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STUDY ON THE OBTAINING OF COBALT OXIDES BY THERMAL DECOMPOSITION OF SOME COMPLEX COMBINATIONS, UNDISPERSED AND DISPERSED IN SiO_2 MATRIX

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In order to obtain cobalt oxides nanoparticles we have used the thermal decomposition of some carboxylate type precursors. These precursors were obtained by the redox reaction between cobalt nitrate and ethylene glycol, either bulk or dispersed in silica matrix. The redox reaction takes place by heating the $Co(NO_3)_2·6H_2O–C_2H_6O_2$ solution or the $Si(OC_2H_5)_4–Co(NO_3)_2·6H_2O–C_2H_6O_2$ gels. Thermal analysis of the $Co(NO_3)_2·6H_2O–C_2H_6O_2$ solution and $Si(OC_2H_5)–Co(NO_3)_2·6H_2O–C_2H_6O_2$ gels allowed us to establish the optimal value for the synthesis temperature of the carboxylate precursors.

By fast heating of the solution $Co(NO_3)_2·6H_2O–C_2H_6O_2$, the redox reaction is immediately followed by the decomposition of the precursor, which represents an autocombustion process. The product of this combustion contains CoO as unique phase. We have obtained a mixture of CoO and Co_3O_4 by annealing the synthesized carboxylate compounds for 2 h at 400°C. With longer annealing time (6 h), we have obtained Co_3O_4 as unique phase.

The XRD study of the crystalline phases resulted by thermal decomposition of the precursors embedded in silica matrix, showed that the formation of Co_2SiO_4 and Co_3O_4, as unique phases, depends on the thermal treatment.

Keywords: *cobalt oxides, ethylene glycol, olivine*

Introduction

Cobalt oxides have large applications in heterogenous catalysis, air pollution control and in the development of rechargable accumulators and CO sensors [1].

Many articles have reported about the synthesis and structure of cobalt oxides nanoparticles (CoO, Co_3O_4) [2].

Cobalt oxides are usually obtained in solid state reactions (mechano-chemical synthesis), pyrolysis, sol–gel process, hydrothermal synthesis, microemulsions precipitation, precipitation with different precipitation agents (urea, ammonia, carbonates) [3].

The systems based on cobalt oxides nanoparticles, dispersed in amorphous silica matrices with high specific surface are very interesting due to their potential applications as optical sensors and catalysts in hydrogenation/dehydrogenation reactions (reformation of methane, hydroformylation of ethene, hydrogenation of arenes and aldehydes) [4].

Recent studies on the system cobalt–silica have shown that the preparation methods and the structure of the silica matrix are very important for the type and dispersion of cobalt oxide species and for the properties of the obtained nanocomposites. There is a great interest in finding new procedures to obtain these systems as well as to study the interactions between the oxidic phase and matrix [5].

In this paper we present a study on the obtaining of cobalt oxides by thermal decomposition of some Co(II) carboxylate type complex combinations [6]. These complex combinations were obtained, bulk or dispersed in SiO_2, as a result of the redox reaction between cobalt nitrate and ethylene glycol. The reaction took place by heating the solutions or the silica gels containing the reactant mixture within the pores. The paper presents the IR and thermal study for the formation and thermal decomposition of these precursors, bulk or dispersed in the silica matrix. The oxidic phases obtained by thermal decomposition of the precursors were studied by XRD.

Experimental

The reagents used in syntheses were: $Co(NO_3)_2·6H_2O$ as cobalt source, ethylene glycol (EG), tetraethylorthosilicate (TEOS) as silicon source and ethanol (EtOH) as solvent, all of purity >98%, Merck.

In order to obtain undispersed precursors, the solution of cobalt nitrate ($Co(NO_3)_2·6H_2O$) in ethylene glycol (molar ratio $Co(NO_3)_2:C_2H_6O_2=1:1$) was

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heated in an oven, until 100°C, when the redox reaction NO_3^- – EG took place.

The obtained coordination compounds, purified with acetone, were used as precursors for the non-dispersed cobalt oxides.

