IOSUD - Universitatea Politehnica Timişoara
Şcoala Doctorală de Studii Inginereşti

NEW METHODS FOR OBTAINING COPPER AND COBALT CHROMITES UNDISPERSED AND DISPERSED IN SILICA MATRIX

PhD Thesis – Summary

to obtain the scientific title of Doctor Chemist at
Politehnica University Timișoara
in CHEMISTRY

author chem. Eniko Berei

Scientific supervisor Prof.univ.dr.chem. Mircea Ștefănescu
November 2019

Nanomaterials are a topical subject, being used in the evolution of science and technology, mainly due to the development of new synthetic strategies and new characterization tools. These materials present a wide range of properties that give them applicability in different fields such as materials science, chemistry, physics, biology, and engineering. For each application it is necessary for the material to have well-defined structural and morphological characteristics (structure, particle size, specific surface area, etc.), as these determine the properties of the material.

The synthesis method has a decisive role in obtaining a material with controlled characteristics, which is why in recent years the research has focused on developing existing synthesis methods and designing new synthesis methods that allow strict control of particle size, structure and properties of nanomaterials.

The aim of the thesis is the synthesis and investigation of nanostructured oxide materials, namely cobalt chromite and copper chromite, both in bulk form and embedded in inorganic/organic hybrid matrix. The study also draws a parallel between the synthesis methods employed, together with the advantages and disadvantages of each method.

The studies carried out in the elaboration of the thesis pursued the following objectives:

- Synthesis and characterization of copper and cobalt chromites from Cr(III) and Cu(II) carboxylate complex combinations and from Cr(III) and Co(II) carboxylate complex combinations used as precursors;
- Synthesis and characterization of chromites from metallic (Cu(II), Co(II)) carboxylate precursors and ammonium dichromate used as Cr(III) source;
- Synthesis and characterization of $CuCr_2O_4$ starting from different precursor mixture:
  - Cu(II) carboxylate-α-Cr_2O_3;
  - Cu(II) nitrate-Cr(III) nitrate;
- Synthesis of copper chromites/SiO_2 nanomaterials (nanocomposites) from Cu(II), Cr(III) carboxylate precursors embedded in SiO_2 matrix;
- Synthesis of $CoCr_2O_4/SiO_2$ nanomaterials from Co(II), Cr(III) carboxylate precursors, respectively from Co(II) carboxylate type complex and ammonium dichromate;

The topic of the doctoral thesis is a topical scientific research subject and makes an important contribution to the study of the synthesis and characterization methods of nanocrystalline oxide compounds. Several synthesis procedures are presented for the copper and cobalt chromites obtained on a nanomaterial scale, both in bulk form and embedded in amorphous silica matrix. In addition to the classical method (ceramic method), a series of original (unconventional) synthesis methods are used, whereby oxide powders are obtained with nanometric particle dimensions at relatively low temperatures and with good yield.

The characterization of these materials was achieved by modern investigation techniques, which have been used throughout the experimental studies (thermal analysis, infrared spectroscopy, X-ray diffraction, UV-VIS absorption spectroscopy, transmission electron microscopy, etc.).

Chapter 1. The current state of research

The first chapter of the thesis presents the literature study of the chosen topic, consisting of a brief introduction in the field of oxide nanomaterials and of their main obtaining methods, with an emphasis on the methods used in the experimental part of this work, followed by a brief presentation of the characterization and investigation methods used.

In the first part of this chapter, nanomaterials are described in a general way. Following is a brief description of the structure and classification of oxides, and then the nanomaterials are detailed in the form of simple and mixed oxide structures formed by the elements chosen for the elaboration of this study: Cu (copper), Co (cobalt) and Cr (chromium). Aspects regarding the simple (CuO, CoO, Cr_2O_3, etc.) and double: spinel type ($CuCr_2O_4$, $CoCr_2O_4$) and delafossite type ($Cu_2Cr_2O_4$) oxide systems were presented.

The following part of this study describes the methods for obtaining copper and cobalt chromites bulk and in mixture with SiO_2, with a detailed description of the synthesis methods used in the experimental part of the thesis. In order to obtain nanocrystalline oxide materials, conventional, classical (ceramic method) methods are used based on the calcination of mechanical mixtures of simple oxides or salts and also the unconventional methods of synthesis, which provide good control over the characteristics of the resulting materials [1-5].

Three synthesis methods were used to obtain the copper and cobalt chromites in bulk form (decomposition of carboxylic complex combinations, combustion method and ceramic method), and the modified sol-gel method was used for the synthesis of nanocomposites: $CuCr_2O_4/SiO_2$, $Cu_2Cr_2O_4/SiO_2$ and $CoCr_2O_4/SiO_2$. The processes involved in obtaining inorganic-organic hybrid gels and the factors that influence the formation of silica gels are described in the following part of the study.

Chapter 2. Synthesis of complex combinations with carboxylate organic ligands used as precursors to obtain copper and cobalt chromites

This chapter presents the synthesis and characterization of copper and cobalt chromites ($CuCr_2O_4$, $Cu_2Cr_2O_4$ and $CoCr_2O_4$) from metal carboxylate complex combinations obtained through the redox reaction between the corresponding metal nitrates and 1,3-propanediol (1,3PD).

