Chemical Bulletin of “Politehnica” University of Timisoara, ROMANIA
Series of Chemistry and Environmental Engineering
Chem. Bull. "POLITEHNICA" Univ. (Timisoara) *Volume 55(69), 2, 2010*

Thermal and FT-IR Studies on the Interaction Between $Cr(NO_3)_3 \cdot 9H_2O$ and Some Diols

M. Barbu, M. Stoia, O. Stefanescu and M. Stefanescu

University “Politehnica” of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Victoriei Square no.2, 300006, Timisoara, Romania

Abstract: This paper presents a study regarding the interaction between $Cr(NO_3)_3$ and 1,2- propanediol, 1,3-propanediol and 1,4-butanediol, respectively. Previous studies on the reaction between metal nitrates and diols showed that the primary C-OH groups of diols are oxidized by NO_3^- to $–COO^-$. The resulted carboxylate anions coordinate to the metal ions forming complexes that can be used as precursors for nanocrystalline metal oxides. The evolution of the redox reaction between $Cr(NO_3)_3$ and the diols was studied by thermal analysis and by FT-IR spectrometry. The FT-IR spectra of the obtained reaction products have confirmed the formation of carboxylate coordination compounds of Cr(III) evidenced by $\upsilon_{ass}(–COO^-)$ at ~1680 cm^{-1} and ~1560 cm^{-1} and $\upsilon_s(–COO^-)$ at ~ 1370 cm^{-1}. These compounds thermally decompose in the range 250-300°C leading to amorphous nonstoechiometric chromium oxide (Cr_2O_{3+x}) which turns into nanocrystalline Cr_2O_3 oxide above 400°C.

Keywords: chromium oxide; diol; carboxylate; nanocrystalline

1. Introduction

In the last decade, the unconventional soft chemical methods such as co-precipitation [1], sol-gel method [2] and the hydrothermal process [3, 4] have been widely used for the synthesis of nanocrystalline simple and mixed metal oxides. These are wet chemical methods that first synthesize an intermediate product (precursor) containing the metal ions which is further converted to simple and mixed oxides by a series of reactions taking place at high temperatures.

Among these unconventional methods, a particular interest is devoted to those using as precursor, complex combinations of metal ions with carboxylate type ligands like citrates [5], oxalates [6, 7], malates [8, 9].

One of the methods that insure the formation of coordination compounds that thermally decompose at relatively low temperatures to the corresponding oxides is based on the redox reaction between transitional metal nitrates and diols [10, 11]. In the redox reaction between nitrate ions and diols, the ≡C-OH (primary) group is oxidized at -COOH leading to carboxylates anions that coordinate to the transition metal ions present in the system.

In our previous studies we have reported the formation of Fe^{3+} [12], Ni^{2+} [7, 15] and Co^{2+} [13, 14] coordination compounds of in the redox reactions between the metal nitrates and different diols: ethane diol (EG), 1,2-propanediol (1,2PG),1,3-propanediol (1,3PG), 1,4-butanediol (1,4BG).

In this paper we present a study regarding the interaction between Cr (III) nitrate and different diols: 1,2PG, 1,3PG, 1,4BG. The formed coordination compounds have been characterized by thermal analysis, FT-IR spectrometry and UV –VIS spectrometry. The formed coordination compounds have been thermally decomposed under a controlled thermal treatment and the decomposition products have been characterized by thermal analysis, FT-IR spectrometry, XR diffractometry.

2. Experimental

The reagents used in synthesis of Cr_2O_3 were: $Cr(NO_3)_3 \cdot 9H_2O$ as chromium source, the diols: 1, 2-propanediol (1,2PG), 1, 3- propanediol (1,3 PG), 1, 4-butanediol (1,4 BG), all of purity >98%, Merck.

The synthesis involves two stages: the synthesis of the precursors and the obtaining of Cr_2O_3 by corresponding thermal treatment of the precursors.

The synthesis of the precursors is based on the redox reaction between Cr (III) nitrate and diol, which takes place during the heating of chromium (III) nitrate – diol solution, with formation of Cr(III) carboxylate type precursors. $Cr(NO_3)_3 \cdot 9H_2O$ was dissolved in the corresponding diol amount and the obtained solution was heated, in the drying stove, up to 130°C when the redox reaction took place with reddish-brown nitrogen oxides emission. The mass reaction was kept at 130°C for 3 hours, in order to obtain the corresponding Cr(III) carboxylate compound, further used as chromium oxide precursor. The obtained precursors were annealed at different temperatures.

