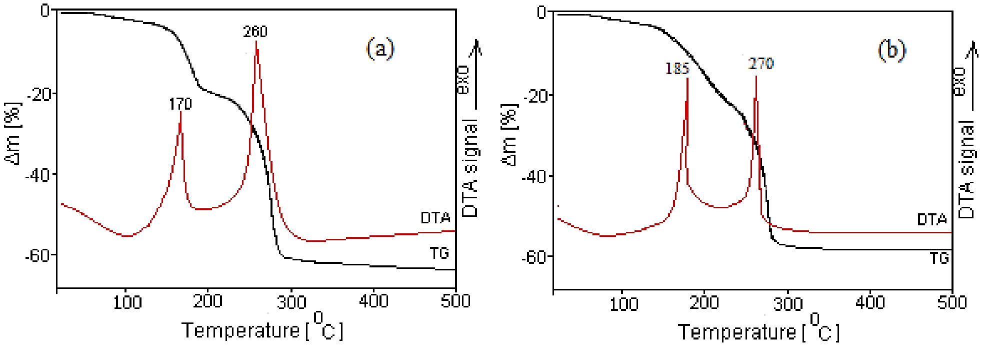


Figure 1. Thermal curves for the Co $(NO_3)_2$-1,2PG (a) and Co $(NO_3)_2$-1,3PG (b) solutions

In the case of 1,3 propanediol, the exothermic effects are slightly carried towards higher temperatures, the formation of cobalt malonate occuring at 185°C, and its decomposition at 270°C. Given the usage of 1,3 propandiol, the mass loss presented on the TG curve amounts to 21% for the first process, and 17% for the second one, a half reduced loss being observed in the case of utilizing a primary diol as opposed to a primary-secondary one.

In the case of 1,2 propanediol, the mass loss seen on the TG curve is 20% for the first process, and 41% for the second one.

Following the thermal analysis, the optimal carboxylate precursors synthesis temperature was established at 140°C. The products obtained at this temperature were characterized by FTIR analysis (fig 2). FTIR spectra of the lactate precursor obtained from 1,2 propanediol and malonate, and 1,3 propanediol, respectively, present all the characteristic bands of the carboxylate anions coordinated at metalic ions: $\nu_{as}(COO^-)$ la 1646 cm^{-1}, $\nu_s(OCO)$ la 1360 cm^{-1}, and $\nu_s(CO) + \delta\ (OCO)$ la ~ 1310 cm^{-1}, confirming the formation of this type of compound [18]. In the case of the lactate procursor's spectra, an intense band can be observed from 1070 cm^{-1}, characteristic to the secondary C-OH group (1,2-propandiol) that does not take part in the redox reaction, thus confirming the formation of the lactate precursor. The absence of bands characteristic to O-H groups suggests the formation of the carboxylate dianion (malonate) [17]. 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 [16-17].

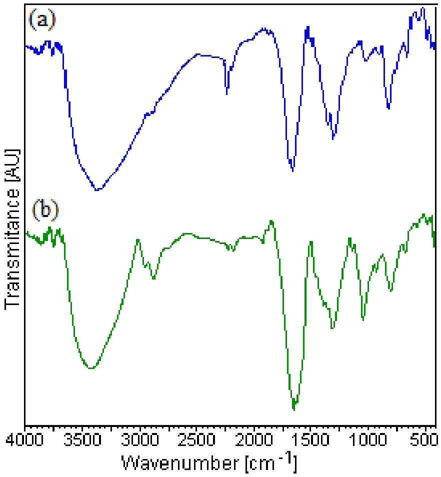


Figure 2. FTIR spectrum of the lactate (a), malonate (b) precursors synthesized at 140°C

Figure 3 presents the comparative thermal curves (TG, DTA) for the decomposition of lactate and malonate precursors, up to 1000°C. The 20% mass loss up to ~210°C can be attributed to the elimination of water from the complex combination. The one from the 220-300°C temperature range (42% for 1,2 propanediol and 21% for 1,3 propanediol), accompanied by an acute exothermic effect (at 280°C for 1,2-propanediol and 240°C for 1,3 propanediol, corresponds to the oxidative decomposition of formed complex combinations (lactate, malonate). This decomposition takes place with an *in-situ* generation of a reductive atmosphere, causing the reduction of Co(II) to metallic Co, followed by its reoxidation to a weakly crystallized oxide with an increased reactivity [21]. Between 950-1000°C, a final mass loss (4%) can be observed, corresponding to the transformations in the oxidic system, the reduction of Co_3O_4 to CoO, an endothermic effect on the DTA curve (950-960°C).