The obtaining method of the complex combinations containing the malonate dianion ligand ($C_3H_2O_4^{2-}$) is based on the oxidation reaction of 1,3PD by the nitrate ions from the metal nitrates ($Cr(NO_3)_3·9H_2O$, $Cu(NO_3)_2·3H_2O$, $Co(NO_3)_2·6H_2O$), simultaneously with the isolation of carboxylate compounds in solid state. From our previous studies we have established the conditions for obtaining the malonate dianion (acidity of the reaction medium, due to the hydrolysis of the metal nitrates in the reaction system which enhances the oxidizing character of the nitrate anion) [6].

The synthesis takes place in two stages; the first stage consists in obtaining the malonate precursors by the redox reaction between the nitrate ions and 1,3PD and the second step consists in the controlled thermal decomposition of these precursors, followed by their thermal treatment at different temperatures.

Thermal decomposition of carboxylate/hydroxycarboxylate precursors was used to obtain the $CuCr_2O_4$, $Cu_2Cr_2O_4$ and $CoCr_2O_4$ nanoparticles [7].

An important role in the way the redox reaction unfolds, with the formation of complex combinations is played by the catalytic effect of the metal ions in the system. The onset temperature of the redox reaction is influenced by the acidity of the metal aquacation and this decreases as the acidic character of the aquacation is more pronounced ($pKa[Cu(H_2O)_4]^{2+}= 8.2$, $pKa[Co(H_2O)_6]^{2+}=12.2$, $pKa[Cr(H_2O)_6]^{3+}= 4$).

Cu(II) and Cr(III) metal nitrates or Co(II) and Cr(III) metal nitrates were dissolved in distilled water. To the obtained solutions were added concentrated HNO_3 and 25% excess 1,3PD compared to the redox reaction stoichiometry between the NO_3^- ions and 1,3PD. The mixtures were heated controlled in an oven until the redox reactions between Cu(II) and Cr(III)/Co(II) and Cr(III) nitrates and 1,3PD were initiated at ~80 °C with massive release of nitrogen oxides (exothermic reaction).

The synthesis temperature of the complex carboxylate combinations was set in the 130-150 °C interval. The carboxylate complex combinations of Cu(II), Co(II) and Cr(III) were studied by FT-IR spectrometry and thermal analysis, in order to obtain information on the function of the coordinated ligand of the complex structure. FT-IR spectrometry confirmed the formation of metal carboxylates by emergence of the bands corresponding to the asymmetric vibration ν_{as} (COO^-) and symmetric vibration ν_s (COO^-) of the carboxylate group [8-9].

This method allows the synthesis of divalent chromites, $CuCr_2O_4$ and $CoCr_2O_4$ (spinels) starting with 400 °C, when the amorphous Cr_2O_{3+x} oxide passes into the crystallized form α-Cr_2O_3, which reacts with the simple oxides of CuO, respectively CoO [7, 10].

The study confirms that the formation mechanism for $CuCr_2O_4$ and $CoCr_2O_4$ has as a first step the transformation of amorphous Cr_2O_{3+x} into α-Cr_2O_3 with the formation of copper chromite germs, or cobalt chromite germs, which have an autocatalytic role thus explaining the formation of chromites at low temperature. The wide temperature interval in which $CuCr_2O_4$ and $CoCr_2O_4$ are obtained offers the possibility to control the structural and textural properties of the oxide systems.

The presence of a copper excess in the Cu:Cr=1:1 sample, favors the formation of $CuCr_2O_4$ at low temperature. Cr_2O_3 reacts completely at 400-600 °C (it was not identified in the RX diffractogram). As confirmed by thermal analysis, the formation of the monovalent copper chromite ($Cu_2Cr_2O_4$) has as a first stage the formation of the bivalent copper chromite ($CuCr_2O_4$), which at temperatures above 800 °C was transformed into $Cu_2Cr_2O_4$.

Copper chromites results as a single phase in the temperature range 800-1000 °C according to the initial composition (Cu:Cr =1:2 and Cu:Cr=1:1). The obtained chromite particles have an average diameter of ~55 nm for $CuCr_2O_4$ and ~115 nm for $Cu_2Cr_2O_4$ and can be used in various applications such as gas sensors, pigments, catalysts, etc.

RX analysis and FT-IR spectroscopy showed $CoCr_2O_4$ formation as a single phase and revealed samples with well-crystallized cubic structure starting from 400 °C, with metal-oxygen vibrations in the tetrahedral and octahedral sites of the spinel structure. The average diameter of the crystallites was in the range 6-50 nm (400-1000 °C), depending on the annealing temperature.

TEM images confirm the formation of crystalline structures and the obtained particle dimensions are in agreement with the data obtained from the X-ray diffraction, and the UV-VIS absorption confirms the potential for use as a pigment.

The advantage of the method is the obtaining of chromites on a nanometric scale with controlled composition, at low temperatures and practically with 100% yield.