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

TABLE 1. Characteristics of the synthesized samples

Sample	Diol	Quantities/mol		Molar ratio NO_3^- : Diol
		$Cr(NO_3)_3.9H_2O$	Diol	
Cr12PG	1,2 PG	0,0394	0,1329	1: 1,1250
Cr13PG	1,3 PG	0,0394	0,0664	1: 0,5625
Cr14BG	1,4 BG	0,0394	0,0664	1: 0,5625

The progress of the redox reactions between chromium (III) nitrate and diols as well as the thermal decomposition of the formed precursors, 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 ^{0}C, with a heating rate of 5 ^{0}C· min^{-1}, using as reference α-Al_2O_3.

The synthesized powders were characterized by FT-IR spectrometry with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 400- 4000 ^{0}C. The phases analysis of the thermally treated samples was achieved on a D8 Advanced- Bruker AXS diffractometer, using Cu- K_α radiation (λ_{Cu}= 1, 54056 Å).

The spectrometric analysis of Cr(VI) in the powders obtained at 320° C was performed on a Perkin-Elmer Spectrometer UV-VIS Lambda 25.

The presence of Cr(VI) in the studied compounds was evidenced by spectrometric analysis on a Perkin-Elmer Spectrometer UV-VIS Lambda 25.

3. Results and Discussion

In the literature only the redox reaction between $Cr(NO_3)_3.9H_2O$ and ethylene glycol [10] has been studied. The reported studies have evidenced that the oxidation of EG by NO_3^- leads to the glyoxylate anion, which coordinates to the Cr^{3+} ions forming the complex $[Cr_2(OH)_2(C_2H_2O_4)_2]$. The thermal decomposition of this compound up to 500°C leads to Cr_2O_3 oxide.

In this paper we are extending the studies on the interaction of $Cr(NO_3)_3.9H_2O$ with diols, by using other three diols: 1, 2- propanediol (1,2PG), 1, 3- propanediol (1,3PG), 1,4- butanediol (1,4BG). This study is motivated by the further studies on the interaction of metal (II) and Cr(III) nitrates mixtures and diols in order to obtain carboxylate type precursors for different chromites with controlled properties. The redox reactions between $Cr(NO_3)_3$ and each diol (1,2PG, 1,3PG, 1,4BG) were studied by thermal analysis of the prepared $Cr(NO_3)_3$ – diol solutions deposed as thin film on Pt plates. The registered TG and DTA curves (Fig.1) have evidenced two exothermic processes with mass losses: the first process in the range 80-100°C assigned to the redox reaction and the second around 300°C assigned to the thermal decomposition of the reaction product.

Fig. 1 presents the TG and DTA curves of the solution $Cr(NO_3)_3$ – 1,4BG.

From the thermal curves presented in Fig.1 we have selected 130°C as optimum temperature for the synthesis of the chromium oxide precursors.

The powders obtained at 130°C have been characterized by FT-IR spectrometry. The FT-IR spectra of the powders Cr12PG, Cr13PG and Cr14BG obtained at 130°C are presented in Fig.2.

All FT-IR spectra of the synthesized compounds exhibit a strong band at around 3400 cm^{-1} which may be assigned to the OH stretching vibration of water and to the secondary –OH group (in case of Cr12PG) [16].