In order to obtain Co_xO_y/SiO_2 composites gels ($Si(OC_2H_5)_4$–$Co(NO_3)_2$–$C_2H_6O_2$) have been synthesized for a final composition of 30% CoO in SiO_2 for a molar ratio r=$Co(NO_3)_2$:$C_2H_6O_2$=1:1. The initial sols were prepared by dissolving $Co(NO_3)_2\cdot 6H_2O$ in the corresponding $C_2H_6O_2$ amount. An ethanolic TEOS solution was dripped to the cobalt nitrate–ethylene glycol solution, under magnetic stirring.

The obtained sols were left gelling at room temperature. The gels were dried at 40°C, in the drying stove, and then heated until 140°C. During this treatment, the redox reaction between EG and nitrate ions takes place with formation of the carboxylate–Co(II) compounds within the matrices pores. These compounds were used as precursors for the cobalt oxide nanoparticles dispersed in silica.

The obtained powders were annealed at different temperatures in order to obtain cobalt oxide nanoparticles embedded in silica matrix.

Thermal analysis was performed on a 1500 D MOM Hungary derivatograph. The experiments have been done with platinum crucibles, in air, in the temperature range 20–500°C, with a heating rate of 5°C min^{-1}, using as reference α-Al_2O_3.

FTIR spectrometry was performed with a Shimadzu Prestige-21 FT–IR, in KBr pellets, in the domain 400–4000 cm^{-1}.

The phases analysis of the annealed samples was achieved on a D8 Advanced-Bruker AXS diffractometer, using CuK_α and MoK_α radiations.

Results and discussions

At controlled heating of the mixture cobalt nitrate–ethylene glycol, until ~115°C, nitrate ions oxidize ethylene glycol to form glyoxylate or oxalate anions (depending on the molar ratio between the reactants) [7, 8]. In the redox reaction resulted Co^{2+} coordinative compounds used as precursors for cobalt oxides.

Figure 1 presents TG and DTA curves of the solutions $Co(NO_3)_2$–$C_2H_6O_2$, deposed as films on platinum crucibles, for a molar ratio $Co(NO_3)_2$: $C_2H_6O_2$= 1:1. The first exothermic process at ~110°C with mass loss, is attributed to the redox reaction between cobalt nitrate and ethylene glycol with formation of the Co(II) carboxylate compounds. The second exothermic process from ~250°C, with mass loss on TG, corresponds to the oxidative decomposition of the complex combination.

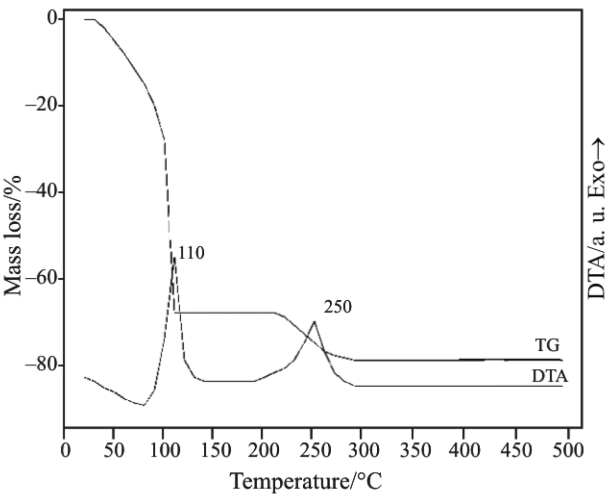

Fig. 1 TG and DTA curves of the solution $Co(NO_3)_2$ – ethylene glycol

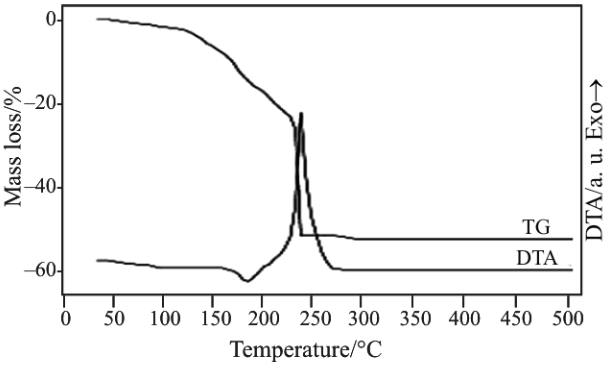

Fig. 2 TG and DTA curves of the Co(II) complex combinations synthesized at 140°C

Based on thermal analysis data, we have established 140°C as synthesis temperature for the Co(II) carboxylate complex compounds.