Chapter 3. Synthesis of copper and cobalt chromites from Cu(II), Co(II) carboxylate complexes and $(NH_4)_2Cr_2O_7$ as a chromium source

This chapter presents a new method for the obtaining of copper and cobalt chromites, which represents the combination of two synthesis procedures: the thermal decomposition of the Cu(II) or Co(II)carboxylate precursors and the combustion method ($(NH_4)_2Cr_2O_7$ decomposition at low temperature). The synthesis method is based on the use of ammonium dichromate as a chromium source and consists in the preparation of a homogeneous mixture of the reagents $Cu(NO_3)_2\cdot 3H_2O$ or $Co(NO_3)_2\cdot 6H_2O$ and 1,3PD, with $(NH_4)_2Cr_2O_7$ followed by its controlled heating.

The method consists of heating an aqueous solution of inorganic salts (usually are used metal nitrates), which act as oxidizing agents ($Cu(NO_3)_2\cdot 3H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $(NH_4)_2Cr_2O_7$) and an organic fuel, the reducing agent (1,3PD), which can be the complexing agent of the metal ions. The homogeneity of the mixture is very important. The complete dissolution of the components is necessary and the mixture is subsequently heated in a controlled manner up to the ignition temperature and gives rise to a rapid exothermic reaction leading to the oxides formation [11-12].

Stoichiometrically dosed reagents ($Cu(NO_3)_2\cdot 3H_2O$, 1,3PD and $(NH_4)_2Cr_2O_7$), for the $CuO:Cr_2O_3=1:1$ oxide ratio, respectively ($Co(NO_3)_2\cdot 6H_2O$, 1,3PD and $(NH_4)_2Cr_2O_7$), for the $CoO:Cr_2O_3=1:1$ oxide ratio, were dissolve in distilled water and a few drops of concentrated HNO_3. After homogenization the mixture was heated controlled in the oven. At ~130 °C the redox reaction between NO_3^- and 1,3PD takes place with the formation of the Cu(II)/Co(II) carboxylate type complex combination and with NOx release. The mixture of Cu(II)/Co(II) carboxylate-$(NH_4)_2Cr_2O_7$ was further heated until the exothermic (energetic) decomposition of ammonium dichromate (180 °C) takes place, also favoring the decomposition of the Cu(II) carboxylate/Co(II) carboxylate, resulting in the homogeneous mixture of amorphous oxides (CuO and Cr_2O_3, respectively CoO and Cr_2O_3). The oxide mixture was thermally treated at temperatures between 400-1000 °C for 3 hours.

Ammonium dichromate contains both oxidizing groups ($Cr_2O_7^{2-}$) and reducing groups (NH_4^+), and upon heating it decomposes autocatalytically with Cr_2O_3 formation. Because the decomposition reaction, which takes place at 180 °C, occurs with massive gas release, the Cr_2O_3 particles obtained are very fine [12].

Thermal analysis and FT-IR spectroscopy show the thermal decomposition of the $(NH_4)_2Cr_2O_7$-Cu(II) carboxylate/$(NH_4)_2Cr_2O_7$-Co(II) carboxylate mixtures. The exothermic effect at 180 °C (DTA curve) was intense because in this case the energetic decomposition of ammonium dichromate ($\Delta H=-476.4\pm0.4$ kJ/mol) was superimposed with that of the Cu(II) carboxylate complex. Decomposition occurred in asimilar way for the case of the ammonium dichromate and Co(II) carboxylate mixture. Following the decomposition, a mixture of amorphous oxides was formed (CuO and Cr_2O_3/CoO and Cr_2O_3), which interacted during the thermal treatments and formed mixed oxide compounds.

The FT-IR spectra confirmed the formation of Cu(II) carboxylate and ammonium dichromate mixture, or of the Co(II) carboxylate and ammonium dichromate mixture by the presence of characteristic bands of carboxylate group: symmetrical vibration ν_s (COO^-) at ~1300 cm^{-1} and the asymmetric vibration ν_{as} (COO^-) at ~1600 cm^{-1}.

For the annealed samples in the 400-1000 °C temperature interval the FT-IR spectra are similar and show the formation of $CuCr_2O_4$/$CoCr_2O_4$ through the presence of the bands located at ~510 cm^{-1} attributed to the bonding vibrations of the Cr^{3+} ions situated in the octahedral positions of the spinel structure and ~630 cm^{-1} attributed to the vibrations of Cu^{2+}/Co^{2+} ions in the tetrahedral sites of the spinel structure [13].

From the results it was found that by this synthesis method, in both cases the chromites form only after the 400 °C temperature, when the non-stoichiometric chromium oxide, Cr_2O_{3+x}, loses the excess oxygen and passes into stoichiometric chromium oxide Cr_2O_3, which reacts with MO (M=Cu, Co).

In the case of copper chromite, it begins to crystallize at 600 °C and at 1000 °C it was the majority phase (96%). The average diameter of the $CuCr_2O_4$ particles was about 50 nm for samples annealed in the 600-1000 °C temperature interval.