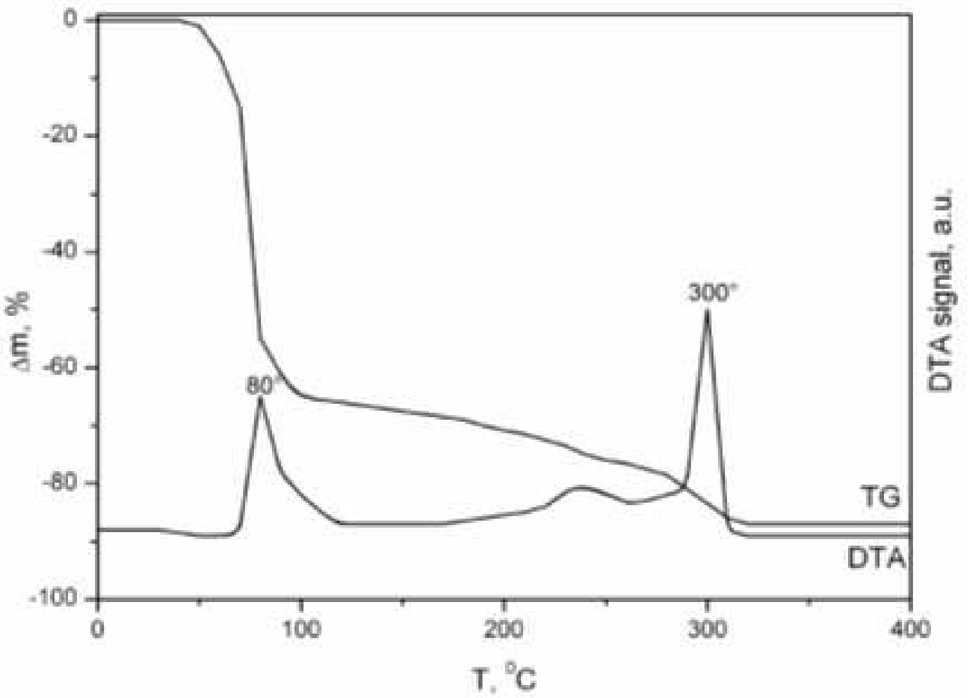

Figure 1. TG and DTA curves of $Cr(NO_3)_3$ – 1,4BG solution

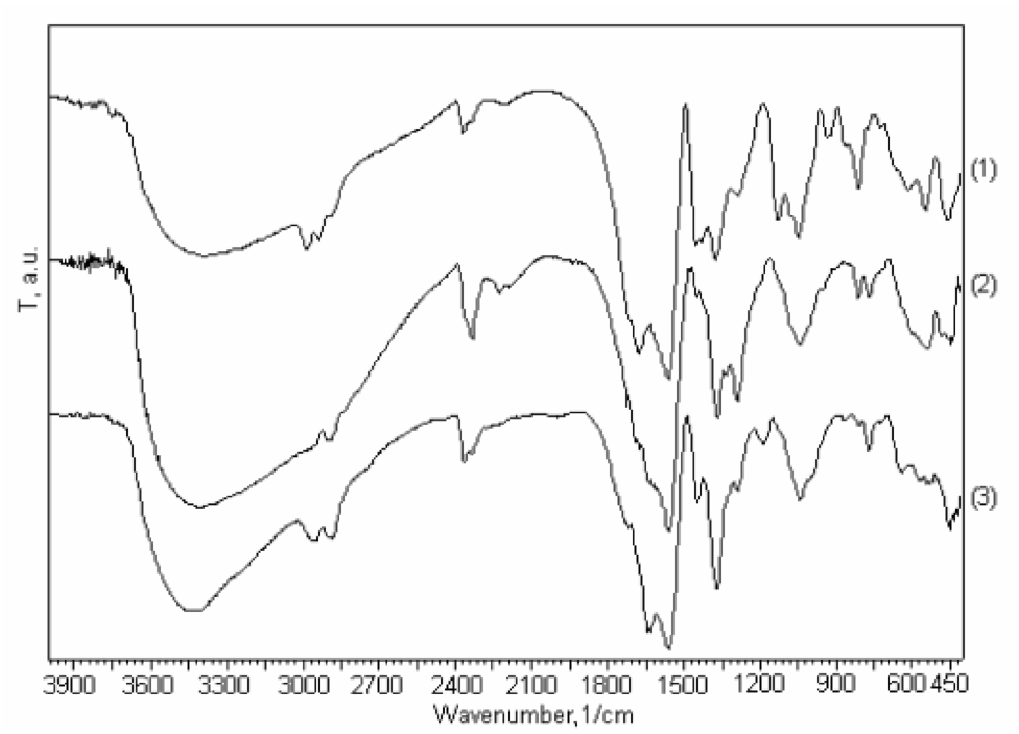

Figure 2. FT-IR spectra of the precursors Cr12PG (1), Cr13PG (2) and Cr14BG (3) obtained at 130°C