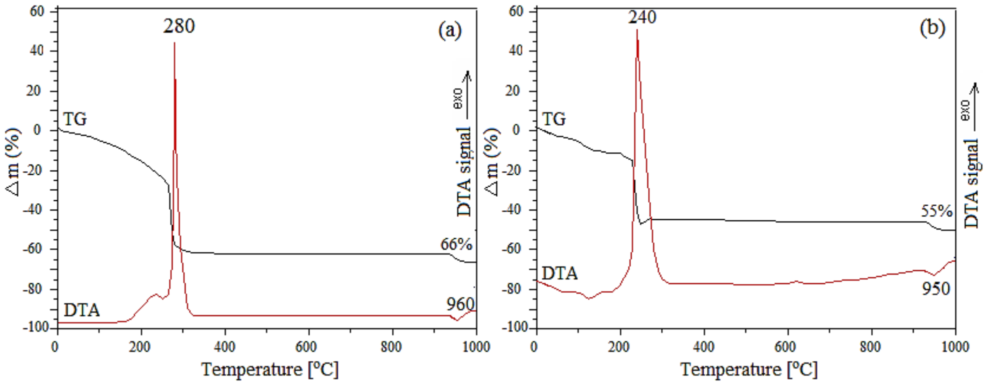
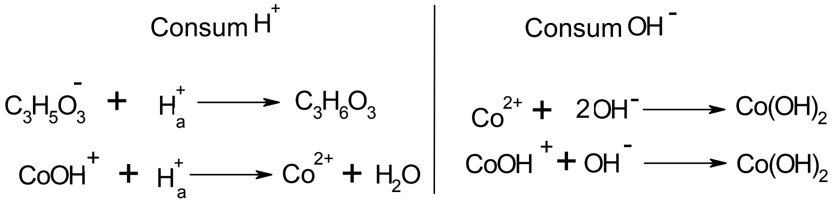


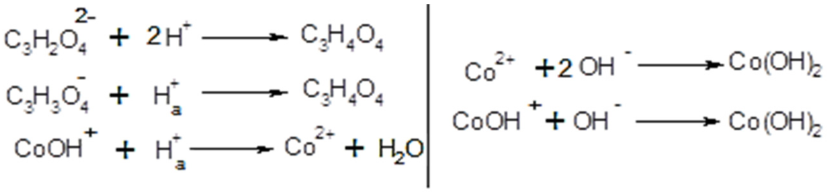
Figure 3. Thermal behaviour of the lactate (a) and malonate (b) precursors synthesized at 140°C

In order to establish if the precursor is a Co(II) lactate or a Co(II) hydroxylactate, and malonate or hydroxymalonate we have studied the acido-basic properties, by using conductometric and pH-metric titrations.

The processes that can take place in the precursor treated with a HCl solution, and NaOH respectively, are presented in schemes 3 and 4.