Via decompositon of Co(II) carboxylate type complex combinations and ammonium dichromate mixture, the $CoCr_2O_4$ spinel was obtained as a single crystalline phase, that occurs at an apparently low temperature (170 °C), after the exothermic decomposition of the ammonium dichromate, which makes the temperature of the system to be much higher ($\Delta H = -476.4 \pm 0.4$ kJ/mol).

RX and TEM analyzes showed that the cobalt chromite samples had a cubic structure and were well crystallized, and the average diameter was between 11 and 50 nm, slightly increasing with the increase of the annealing temperature.

The disadvantage of this synthesis procedure is the difficult control of the decomposition reaction which can lead to the loss of certain amounts of substance during the energetic decomposition reaction. For this reason, a procedure has been developed to isolate the reaction mixture, in order to prevent the loss of substance.

Chapter 4. Synthesis of copper chromites from mechanical mixing

This chapter includes a study on the formation of copper chromite ($CuCr_2O_4$) starting from the mixture of Cu(II) carboxylate and α-Cr_2O_3 on the one hand and starting from a mixture of salts (copper nitrate and chromium nitrate) on the other hand.

The reactants $Cu(NO_3)_2 \cdot 3H_2O$, 1,3PD and α-Cr_2O_3, stoichiometrically dosed ($CuO:Cr_2O_3=1:1$) were mixed and homogenized with distilled water and the mixture obtained was heated controlled in the oven. At 130 °C the redox reaction between NO_3^- ions and 1,3PD took place with the formation of the copper carboxylate type complex combination in mixture with α-Cr_2O_3 and gas emission (NOx).

Controlled heating of the Cu(II) malonate-α-Cr_2O_3 mixture led to Cu(II) carboxylate complex combination decomposition at 220 °C, with the obtaining of CuO (amorphous) in mixture with α-Cr_2O_3. The obtained powder was annealed at different temperatures in the 400-1000 °C temperature interval, for 3 hours.

The FT-IR spectra of the Cu(II) carboxylate type complex combination, simple and mixed with α-Cr_2O_3, obtained at 130 °C contained the characteristic bands from 1625 cm^{-1} and 1390 cm^{-1}, which can be attributed to the carboxylate bonds vibrations ν_{as} (COO^-) and ν_s (COO^-) coordinated to metal ions (Cu^{2+}), confirming the formation of the copper carboxylate (malonate) combination.

FT-IR analysis of the annealed samples demonstrated the formation of M-O bonds, and the X-ray diffraction confirmed the formation of the oxide structures in the samples. At 800 °C, CuO reacted with Cr_2O_3, forming a mixture of copper (I) chromite and copper (II) chromite. This can be attributed to the good stability of chromium oxide. The presence of α-Cr_2O_3 together with the chromites mixture can be explained by the fact that part of CuO (it was consumed) reacted with $CuCr_2O_4$ to form monovalent chromite.

The copper chromite obtained from the Cu(II) and Cr(III) nitrates mixture was similar. The salt mixture was milled with 1mL distilled water, heated under controlled conditions up to 90 °C and kept for two hours at this temperature. Subsequently, the temperature was raised to 170 °C and maintained for two hours, and then the sample was annealed at different temperatures in the 400-1000 °C temperature interval, for 3 hours.

This synthesis resulted in a mixture of oxides. The reaction mechanism for the formation of the copper chromite from the mechanical mixture of nitrates took place through the copper chromate (reaction intermediate), recorded in the diffractogram of the sample annealed at 400 °C, and the copper chromite was formed starting with the 500 °C temperature. At 800 °C, $Cu_2Cr_2O_4$ was also formed from $CuCr_2O_4$ and the mixture of oxide phases (Cr_2O_3, $CuCr_2O_4$ and $Cu_2Cr_2O_4$) was maintained up to 1000 °C.

Chapter 5. Preparation of nanocomposites from carboxylate complexes of malonate type through the modified sol-gel method

The method used to obtain the nanocomposites represents an original synthesis method that combines the decomposition of carboxylate precursors with the classical sol-gel method. The formation and decomposition of carboxylate precursors takes place inside the silica matrix at low temperatures and leads to the formation of nanocomposites of the $M^{II}Cr_2O_4/SiO_2$ type.

The modified sol-gel method was developed within the research group led by Professor M. Ştefănescu and his colleagues, who have carried out numerous studies regarding the interaction between different diols with the hydrolysis products of TEOS (Tetraethyl orthosilicate), as well as the effect of these interactions on of the silica matrix morphology and have established the optimal parameters for the synthesis of these gels [14-16].

The modified sol-gel method consists in the preparation of gels by hydrolysis and condensation of TEOS-diol-metal nitrate precursors, which are subsequently subjected to thermal treatments, and following the decomposition of these precursors, metal oxides embedded in SiO_2 are formed.

The diol has a dual role in this synthesis method because in the gelling step it interacts with the TEOS, leading to the formation of an inorganic-organic hybrid gel and in the thermal treatment stage, it interacts with the metal nitrate and forms metal-carboxylate type combinations embedded in the silica matrix.

The decomposition of the precursors takes place at low temperature and leads to the formation of a homogeneous mixture of metal oxides in amorphous state, with high reactivity and offers the possibility of obtaining very fine particles (nanoparticles).