Figure 2 presents the thermal behaviour of the complex combination prepared at 140°C. The mass loss until 200°C, with endothermic effect corresponds to the elimination of the coordinated water. The pronounced exothermic effect from 240°C, corresponds to the oxidative decomposition of the organic ligand, leading to the formation of the oxidic system.

Figure 3 presents the FTIR spectrum corresponding to the Co(II) complex combination, synthesized at 140°C. The FTIR spectrum presents bands characteristic to the coordinated carboxylate group at 1617 cm^{-1} ($\nu_{as(COO^-)}$) and 1317 cm^{-1} ν_{CO}. The band from 1384 cm^{-1} is characteristic for the residual nitrate ion. The band from 816 cm^{-1} is characteristic for the anti-symmetric vibration δ_{OCO} and the band from 543 cm^{-1} can be attributed to the vibrations ν_{M-O_x} [9].

FTIR spectrum (Fig. 4) of the complex combinations decomposition residue from 300°C presents characteristic bands for water (~3400 and 1636 cm^{-1})

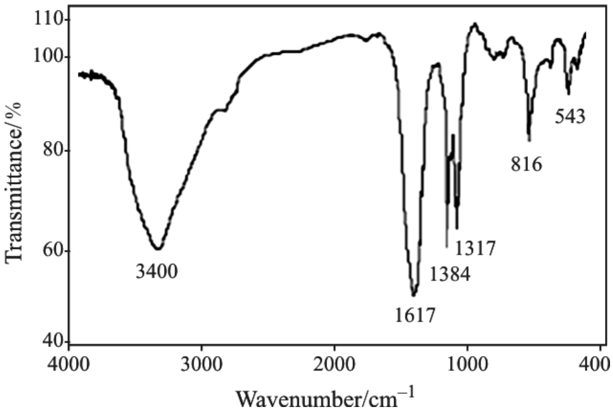

Fig. 3 FTIR spectrum of the complex combination synthesized at 140°C

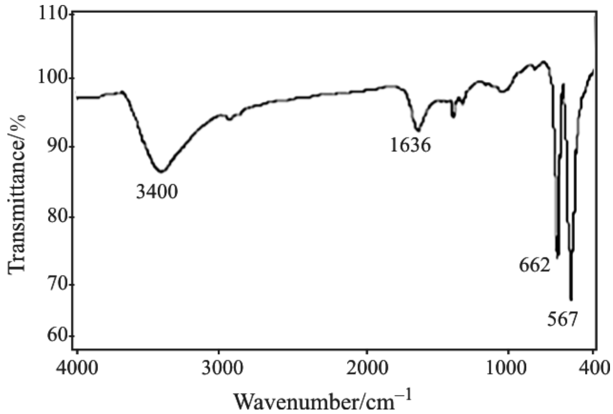

Fig. 4 FTIR spectrum for the decomposition residue of the complex combination from 300°C

but it does not present the characteristic carboxylate groups, anymore. This indicates the complete decomposition of the complex combination, at 300°C, with formation of the metallic oxide, evidenced by the intense bands from 662 and 567 cm^{-1}.

If the solutions $Co(NO_3)_2–C_2H_6O_2$ are rapidly heated at ~130°C, the strong exothermic redox reaction induces the thermal decomposition of the complex combination (auto-combustion). The as-obtained product contains CoO as unique phase (Fig. 5a). This can be explained by the reducing atmosphere generated in situ (NO_x-redox reaction and CO-thermal decomposition) which maintains the oxidation state of Co(II).

According to the literature, the obtaining of CoO, as unique phase, needs the use of some precursors and special thermal treatment conditions (reducing or inert atmosphere) [4, 10, 11].

By annealing the complex combination synthesized at 140°C, for 2 h, at 400°C, one obtains a mixture of CoO and Co_3O_4 (Fig. 5b), due to the partial oxidation of CoO to Co_2O_3, with formation of Co_3O_4.

By increasing the annealing time to 6 h (400°C), we have obtained Co_3O_4 as unique phase (Fig. 6).