The bands in the range 2800-2900 cm^{-1} correspond to the vibrations of the C – H bond from the -CH$_2$- groups and -CH$_3$ group. All compounds exhibit two bands characteristic to the asymmetric stretching vibrations υ_{ass}(–COO$^-$) at ~1680 cm^{-1} and ~1560 cm^1 [16]. This evidences the presence of the carboxylate group coordinated bidentate and monodentate to the Cr(III) cations, in the synthesized compounds. In the range 1400-1450 cm^{-1} some weak bands are present, corresponding to bending vibration of CH$_2$ and CH groups [17]. The band characteristic to the symmetric stretching vibration of the group –COO$^-$ appears in all spectra at ~ 1370 cm^{-1}. The band from 1280 cm^{-1} can be assigned to the υCC(O)O vibrations [17]. The region 1200-1000 cm^{-1} is characterized by the vibration frequency of the –OH groups. Spectrum (1) for the precursor Cr12PG presents, in this region, a supplementary band at 1124 cm^{-1} due to the presence of the un-oxidized secondary –OH group. The bands which appear in the range 563 - 500 cm^{-1} are assigned to M – O stretching vibrations.

Thus, the FT-IR study evidenced the formation of carboxylate coordination compounds of Cr(III) in all synthesized products.

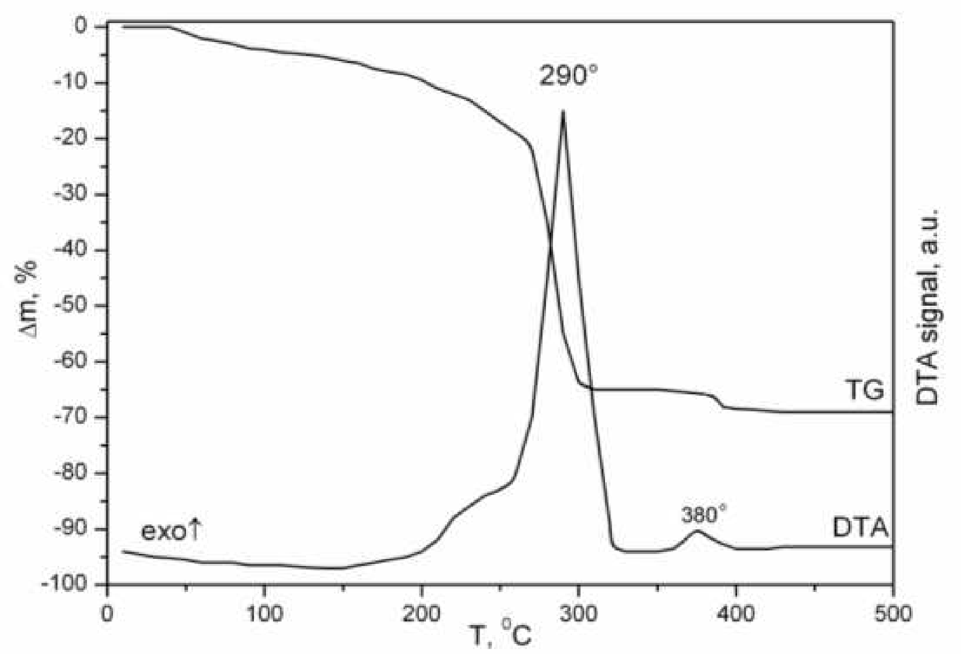

Figure 3. TG and DTA curves of sample Cr12PG synthesized at 130°C

TABLE 2. The results of thermal analysis of all compounds

Sample	Δm_t/% 20-500°C	Δm_t/% 20-250°C	Δm_t/% 250-350°C	Δm_t/% 350-400°C	$m_{resCr2O3,}$ % (500°C)
Cr12PG	70	14	52	4	30
Cr13PG	71	15	52	4	29
Cr14BG	69	17	48	4	31