The precursors nature (carboxylate complex combinations) plays an important role in the synthesis of oxide nanoparticle systems. In addition to the precursors nature, the conditions under which the decomposition is performed (heating rate, temperature and annealing time, the atmosphere in the oven) play a decisive role and allow the control of the structural and morphological characteristics of the decomposition products [17-18].

In the case of the studied systems, the conditions of solubilization of metallic nitrates in distilled water and ethanol by magnetic stirring were established. The required amount of 1,3PD, concentrated nitric acid and the TEOS-ethanol solution were added and stirring continued for one hour. The resulted clear solution was allowed to rest, and after some time a gel was obtained. This gel was dried at 40 °C, then milled and thermally treated in the oven at 90 °C and 200 °C, for 3 hours, when a powder was obtained which contained in its pores the reagents mixture (90 °C) or the carboxylate precursors (200 °C).

By controlled heating in the 90-150 °C interval, the redox reaction occurred depending on the metal nitrate type, with the formation of the carboxylate which was isolated and stabilized in the pores of the hybrid silica gel.

Thermal analysis and FT-IR revealed the formation of Cu(II), Co(II) and Cr(III) carboxylate precursors. Thermal analysis showed that in the 250-350 °C temperature interval the decomposition of carboxylated precursors took place inside the gel pores, with the formation of simple or mixed metal oxides.

According to the synthesis procedure, two series of gels $Cu(NO_3)_2 \cdot 6H_2O$-TEOS-1,3PD, with different compositions 50% oxide/SiO_2 (molar ratios Cu(II):Cr(III)=1:1 and Cu(II):Cr(III)=1:2) were prepared.

The gels obtained at 90 and 200 °C were characterized by thermal analysis and FT-IR.

By thermal analysis of the gels, in the 200-270 °C temperature interval, on the TG curves the loss of water from the composition of the complexes was recorded, when their structure was reorganized. All samples show a strong exothermic effect at 270-310 °C, on the DTA curve, attributed to the oxidative decomposition reaction of the carboxylate mixture. During the decomposition reaction, an amorphous mixture of oxides (Cr_2O_{3+x} and CuO) was formed in the pores of the gels. At 400 °C, Cr_2O_{3+x} (amorphous) passes into α-Cr_2O_3 (crystalline), which in the 400-500 °C temperature interval interacts with CuO and results in $CuCr_2O_4$ formation [10].

At higher temperatures (~800 °C), $CuCr_2O_4$ changed its structure and $Cu_2Cr_2O_4$ was formed. Both samples exhibited a weak exothermic effect on the DTA curve associated with structural changes and rearrangement of the crystalline network from the spinel structure ($CuCr_2O_4$) to the delafossite structure ($Cu_2Cr_2O_4$). In the case of a CuO excess, the ratio Cr_2O_3:CuO=1:2, starting with the 800 °C temperature, the formation of the Cu(I) chromite from the Cu(II) chromite started, in air atmosphere.

FT-IR spectra, in the 40-200 °C temperature interval, highlighted the presence of nitrate (NO_3^-) through the specific band from ~1380 cm^{-1}, which at higher temperatures disappeared due to the consumption of nitrate in the NO_3^--diol redox reaction. The gels presented two characteristic bands of the asymmetrical and symmetrical stretching vibrations of the carboxylate groups coordinated to the metal ions: ν_{as} ($-COO^-$) at about 1.560 cm^{-1} and ν_s ($-COO^-$) around 1.350 cm^{-1}. These bands disappeared in the annealed samples (400-1000 °C) due to the carboxylate precursors decomposition.

The silica matrix plays a decisive role in the formation of copper chromates because it prevents contact between oxides (CuO and Cr_2O_3) and the reaction was delayed, and also limits the oxygen diffusion into the system.

Even if the syntheses started from different molar ratios, $CuCr_2O_4$ was formed in both samples at low temperature (600 °C). At 800 °C, in the RX diffractograms, CuO and $CuCr_2O_4$ are registered, which reacted as temperature increased at 1000 °C with the formation of monovalent copper chromite, due to the influence of the silica matrix.

The synthesis procedure of $CoCr_2O_4/SiO_2$ nanocomposites was similar to that of the $CuCr_2O_4/SiO_2$ system and 20%, respectively 50% $CoCr_2O_4/SiO_2$ (molar percent) mixtures were synthesized. The gels obtained at 70 °C and 150 °C were subjected to thermal analysis.

Thermal analysis of the gels followed the redox reaction 1,3PD-metal nitrates unfolding with the formation of Co(II) and Cr(III) complex combinations in the pores of the hybrid gels and 150 °C temperature was proposed as a synthesis temperature of the precursors. FT-IR spectrometry revealed the formation of Co(II) and Cr(III) carboxylate complex combinations in the pores of hybrid gels.

On the DTA curves there was a weak exothermic effect at 90-130 °C attributed to the redox reaction between $Co(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_2{\cdot}9H_2O$ and 1,3PD, which occurred in the gel pores with the Co(II) and Cr(III) carboxylate mixture formation. The second exothermic effect registered on the DTA curve (250-350 °C) was stroger and was associated with the decomposition of the carboxylate mixture and the formation of cobalt chromite.