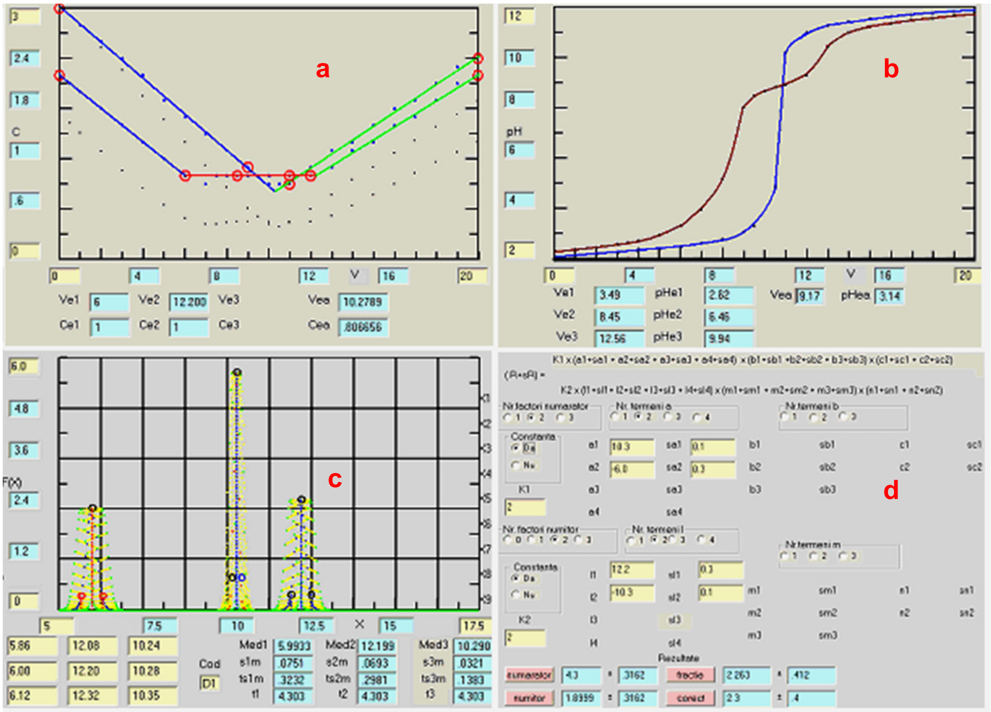


Scheme 3. The processes that can take place in the precursor (lactate) treated with HCl (left) and with NaOH (right)



Scheme 4. The processes that can take place in the precursor (malonate) treated with HCl (left) and with NaOH (right)

The consumed acid amount is calculated from the difference between the initial and the unreacted HCl volume (corresponding to the first point of equivalence). The utilized amount of NaOH is evaluated through the difference between the NaOH volume corresponding to the second point of equivalence and the volume of initial HCl. When the consumed HCl quantity (for the protonation of the lactate ion) is equal to the quantity of consumed NaOH (for the precipitation of Co(II) to $Co(OH)_2$) ($H^+/OH^-=1$), it can be considered that cobalt (II) lactate ($Co(C_3H_5O_3)_2$) is the precursor. Cobalt (II) hydroxylactate precursor ($Co(OH)C_3H_5O_3$) is formed when the volume of consumed HCl (for the precipitation of lactate and hydroxide ions) is double ($H^+/OH^-=2$) when compared to the consumed NaOH (for the precipitation of Co(OH) to $Co(OH)_2$). The precursor of cobalt malonate ($CoC_3H_2O_4$), has a similar formation, when the quantity of consumed HCl is equal with the quantity of consumed NaOH (for the precipitation of Co(II) as $Co(OH)_2$). To confirm the formation of the hydroxycarboxylate anion (lactate), and dicarboxylate (malonate), neutral, basic or hydroxyde, studies on the acido-basic properties were carried out (conductometric and pH-metric titrations) Figure 4 presents the conductometric titration (Figure 4a), and pH-metric titration (Figure 4b) curves of the acid solutions of the sample with 1,2 propanediol and HCl solution (volume used to disolve the precursor and process the experimental results).