The thermal decomposition of the Cr(III) carboxylates synthesized at 130°C was studied by means of thermal analysis, in air atmosphere up to 500°C. The registered thermal curves have evidenced a similar thermal behavior for all three samples. Up to 200°C a slow mass loss occurs associated to the loss of both crystallization and coordinated water. In the range 250-320°C a significant mass loss takes place with a strong exothermic effect due to the oxidative decomposition of the organic ligands, with formation of a nonstoechiometric Cr_2O_{3+x} oxide, according to the literature [18]. The mass remains constant up to 380°C, when a mass loss occurs due to the transition $Cr_2O_{3+x} \rightarrow Cr_2O_3 + xO$, associated to an exothermic effect attributed to the crystallization of Cr_2O_3. Figure 3 presents the TG and DTA curves obtained for the sample Cr12PG. The results of thermal analysis of all synthesized compounds are listed in Table 2.

In order to elucidate the thermal evolution of the synthesized compounds we have annealed them at different temperatures and studied the as obtained powders by thermogravimetry and FT-IR spectrometry. Figure 4 presents the TG curves of the sample Cr13PG annealed at different temperatures. From the TG curves (1) and (2) results that by the thermal treatment of the powder at 250°C only small changes in the thermal behavior of Cr(III) carboxylate occur. Thus, up to 250°C a very small mass loss is registered, compared to the TG (1) for the as synthesized sample, due to the loss of crystallization and coordinated water and –OH groups. The thermal behavior in the range 250-500°C is almost identical, due to the fact that the organic part does not change by heating up to 250°C.

By annealing of the sample at 320°C, the major part of the organic ligand decomposes, as it results from the slow and little mass loss registered up to 350°C. The mass loss registered in the range 350-400°C corresponds to the loss of oxygen, during the transition: $2CrO_3 \rightarrow Cr_2O_3 + 3/2O_2$. TG curve (4) of the sample annealed at 500°C evidences no mass losses, due to the complete transition of Cr_2O_{3+x} to Cr_2O_3..

The FT-IR spectra of the samples annealed at different temperatures are presented in Figure 5.

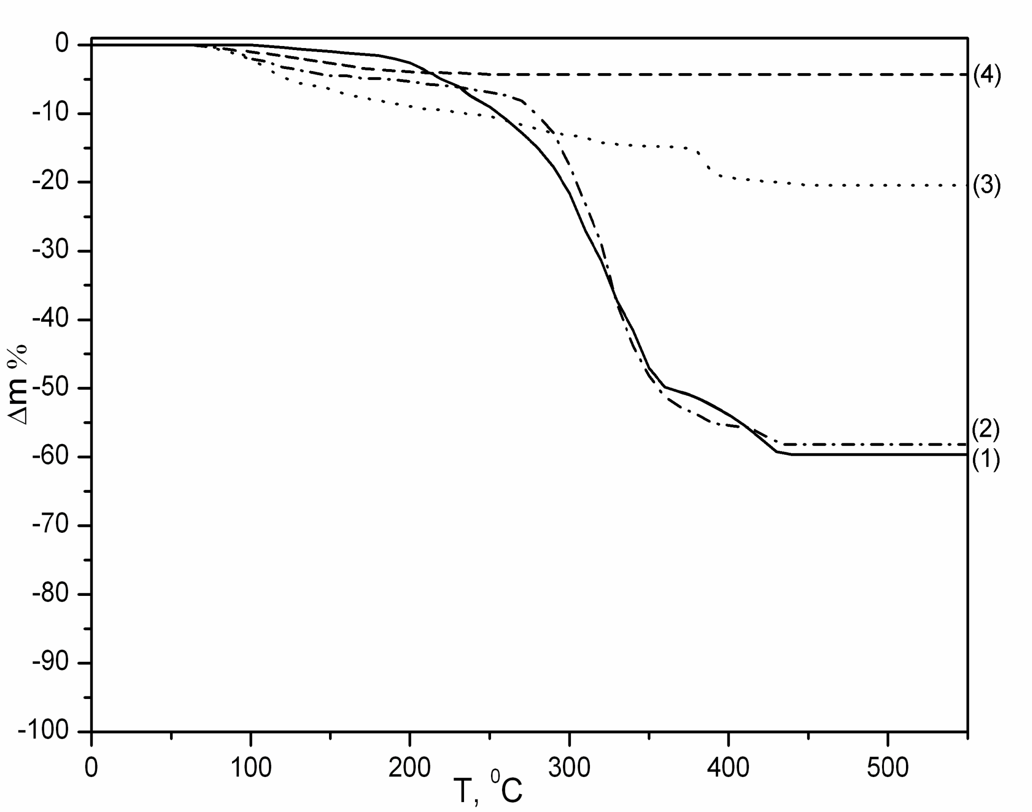

Figure 4. TG curves of sample Cr13PG thermally treated at different temperatures:
(1) 130°C, (2) 250°C, (3) 300°C, (4) 500°C