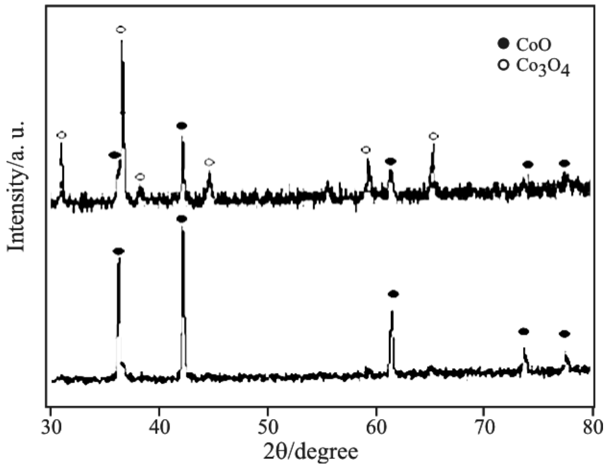

Fig. 5 XRD patterns (CuK_α radiation) of residues obtained after a – autocombustion and b – by annealing 2 h at 400°C

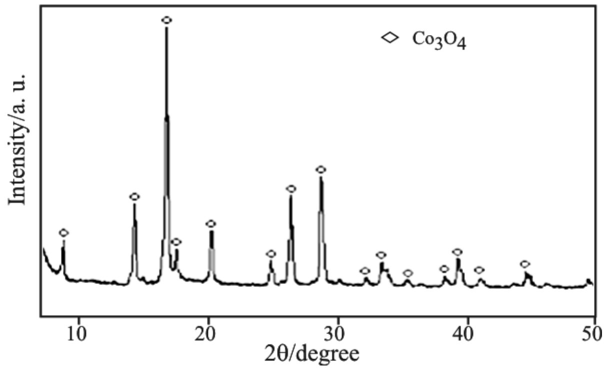

Fig. 6 XRD patterns (MoK_α radiation) of the powder obtained by annealing the precursor for 6 h at 400°C

From the XRD data for the samples annealed at 400°C, for 6 h (Fig. 6), we have calculated, with the Scherrer formula, the average diameter of the Co_3O_4 crystallites, and we have obtained ~20 nm [12].

In order to obtain cobalt oxides nanoparticles dispersed in SiO_2, we have used a modified sol–gel method [6]. This method consists in the formation of the Co(II) complex combination inside the pores of the silica matrix by the redox reaction $Co(NO_3)_2–C_2H_6O_2$.

In this respect, we have prepared gels with molar ratio TEOS:$Co(NO_3)_2$:EG=3:1:1. The gels obtained after drying at 40°C, were studied by thermal analysis.

The obtained TG and DTA curves are presented in Fig. 7.

On DTA are registered two exothermic effects similar to those registered for the solution $Co(NO_3)_2–C_2H_6O_2$ (Fig. 1). The first exothermic effect from ~115°C is attributed to the redox reaction $Co(NO_3)_2–C_2H_6O_2$ which takes place within the gels pores, with formation of the Co(II) complex combination dispersed inside the matrix. The second exothermic effect from ~250°C, is due to the oxidative de-