The FT-IR spectra of the samples obtained at 70 and 150 °C showed the characteristic bands for the asymmetrical ν_{as} ($-COO^-$) and symmetrical ν_s ($-COO^-$) carboxylate group vibrations. The carboxylate band from 1380 cm^{-1} overlapped with the NO_3^- vibration, indicating that NO_3^- was not completely consumed in the redox reaction at 70 °C [19].

The sample heated to 150 °C was annealed in the 300-1000 °C temperature interval. The diffractograms of the annealed gels showed the formation of the $CoCr_2O_4$ structures embedded in SiO_2. $CoCr_2O_4$ was identified by X-ray diffraction starting with the 300 °C temperature for both compositions of nanocomposites (20% and 50% molar percent $CoCr_2O_4/SiO_2$), but it was well crystallized only for the 50% $CoCr_2O_4/SiO_2$ composition at this temperature.

The average diameter of $CoCr_2O_4$ crystallites was of 4-15 nm, for both series of samples. TEM images show the distribution of cobalt chromite in the silica matrix and the maps of the elements distribution in the $CoCr_2O_4/SiO_2$ nanocomposites (20% cromite) showed the uniform distribution of Co and Cr atoms throughout the scanned area.

Chapter 6. Synthesis of $CoCr_2O_4/SiO_2$ nanocomposites from Co(II) malonate type complex combinations and $(NH_4)_2Cr_2O_7$ through the modified sol-gel method

The study presented in this chapter presents the synthesis of $CoCr_2O_4/SiO_2$ nanocomposite. The method represents a changed procedure of the modified sol-gel method. The synthesis method aims to combine the advantages of decomposition of the carboxylate precursors and those of the decomposition of the ammonium dichromate, with those of the sol-gel method. The method consists in obtaining gels in the TEOS-1,3PD-$Co(NO_3)_2 \cdot 6H_2O$-$(NH_4)_2Cr_2O_7$ system, that are subsequently subjected to controlled thermal treatments.

As showed in the previous chapter, where the modified sol-gel method was presented, the diol has a dual role, interacting both with the metal alkoxide (TEOS) and with the cobalt nitrate. The interaction of the diol with the TEOS, during the gelling process, influences the characteristics of the obtained matrix, and upon heating, as a result of the interaction with the cobalt nitrate, the Co(II) malonate type complex combinations are formed *in situ*, during the nitrate-diol redox reaction. The corresponding $CoCr_2O_4$ oxide phase, embedded in the amorphous silica matrix, was formed by appropriate thermal treatments.

Three sets of samples with different oxide content were prepared (20%, 50% and 80% $CoCr_2O_4/SiO_2$-weight percent, for which the following notations were used:G_{20}, G_{50} and G_{80}). For the gel precursor synthesis, the amounts of $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_2Cr_2O_7$ and 1,3PD with 25% excess were dissolved. After homogenization a ethanol-TEOS solution was added dropwise. The obtained samples were allowed to gel. The obtained samples were dried at 80 °C for two hours and then were milled. Then the gels were the thermally treatmented at 170 °C, for two hours, to complete the redox reaction between $Co(NO_3)_2 \cdot 6H_2O$ and 1,3PD, which occurred with gas emission (NOx) and the Co(II) carboxylate complex formation. At this temperature (170 °C) the samples contained a mixture of Co(II) carboxylate complex and $(NH_4)_2Cr_2O_7$, embedded in the gel pores. The samples thus obtained were annealed at different temperatures (400-1000 °C) for three hours.

The samples obtained at 80 °C were subjected to thermal analysis. The strong exothermic effect recorded on the DTA curve at 167 °C corresponds to the decomposition of $(NH_4)_2Cr_2O_7$, which occurs at ~170 °C [12], together with the decomposition of the Co(II) carboxylate complex and the formation of the mixed oxide. The second effect, recorded at 293 °C, was wider and less intense and may be associated with the decomposition of the Co(II) complex. The thermal analysis for the G_{50} sample obtained at 80 °C had a similar thermal behavior to the G_{20} sample, and for G_{80} the thermal analysis could not be performed.

Due to the presence of the SiO_2 matrix, not all the amount of Co(II) carboxylate decomposed in the first decomposition step associated with the $(NH_4)_2Cr_2O_7$ decomposition. During the formation of the matrix, a series of pores were formed in its structure that incorporated the reagents mixture, which led to a smaller exothermic effect and a controlled decomposition process. When the amount of $(NH_4)_2Cr_2O_7$ was higher, as in G_{80}, the behavior of the sample was different. The decomposition reaction for this sample was violent and the energetic decomposition reaction occurred at 170 °C with particle scattering.

FT-IR spectroscopy showed the presence of Co(II) carboxylate precursor in combination with ammonium dichromate in all samples obtained at low temperature (80 °C). The Co(II) carboxylate precursor is of the malonate type [20] and was formed in the redox reaction between NO_3^- and -OH groups of 1,3PD.