Ve1 6
Ve2 12.200
Ve3
Veo 10.2789
Ce1 1
Ce2 1
Ce3
Ceo .806656

Ve1 3.49
pHe1 2.62
Veo 9.17
pHeo 3.14
Ve2 8.45
pHe2 6.46
Ve3 12.56
pHe3 9.94

5.86	12.08	10.24
6.00	12.20	10.28
6.12	12.32	10.35

Cod D1

Med1	5.9933	Med2	12.199	Med3	10.290
s1m	.0751	s2m	.0693	s3m	.0321
ts1m	.3232	ts2m	.2981	ts3m	.1383
t1	4.303	t2	4.303	t3	4.303

(A±sA) = K1 x (a1±sa1 · a2±sa2 · a3±sa3 · a4±sa4) x (b1±sb1 · b2±sb2 · b3±sb3) x (c1±sc1 · c2±sc2) / K2 x (l1±sl1 · l2±sl2 · l3±sl3 · l4±sl4) x (m1±sm1 · m2±sm2 · m3±sm3) x (n1±sn1 · n2±sn2)

Nr.factori numarator ○ 1 ● 2 ○ 3
Nr. termeni a ○ 1 ● 2 ○ 3 ○ 4
Nr.termeni b ○ 1 ○ 2 ○ 3
Constanta ● Da ○ Nu
K1 2
a1 10.3 sa1 0.1
a2 -6.0 sa2 0.3
a3 sa3
a4 sa4
b1 sb1 c1 sc1
b2 sb2 c2 sc2
b3 sb3

Nr.factori numitor ○ 0 ○ 1 ● 2 ○ 3
Nr. termeni l ○ 1 ● 2 ○ 3 ○ 4
Nr.termeni m ○ 1 ○ 2 ○ 3
Constanta ● Da ○ Nu
K2 2
l1 12.2 sl1 0.3
l2 -10.3 sl2 0.1
l3 sl3
l4 sl4
m1 sm1 n1 sn1
m2 sm2 n2 sn2
m3 sm3

Rezultate
numarator 4.3 ± .3162
numitor 1.8999 ± .3162
fractie 2.263 ± .412
conect 2.3 ± .4

Figure 4. Conductometric titration curve (a), pH-metric titration curve (b), calculation of the medium equivalence volume (c), calculation of the reaction ratio (d) for the 1,2 propanediol sample

Figure 4c shows the statistical calculus method for the equivalence volumes, while figure 4d, presents the statistic calculus method for the consumed acid/ consumed base ratios from the equivalence volumes. In the case of using 1,2 propanediol, a mixture of neutral and basic salts is obtained, whereas in the case of 1,3 propanediol isomer, only hydroxymalonate is obtained. Similarly, the acido-basic curves in the case of 1,3-propanediol are presented (Figure 5a and 5b), followed by the statistical calculation of the acid/ base ratio (Figure 5c and 5d).

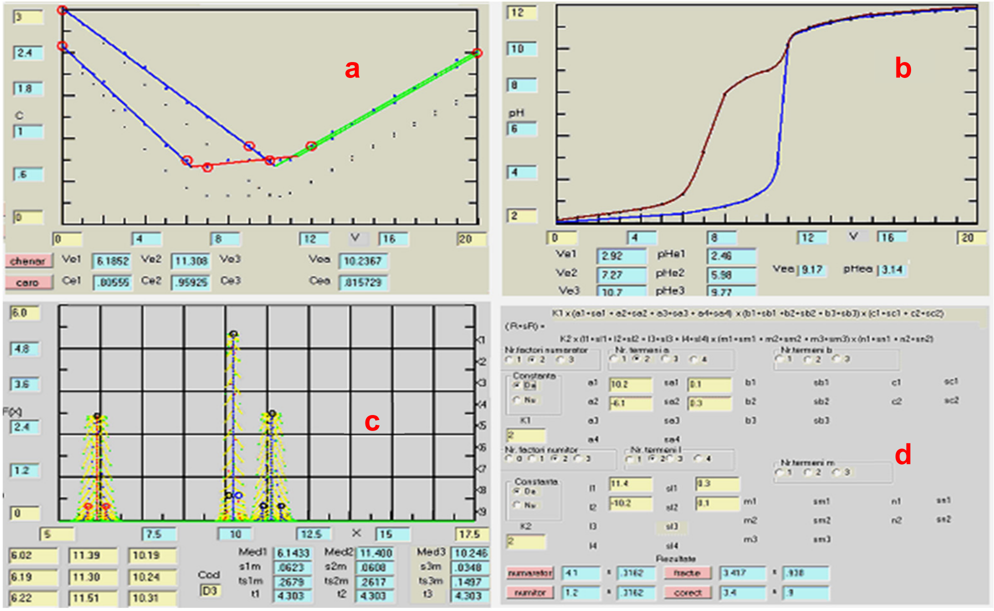


Figure 5. Conductometric titration curve (a), pH-metric titration curve (b), calculation of the medium equivalence volume (c), calculation of the reaction ratio (d) for the 1,3 propanediol sample

The results obtained following the conductometric and pH-metric titrations are presented in table 1.