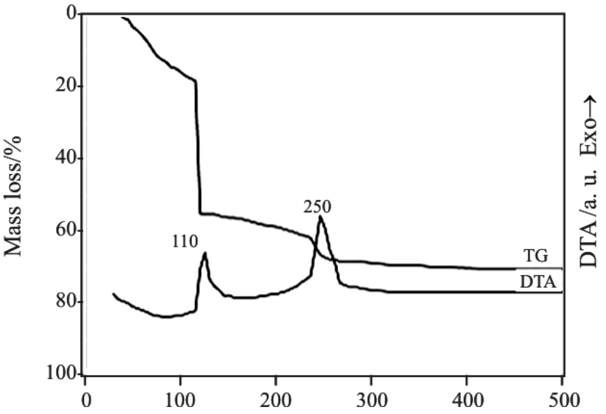

Fig. 7 TG and DTA curves of the gel dried at 40°C

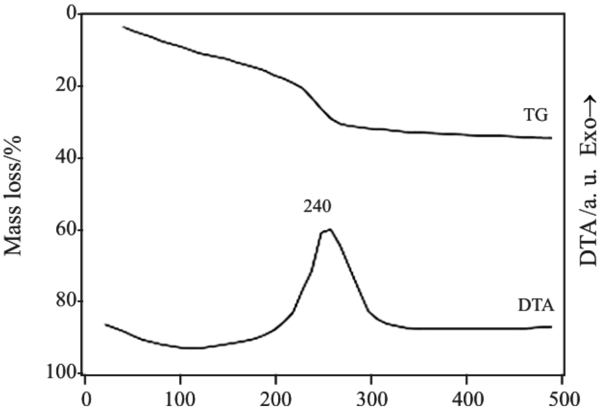

Fig. 8 TG and DTA curves of the gel thermally treated at 150°C

composition of the complex combination within the matrices pores.

Based on the thermal analysis studies performed on the gels dried at 40°C, we have established 150°C as optimal synthesis temperature for the precursors dispersed in the pores of the matrix.

The thermal behaviour of the gels obtained at 150°C was studied by thermal analysis, in air, until 500°C (Fig. 8). The slow mass loss until 200°C is due to the promotion of the polycondensation reaction of the matrix. The mass loss from the range 200–300°C, accompanied by an exothermic effect (DTA), is due to the oxidative decomposition, in the pores of the silica matrix [13].

FTIR spectra of the gel dried at 40°C (spectrum 1) and thermally treated at 150°C (spectrum 2) and 300°C (spectrum 3) are presented in Fig. 9. All spectra present the characteristic bands for the silica matrix: 3460, 1640, 1075, 960, 800 and 475 cm^{-1}. The spectrum of the gel dried at 40°C presents also characteristic bands for the nitrate ion (at 1380 cm^{-1} – intense band, 825 cm^{-1} – weak band) which is present in the pores of the gel, at this temperature [6, 14].

In the FTIR spectrum of the gel thermally treated at 150°C, we can observe the disappearence of the band from 1380 cm^{-1} characteristic for NO_3^-. At this temperature, appear the bands characteristic for the group (COO$^-$) coordinated to the Co(II) ion (1300–1400, 1620 cm^{-1}) [6], as a result of the formation of Co(II) carboxylate type compounds within the matrices pores.

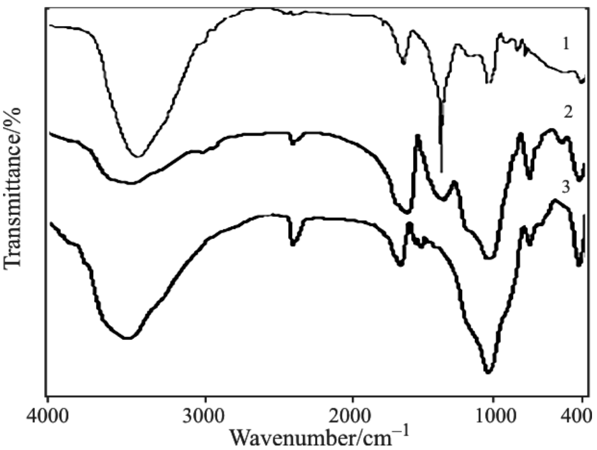

Fig. 9 FTIR spectra of the gel dried at 1 – 40°C and thermally treated at 2 – 150°C and 3 – 300°C

Spectrum 3 corresponding to the gel annealed at 300°C evidences the disappearence of the bands characteristic for the carboxylate type precursors and presents only the bands characteristic for the silica matrix.

In order to obtain cobalt oxides dispersed in SiO$_2$, the powders obtained at 150°C, which contain the carboxylate type precursors within the pores of the matrix, were annealed for 2 h at 400, 700 and 950°C. The obtained XRD petterns are presented in Fig. 10.