X-ray analysis confirmed the crystallization of $CoCr_2O_4$ inside the silica matrix as a single cubic phase, at 400 °C. RX diffractograms and TEM images showed relatively spherical $CoCr_2O_4$ nanoparticles, with dimensions ranging from 3.9 to 12.4 nm.

General conclusions

The studies carried out in the thesis aimed to obtain oxide nanomaterials based on Cu, Co, and Cr, bulk and mixed with SiO_2 through four synthesis methods:

- **The thermal decomposition of carboxylate type complex combinations method** obtained by the redox reaction between metal nitrates and diols;
- **The combustion method** which consists in the thermal decomposition of the M(II) metallic carboxylate complex combinations in mixture with the ammonium dichromate, used as a chromium source;
- **The ceramic method**, mixtures of:
    - Cu(II) carboxylate-α-Cr_2O_3;
    - Cu(II) nitrate-Cr(III) nitrate;
- **Modified sol-gel method** which consists in the obtaining and thermal decomposition of carboxylate type complex combinations inside the silica gel pores.

The optimal conditions for the redox reaction between $Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and 1,3PD were established.

The Cr(III), Cu(II) and Cr(III), Co(II) hydroxycarboxylate complex combinations were obtained in the mixture at ~130 °C and were decompose in the 270-380 °C temperature interval, with an oxide mixture formation Cr_2O_{3+x} and CuO, respectively Cr_2O_{3+x} and CoO.

At about 400 °C amorphous Cr_2O_{3+x} transformed into crystalline α-Cr_2O_3, when it reacted with the simple oxides (CuO, CoO) forming mixed oxides. The formation of carboxylate complex combinations was highlighted by thermal analysis and FT-IR spectroscopy.

$CoCr_2O_4$ and $CoCr_2O_4$ were obtained by **the thermal decomposition of carboxylated precursors method** at low temperature, starting at 400 °C.

The presence of an excess of copper (Cu:Cr=1:1) favored the formation of $CuCr_2O_4$ at low temperature. Copper chromites ($CuCr_2O_4$ and $Cu_2Cr_2O_4$) formed as a single phase at temperatures above 800 °C, when $CuCr_2O_4$ interacted with excess CuO to form $Cu_2Cr_2O_4$.

Cobalt chromite was obtained as a single, well crystallized cubic phase at temperatures above 300 °C and the obtained cobalt chromite particles had an average particle diameter of 6-50 nm.

TEM images showed that the obtained copper and cobalt chromite nanoparticles ($CuCr_2O_4$ and $CoCr_2O_4$) had a good crystallinity, with fine spinel structure, and $Cu_2Cr_2O_4$ had a hexagonal structure.

The combustion method is an original synthesis procedure that uses ammonium dichromate as the chromium source and the M (II) carboxylate combinations as the divalent metal source (M=Cu, Co).

$CuCr_2O_4$ was formed starting with the temperature of 600 °C, and at 1000 °C it was the majority phase (96%).

$CoCr_2O_4$ was obtained by the thermal decomposition of $(NH_4)_2Cr_2O_7$, starting with a temperature of 170 °C, which also triggers the decomposition of the Co(II) carboxylate complex.

According to the values of the average crystallite diameters (d_{XRD}), it was found that the two chromites were nanocrystalline (d_{XRD}=48-51 nm for $CuCr_2O_4$ and d_{XRD}=11-46 nm for $CoCr_2O_4$).

The modified sol-gel method was used to obtain the $CuCr_2O_4/SiO_2$, $Cu_2Cr_2O_4/SiO_2$ and $CoCr_2O_4/SiO_2$ nanocomposites.

The formation of hybrid gels took place within the SiO_2 matrix and was highlighted by FT-IR and thermal analysis. In the pores of the gels, the redox reaction between metal nitrates and diol (1,3PD) occurred in a controlled maner due to the presence of the silica matrix.

The study of the thermal decomposition of the Cu(II), Co(II) and Cr(III) carboxylate type complex combinations, in the pores of the silica matrix revealed that it unfolds in steps, in the 250-360 °C temperature interval and was not influenced by the concentration of the oxide precursors.

$CuCr_2O_4$ started to form at temperatures higher than 400 °C, for both compositions considered (Cu:Cr=1:2 and Cu:Cr=1:1), together with α-Cr_2O_3 formation.

At temperatures above 800 °C, $CuCr_2O_4$ passed into $Cu_2Cr_2O_4$, in both cases due to the influence of the SiO_2 matrix, which prevented the contact between particles and limited the diffusion of oxygen into the system.

$CoCr_2O_4$ began to form at temperatures above 300 °C, for both compositions (20% and 50% molar percent $CoCr_2O_4/SiO_2$); $CoCr_2O_4$ was obtained as a single phase, and the average diameter of the obtained particles was between 5-15 nm.

The method used to obtain $CoCr_2O_4/SiO_2$ nanocomposites is an original synthesis method, **a different procedure of the modified sol-gel method**.

The decomposition of the precursor mixture was controlled by the presence of the SiO_2 matrix, which took up a significant amount of the reaction enthalpy, which led to the lowering of the mixture's temperature and to a better control over the energetic decomposition process of the precursor mixture (Co(II) carboxylate and $(NH_4)_2Cr_2O_7$).