Table 1. H^+/OH^- molar ratios and the compounds formed following the acido-basic titrations

Experimental molar ratio H^+/OH^-			Corresponding compound
Sample obtained from	Conductometric	pH-metric	$Co(C_3H_5O_3)_2$ $(CoOH)C_3H_5O_3$
1.2 propanediol	2.3 ± 0,4	1.5 ± 0.3	
1.3 propanediol	4.0± 0.2	4,2 ± 0.3	$n(CoOH)_2 .CoC_3H_2O_4$

The acido-basic properties of the synthesized compounds confirm the results of thermmal analysis and FTIR, advocating that the redox reaction forms carboxylate or hydroxycarboxylate compounds, that coordinate Co(II) ions in the form of a compound with either a basic or a neutral character.

The precursor was thermally decomposed at 300°C for 6 hours and then annealed for 3 hours at 500°C, at 800°C and at 1000°C. Following the thermal analysis, it was observed that the thermal decomposition of the carboxylate precursors occured up until 300°C with the formation of cobalt oxides through the in situ generation of a reductive atmosphere (C,CO) depending on the nature of the presumed complex combination. The reductive atmosphere can be influenced by the nature of the diol and the manner in which the decomposition (thermal treatment) takes place. The annealing products were studied by XRD analysis (fig. 6). Following the 500°C decomposition of cobalt lactate, a mixture of cobalt oxides (CoO and Co_3O_4) is formed. At 800°C Co_3O_4 is obtained as a single phase, while at 1000°C, CoO forms as a single phase (JCPDS 75-0393 chart [18]). In the case of cobalt malonate decomposition, Co_3O_4 is obtained as a single, crystalline phase (JCPDS 42-1467 chart [18]), both at 500 and 800°C, while at 1000°C, CoO becomes the unique crystalline phase. The reduction of Co_3O_4 to CoO takes place following the reaction:

$$Co_3O_4 \rightarrow 3\ CoO + \tfrac{1}{2}\ O_2$$

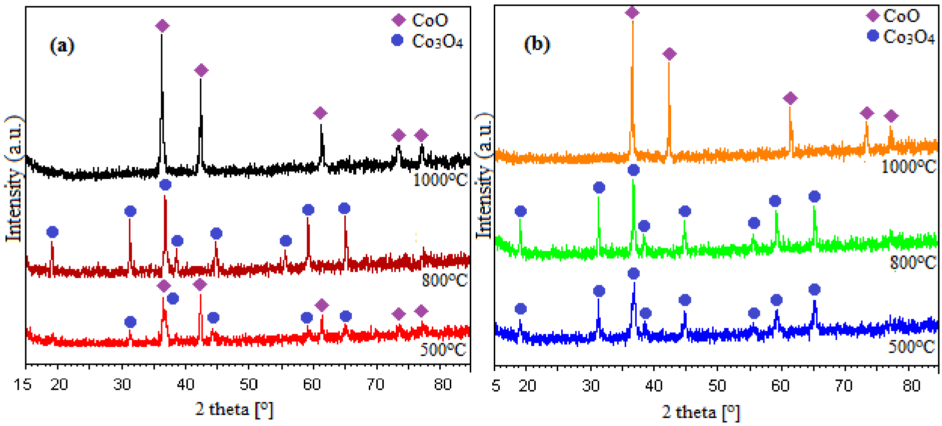


Figure 6. XRD difractogram of samples obtained from 1-2-propanediol (a), 1,3-propanediol (b) at 500°C, 800°C and 1000°C

The average crystallite size (D) of CoO and Co_3O_4 was calculated from the XRD data using Debye-Scherrer formula ($D=C\cdot\lambda/\beta_{1/2}\cdot\cos\theta$) [19] and is presented in table 2.