The XRD patterns of the sample annealed at 400°C, does not evidence crystalline phases, presenting an aspect characteristic for the amorphous phase. The XRD patterns of the samples annealed at 700 and 950°C, evidence Co_2SiO_4 (olivine) as unique crystalline phase, inside the amorphous silica. The difficult

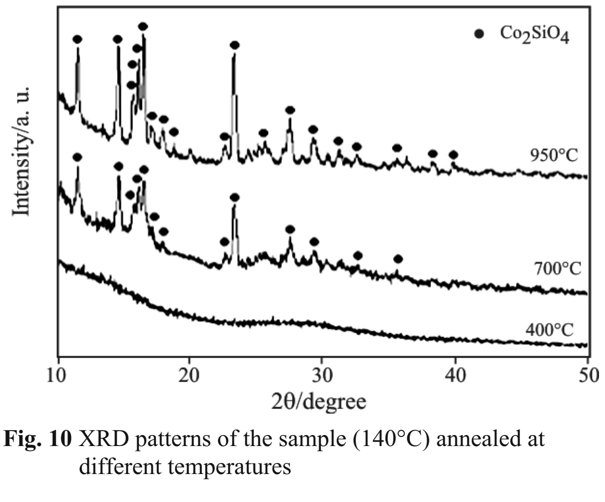

Fig. 10 XRD patterns of the sample (140°C) annealed at different temperatures

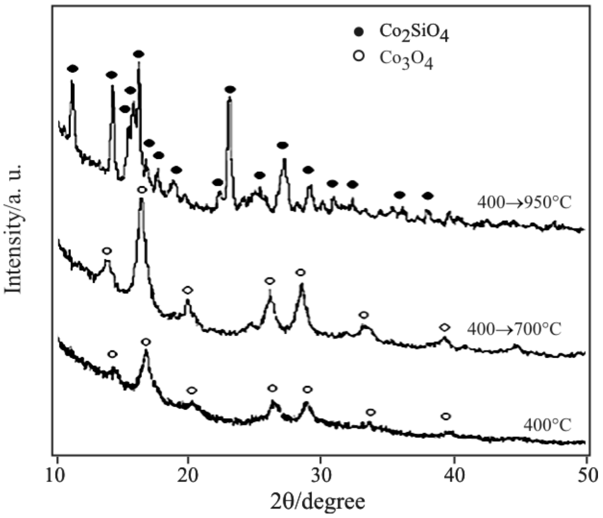

Fig. 11 XRD patterns of the sample decomposed at 400°C, then annealed at 700 and 950°C

diffusion of oxygen within the pores of the silica matrix and the reducing atmosphere generated by thermal decomposition of the carboxylate precursors, insured the maintenance of the oxidation state Co(II). This fact explains the formation of olivine at this temperature.

At 950°C, olivine is much better crystallized according to the formation mechanism presented above.

By annealing the gel for 6 h at 400°C, conditions in which Co(II) is oxidized to Co(III), we obtain Co_3O_4 as unique phase within the silica matrix (Fig. 11). By ulterior annealing at 700°C of the product resulted at 400°C (Co_3O_4/SiO_2), Co_3O_4 remains as well crystallized unique phase (Fig. 11).

By annealing at 950°C of the product from 400°C (Co_3O_4/SiO_2), Co_2SiO_4 forms well crystallized, as unique phase within the silica matrix. This is due to the transformation of Co_3O_4 in CoO (900°C), which interacts with SiO_2 to form Co_2SiO_4 [15, 16].

The average diameter of the Co_3O_4 crystallites embedded in silica matrix, calculated from the XRD data using the Scherrer [12] formula is about 10 nm, suggesting that by the used synthesis method we can obtain fine oxidic nanocrystalites, dispersed in SiO_2.

The obtaining of Co_3O_4/SiO_2 and Co_2SiO_4/SiO_2 nanocomposites, by this synthesis method, at low temperatures, offers an economical variant in order to use these nanomaterials as catalysts, pigments and magnetic materials [15, 17].

Conclusions

This paper presents the obtaining of some carboxylate coordination compounds of Co(II) by the redox reaction between cobalt nitrate and ethylene glycol.

Depending on the applied thermal treatment, the undispersed precursors lead, by thermal decomposition, to the formation of different cobalt oxides (CoO, Co_3O_4) as unique nanocrystalline phases.

When the precursors are dispersed in silica matrix, depending on the thermal treatment, we obtain either Co_3O_4, or Co_2SiO_4 (olivine) as unique phase in amorphous SiO_2. Owing to the homogeneous distribution of the precursors in the gels and their particular thermal decomposition Co_2SiO_4 nanocrystallites are obtained in silica matrix, at substantial reduced annealing temperatures (700°C).

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