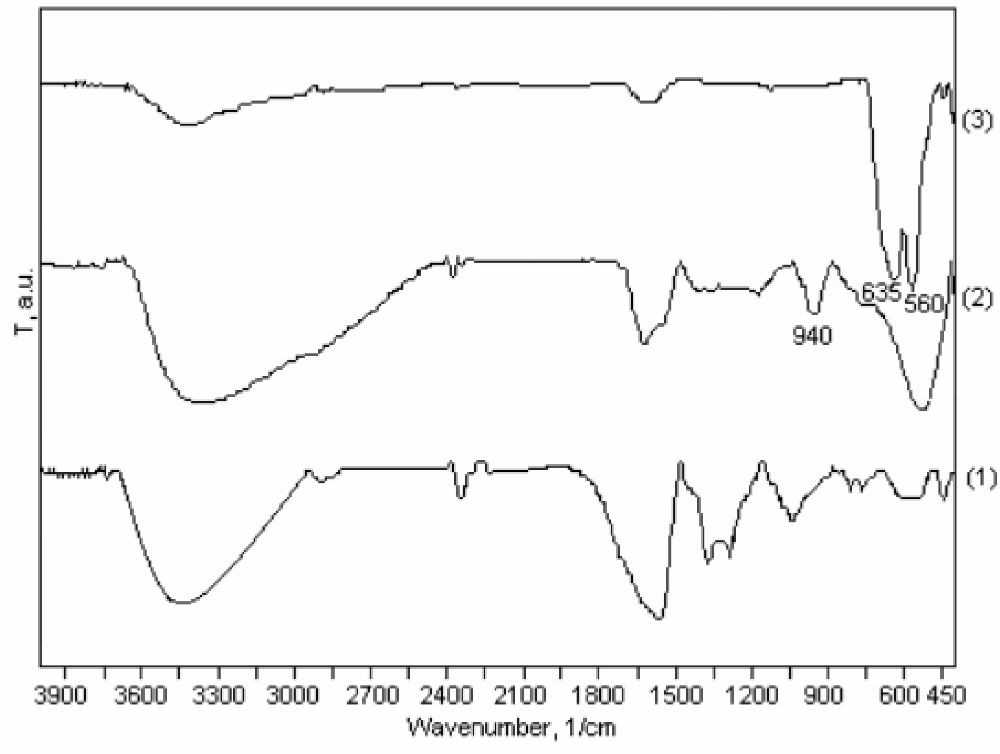

Figure 5. FT-IR spectra of sample Cr13PG thermally treated at different temperatures: (1) 130°C, (2) 320°C; (3) 500°C

The thermal treatment of the synthesized compounds at 250°C had minor effects on the FT-IR spectra. By raising the annealing temperature at 320°C (spectrum (2)), the organic part decomposes, thus the bands from the range 2900-2800 cm^{-1}, 1700-1500 cm^{-1} and 1400-1200 cm^{-1} almost disappear. A large band appears in the range 450-700 cm^{-1} that can be assigned to the Cr – O bond vibrations, due to the formation of the corresponding chromium oxide. Another new band assigned to CrO_3 appears at ~940 cm^{-1} [18], but disappears from the spectrum of the sample annealed at 500°C (spectrum (3)). By annealing of the sample at 500°C, the transition CrO_3 to Cr_2O_3 takes place with appearance of two strong bands at ~560 cm^{-1} and ~ 635 cm^{-1}, which can be attributed to hexagonal Cr_2O_3 [8, 19]. Thus, the FT-IR spectrometry confirms the results of the thermal analysis.