Nanocomposites with different oxide ratios (20%, 50% and 80% $CoCr_2O_4/SiO_2$) were obtained, with average diameter of cobalt chromite particles between 4-13 nm.

The materials obtained can be used as inorganic pigments and catalysts.

REFERENCES

1. N. Dupont, A. Kaddouri, P. Gelin, Physicochemical and catalytic activity properties of sol gel-prepared copper-chromium oxides, J Sol-Gel Sci Tehnol, 58, 302-306, 2011.
2. S.M. El-Sheikh, M. Rabbah, Novel low temperature synthesis of spinel nano-magnesium chromites from secondary resources, Thermochim Acta, 68, 13-19, 2013.
3. S. Naz, S.K. Durrani, M. Mehmood, M. Nadeem, A.A. Khan, Study of thermal, structural and impedance characteristics of nanocrystalline copper chromite synthesized via hydrothermal process, J Therm Anal Calorim, 126, 381-389, 2016.
4. M.H. Habibi, H. Fakhri, Sol–gel combustion synthesis and characterization of nanostructure copper chromite spinel, J Therm Anal Calorim, 115, 1329-1333, 2014.
5. P.M. Pimentel, A.E. Martinelli, D.M.A. Melo, A.M.G. Pedrosa, J.D. Cunha, J.C.N. Silva, Pechini synthesis and microstructure of nickel-doped copper chromites, Mater Res, 8(2), 221-224, 2005.
6. M. Niculescu, R. Dumitru, A. Magda, G. Bandur, E. Șișu, Noi metode de obținere a unor acizi carboxilici prin reacții de oxidare a poliolilor cu azotați de metal (II) I. Reacții de oxidare a 1,2-propandiolului cu azotați de metal (II), Rev Chim București, 58(10), 2007.
7. M. Ştefãnescu, V. Sasca, M. Bîrzescu, Studies on the thermal decomposition of heteropolynuclear glyoxyates of Cr(III) and Cu(II), J Therm Anal Calorim, 56, 579-586, 1999.
8. H.Y.N. Holman, D.L. Perry, M.C. Martin, G.M. Lamble, W.R. McKinney, J.C. Hunter-Cevera, Real-time characterization on biogeochemical reduction of Cr(VI) on basalt surfaces by SR-FTIR imaging, Geomicrobiol J, 16, 307-324, 1999.
9. K. Nakamoto, Infrared spectra of inorganic and coordination compounds, New York: John Wiley and Sons, 1970.
10. M. Ştefãnescu, Considerațiuni asupa modului de formare a oxizilor micști din substanțe inițiale cu reactivitate crescută, Teză de doctorat, Universitatea Politehnica Timișoara, România, 1993.
11. Z-L. Luo, B. Geng, J. Bao, C. Gao, Parallel solution combustion synthesis for combinatorial materials studies, J Comb Chem, 7, 942-946, 2005.
12. M.D. Lima, R. Bonadimann, M.J. Andrade, J.C. Toniolo, C.P. Bergmann, Nanocrystalline Cr_2O_3 and amorphous CrO_3 produced by solution combustion synthesis. J Eur Ceram Soc, 26, 1213-1220, 2006.
13. A.V. Salker, S.M. Gurav, Electronic and catalytic studies on $Co_{1-x}Cu_xMn_2O_4$ for CO oxidation, J Mater Sci, 35, 4713-4719, 2000.
14. O. Ştefãnescu, M. Stoia, M. Ştefãnescu, T. Vlase, Study on the influence of teos-diol molar ratio on their chemical interaction during the gelation process, J Therm Anal Calorim, 97(1), 251-256, 2009.
15. M. Ştefãnescu, M. Stoia, O. Ştefãnescu, A. Popa, M. Simon, C. Ionescu, The interaction between TEOS and some polyols-Thermal analysis and FTIR, J Therm Anal Calorim, 88(1), 19-26, 2007.
16. M. Ştefãnescu, M. Stoia, O. Ştefãnescu, Thermal and FT-IR study of the hybrid ethylene-glycol-silica matrix, J Sol-gel Sci Technol, 41(1), 71-78, 2007.
17. C.J. Brinker, G.W. Scherer, Sol-Gel Science. Physics and Chemistry of Sol-Gel Processing, Academic Press, New York, 1990.
18. A. Pathak, P. Pramanik, Nano-particles of oxides through chemical methods, PINSA, 67(1), 47-70, 2001.

19. S.A. Hosseini, M.C. Alvarez-Galvan, J.L.G. Fierro, A. Niaei, D. Salari, MCr_2O_4 (M=Co, Cu, and Zn) nanospinels for 2-propanol combustion: Correlation of structural properties with catalytic performance and stability, Ceram Int, 39, 9253-9261, 2013.
20. O. Ștefãnescu, M. Ștefãnescu, New Fe(III) malonate type complex combination for development of magnetic nanosized ɤ-Fe_2O_3, J Organomet Chem,740, 50-55, 2013.