Table 2. Average diameters of nanoparticles calculated with Scherrer equation

Temperature / °C	Average diameter / nm			
	din 1.2 propandiol		din 1.3 propandiol	
	CoO	Co_3O_4	CoO	Co_3O_4
500	20	23	-	26
800	-	28		30
1000	32	-	35	-

According to the data in table 2, the dimension of the nanoparticles increases with the increase in temperature and with that of the crystallization degree. In addition, purer oxides with larger nanoparticles are obtained from 1,3 propanediol when compared to those synthesized from 1,2 propanediol.

CONCLUSIONS

The redox reaction $Co(NO_3)_2$–1,2-propandiol and $Co(NO_3)_2$–1,3-propandiol, as evidenced by thermal analysis, takes place in the range of 160-190°C. The cobalt lactate and cobalt malonate formation of the redox reaction was confirmed by means of FT-IR spectrometry, thermal analysis and acido-basic analysis (conductometric and pH-metric). All techniques have evidenced the formation of coordination compounds of Co(II) with the lactate anions, resulted through 1,2-propandiol oxidation. According to the study of acido-basic properties of the product obtained from 1,2-propandiol, a mixture of Co(II) lactate and Co(II) hydroxylactate was obtained, while from 1,3-propandiol only cobalt malonate was synthesized. By thermal treatment of this product at 500°C, through the decomposition of cobalt lactate, a mixture of CoO and Co_3O_4 is obtained, while at at 800°C only the Co_3O_4 crystalline phase results, phase that at 950°C reduces to the well crystallized CoO. In the case of cobalt malonate decomposition, Co_3O_4 results as a single phase, while at 1000°C the unique phase is CoO, the crystallization degree increasing with the increase in temperature. The size of nanoparticles increases with temperature, where Co_3O_4 obtained from 1,2 propanediol at 800°C has 28 nm, and from 1,3 propanediol, 30 nm. In a similar manner, the dimensions of CoO obtained through the decomposition of cobalt lactate, following the 1000°C thermal treatment, increases from 32 to 35 nm from the decomposition of malonate. In conclusion, it can be stated that the position of the second OH group can influence the conditions related to the formation of the carboxylic precursor, as well as the nature of oxides formed by advanced treatments.

EXPERIMENTAL SECTION

The reagents used in synthesis were: $Co(NO_3)_2 \cdot 6H_2O$ and 1,2 propanediol respectively 1,3-propandiol of purity p.a. (Merk). The synthesis method consists in dissolving cobalt nitrate in the corresponding 1,2PG respectively 1,3-propanediol in stoichiometric ratio, amount followed by controlled heating at 140°C. At these temperatures, the redox reaction begins accompanied by nitrogen oxide emission (brown-reddish gas). The isolated reaction products were maintained at 140°C until the emission of brown gas stops (reaction end). The powder obtained at 140°C was washed with acetone for removing of the reactant excess. The obtained products were characterized by thermal analysis, FT-IR spectrometry and conductometric/pH-metric acido-basic titrations

For the conductometric and potentiometric titrations 0.2 mmoli Co(II) were used, adding volumes of 10,0 cm^3 HCl 0.1M and subjected to titrations with NaOH 0.1M. The acido-basic properties of the precursors were studied through conductometric and pH-metric titrations using a Crison MM41 multimeter. The formation process of cobalt oxides was followed with thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) using a SDT Q600 type instrument, in air up to 1000^{o}C at 10 ^{o}C min^{-1} and alumina standards. The FTIR spectra were recorded on 1% KBr pellets using a Spectrum BX II spectrometer. The XRD patterns were recorded using a high resolution Bruker D8 Advance diffractometer with Cu ($\lambda_{CuK\alpha1}$=1,54056 Å) radiation.

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