The presence of Cr(VI) in the powders obtained at 320°C was confirmed qualitatively by the reaction with the diphenylcarbazide [20]. The reaction was negative in the case of the as synthesized precursor (130°C) and of the powders obtained at 500°C, confirming the interpretation of both thermal analysis and FT-IR spectrometry. In the table 3 we present the composition of the oxide powders obtained at 320°C, according to the experimental data of thermogravimetric analysis.

From the data presented in table 3 it results that the CrO_3 content does not depend on the precursors nature.

TABLE 3. The composition of the powders obtained at 320° obtained from TG curves

Sample	m_{rez} (320°C)	Mass loss (350-400°C)	%CrO_3	%Cr_2O_3
Cr12PG	31	4	54	46
Cr13PG	33	4	50	50
Cr14BG	35	4	48	52

The powders obtained by annealing the synthesized precursors at 320° C and 500°C have been characterized by XR diffraction. The XRD patterns obtained for the powders at 320°C evidenced no crystalline phases, the oxides Cr_2O_{3+x} being amorphous. By annealing the precursors at 500°C, Cr_2O_3 appears as single phase, well crystallized in all samples. Figure 6 presents the XRD patterns of the sample Cr13PG annealed at 320°C (pattern 2) and 500°C (pattern 1).

From the full width at half maximum (110) of the main diffraction peaks results that the average of the crystallites size obtained at 500°C is ~ 25 nm. This proofs that the thermal decomposition of the synthesized precursors leads to nanocrystallites oxides.

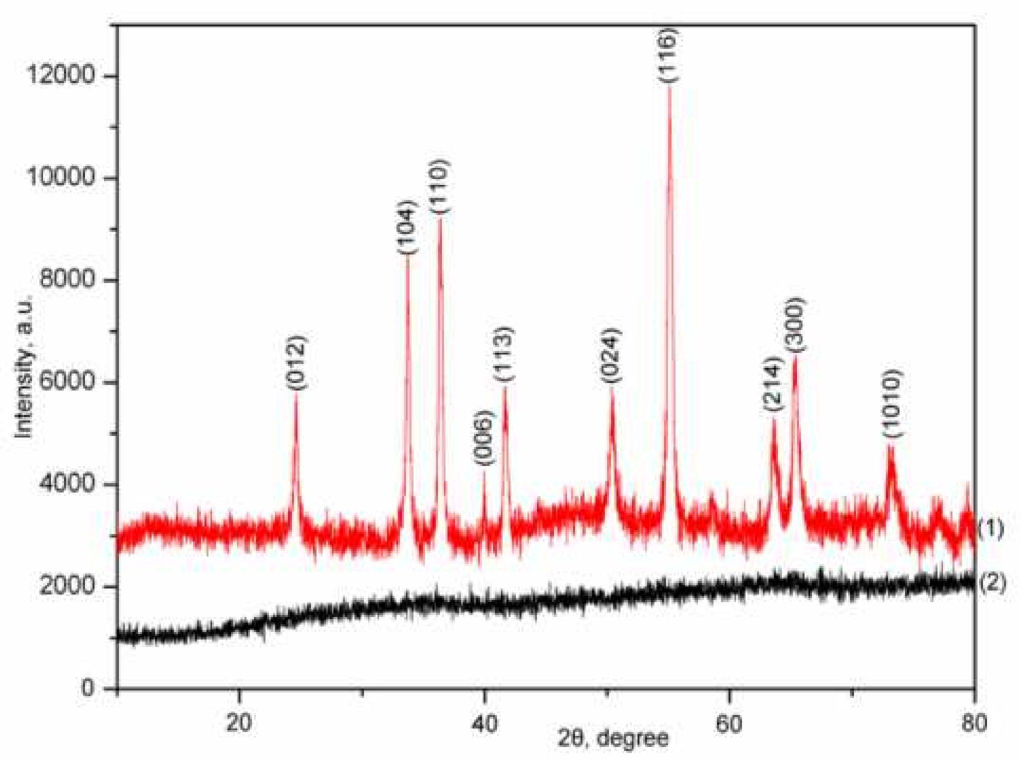

Figure 6. XRD patterns of sample Cr13PG annealed at 320°C (2) and 500°C (1)

4. Conclusions

In the reported research, nanocrystallites of Cr_2O_3 were successfully prepared via the thermal decomposition of some carboxylate type coordination compounds of Cr(III). The studied carboxylate type precursors have been obtained in the redox reaction between chromium nitrate and three different diols: 1,2- propanediol, 1,3- propanediol and 1,4- butanediol. All synthesized precursors present similar thermal behaviour, leading by thermal decomposition to the formation of an amorphous oxide $Cr_2O_3 \cdot xCrO_3$, which turns to nanocrystalline Cr_2O_3 arround 400°C. The obtained nanocrystallites have the average size of ~25 nm. This type of precursors will be used in the further works for the preparation of nanocrystalline chromites with controlled properties.

ACKNOWLEDGMENT

This work was partially supported by the strategic grant POSDRU/88/1.5/S/50783, Project ID50783 (2009), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013 and partially supported by the grant POSDRU 107/1.5/G/13798, inside POSDRU Romania 2007-2013 co-financed by the European Social Fund – Investing in People.

REFERENCES

1. Wojciechowska M., Tomska-Foralewska I., Przystajko W., and Zielinski M., *Catalysis Letters*, 104, **2005**, 3–4.
2. Zhigaikina I. A., Nikolaeva T.D. , Suponitskii Yu. L. and Polyak t B. I., *Glass and Ceramics*, 55, **1998**, 5 - 6.
3. Ovenstone J., Chan K.C. and Ponton C.B., *Journal of Materials Science*, 37**, 2002**, 3315 – 3322.
4. Zhenzhao P., Xu H. and Y. Zhang, *J. of Alloys and Compounds*, 468, **2009**, L5-L8.
5. Varma H.K., Kumar K.P., Warrier G.K. and Damodaran A.D., *Journal of Materials Letters*, 8, **1989,** 1313-1316.
6. Birzescu M., Niculescu M., Dumitru R., Carp O. and Segal E, *J. Therm Anal Calorim*, 96, **2009**, 979-986.
7. Niculescu M., Vaszilcsin N., Birzescu M., Budrugeac P. and Segal E., *J Therm Anal Calorim*, 63, **2001**, 181-189.
8. Carp O., Patron L., Mindru I., Marinescu G., Diamandescu L. and Banuta A., *J. Therm. Anal. Calorim*., 74, **2003** , 789-799.
9. Prasad R., Sulaxna and Kumar A., *J. Therm. Anal. Calorim*, 81, **2005**, 441-450.
10. Stefanescu M., Sasca V. and Birzescu M., *J. Therm. Anal. Calorim*, 72, **2003**, 515-524.
11. Niculescu M., Kellenberger A., Maghet T., Dumitru R., Birzescu M. and Vaszilcsin N., Chem Bull Politehnica Univ. Timisoara, 47(61), **2002**, 1-6.
12. Stefanescu M., Stefanescu O., Stoia M. and Lazau C., *J. Therm. Anal. Calorim*, 88, **2007**, 1, 27-32.
13. Niculescu M., Vaszilcsin N., Birzescu M., Budrugeac P. and Segal E., *J Therm Anal Calorim*, 65, **2001,** 881-889.
14. Stefanescu M., Stoia M., Caizer C., Dippong T. and Barvinschi P., *J. Therm. Anal. Calorim*., **2009**, 245-250.
15. Stefanescu M., Stoia M., Dippong T., Stefanescu O. and Barvinschi P., *Acta Chim. Slov*., 56, **2009**, 379-385.
16. Pocol V., Patron L., Carp O., Brezeanu M., Segal E. and Stanica N., *J. Therm. Anal. Calorim*., 55, **1999,** 143-154.
17. Castro E. A., Bustillo S., Romero J. M., Leiva L. C., Jorge N. L. and Gomez Vara M., *American J. of Biochemistry and Biotechnology*, 1(1), **2005**, 47-49.
18. Stefanescu M., Teza de doctorat, Universitatea din Timisoara, **1993**.
19. El-Sheikh S. M., Mohamed R. M. and Fouad O. A., *J. of Alloys and Compounds*, 482, **2009**, 302-307.
20. Xu G.Z., Wen X.H. and Wu Q.Z., *Chinese Chemical Letters*, 12, **2001**, 635-636.

Received: 08 April 2010
Accepted: 15 December 2010