

To the memory of Academician Maria Brezeanu, who intuited thirty years ago the great potential of using coordination compounds as precursors for different materials, starting the research in the field named today materials science

REVIEW

THERMAL PROPERTIES OF SOLID COORDINATION COMPOUNDS. IV. SOME APPLICATIONS IN MATERIALS SCIENCE

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The paper consists in a critical review of the main applications of the thermal reactions of solid coordination compounds in the field of materials science, namely generation of tailor made materials with specific physical/or chemical properties. As the synthesis of mixed oxides with various structures (spinelic, garnet, hexagonal, perovskitic) represents definitely the main application in this field, the corresponding paragraph is the most extensive of the paper. The synthesis of sulfides, metals, nitrides, composite materials and new complexes (which cannot be synthesized in aqueous solutions) is also reviewed.

INTRODUCTION

Thermal reactivity of solid coordination compounds is a topic of general importance ranging from fundamental scientific aspects to application-oriented problems. Whereas in the field of pure science the interest is focused on the mechanistic course, the generation of tailor-made materials with specific chemical/or physical properties at optimum conditions is of crucial relevance for industrial processes.

In previous papers¹⁻³ we presented some theoretical aspects of the thermoreactivity of coordination compounds, emphasising some general features such as the influence of experimental conditions and coordination compounds' nature on their thermal behaviour. Based on this knowledge, the aim of this paper is to present some practical applications of the thermal decompositions reactions of these compounds in materials science (synthesis of oxides, sulfides, nitrides, composites materials, metals and new complexes).

1. Oxides synthesis

The use of coordination compounds as raw materials for simple and mixed oxides with various structures (spinelic,^{4,5} garnet,⁶⁻⁷ hexagonal,⁸ perovskitic^{9,10}) constitutes by far, the main application of their thermal decomposition reactions.¹¹⁻¹³ Such a synthetic route is considered as an efficient method due to the valuable benefits¹³⁻¹⁵ related to the:

- synthesis reproducibility;
- accessibility (most raw materials have moderate costs);
- diversity of metallic ions combinations (coordination abilities with a variety of ligands and versatile combination ratios);

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- homogeneity of the mixed oxides (the metallic cations are built up on an atomic scale in an ordered precursor and during the thermal decomposition the uniform distribution is largely preserved);
- oxides particles with sizes lower than 500 Å, inferior to obtained through conventional or other nonconventional synthesis methods, due to low decomposition temperatures (the mixed oxide lattice is often already available for decomposition completion).

The coordination compounds used as precursors in the synthesis of mixed oxides belong to the following groups:

- complex anion–complex cation (mixed complexes);
- polynuclear coordination compounds.

The decomposition processes of various metal carboxylates (mono, poly and hydroxy) were the most studied reactions during the last decades in this topic. The simplest compounds, formates and oxalates were scrutinized, but the complex of unsaturated and aromatic carboxylic acids (such as maleates and phthalates) were also investigated.

As compared to the aliphatic monocarboxylates (formate,^{13,16-18} acetate,¹⁹ propionate,²⁰ malonate,^{21,22} succinate²²), the dicarboxylates show promising results²¹⁻²⁴ due to their exothermicity during decomposition. Additional, poly(hydroxy)carboxylic acids (oxalic²⁵⁻²⁸ malonic,²⁹ malic,^{8,30-32} tartarate,^{30,33} gluconate,^{6,34,35} citric^{36,37} acids) act as versatile complexing agents with different oxygen donor atoms and exhibiting distinct affinity towards metal ions (forming different coordination geometries depending on the chemical environment).

Usually found residia are metal oxides (in air atmosphere) or pure metals (in inert atmosphere). In addition to metals, metal carbides and dispersed carbon were also found as solid products^{38,39}. In air atmosphere, CO₂ and H₂O were found as mainly gaseous evolved products.⁴⁰ In inert atmosphere, as gas-phase products carbon dioxide, hydrocarbons, aldehydes, ketones, acids (and acid anhydrides) were identified.^{38,39}

Generally, the carboxylate ligands of coordination compounds undergo degradative oxidation on heating, being possible to isolate several reaction intermediates as oxalates^{8,41,42} and malates⁴³ in tartarates complexes, malonates^{5,8,44-47} and acetates^{5,8,45,48} in malates compounds, acetonedicarboxylates in citrates complexes,^{49,50} oxalates in 4,5 imidazoloedicarboxylates,⁵¹ mixed imidazole-carboxylates⁵² (phthalates and malates), and glyoxalates⁵³ complexes decomposition.

Formation of mixed oxycarbonate (Ln₂O(CO₃)₂) or dioxycarbonate (Ln₂O₂CO₃), as intermediate are reported in the thermal decomposition of yttrium and lanthanide coordination compounds with several carboxylic acids. Thus, Ln₂O(CO₃)₂ is obtained as intermediate in the thermal decomposition of 3-methyladipates complexes,⁵⁴ 1,1-cyclobutamedicarboxylates.⁵⁵ Ln₂O₂CO₃ is identified in the thermal decomposition of 4-dimethylaminobenzylidenepyruvates and 4-methoxybenzylidenepyruvates,^{56,57} 1-hydroxy-2-naphthoates,⁵⁸ mesoconates,⁵⁹ 4-methoxy-2-methylbenzoates,⁶⁰ dimethoxybenzoates,⁶¹ 2,3,4-trimethoxybenzoates,⁶² 2,4,6-trimethylbenzoates,⁶³ 3-methyladipates,⁵⁴ cinnamates,⁶⁴ 3-methylglutarates,⁶⁵ 2,5-dihydroxybenzoates,⁶⁶ sodium and potassium oxalatometallates of rare earth.^{67,68} LnCo(CO₃)₂O_{0.5}, LnCo(CO₃)O_{1.5} and LnCo(CO₃)_{0.5}O₂ are separated in the thermal decomposition of some [LnCo(C₂O₄)_n·nH₂O]⁶⁹ coordination compounds.

Oxalate complexes (oxalic acid, HOOC-COOH) are considered as “pioneer precursors” in the synthesis of mixed oxides and their thermal properties have been extensively studied.^{15,70} The first investigation concerning the synthesis of mixed oxides through thermal decomposition of coordination compounds mentioned in literature belongs to Paris and Paris.⁷¹ They obtained some aluminates, vanadates and chromites starting from A(I)[M(III)(C₂O₄)₃] (A(I)=H⁺, NH₄⁺, M(III)=Al³⁺, Cr³⁺, V³⁺) compounds.

The Romanian school of coordination chemistry approached this field as far as the seventies. Macarovici *et al.*⁷² synthesized compounds of Aⁿ_x[M^m_y(C₂O₄)_z], (A=Bi³⁺, La³⁺, Ce³⁺, In³⁺ and M=Ti⁴⁺, Co³⁺, Cr³⁺) and some anion complex – cation complex coordination compounds types as precursors for mixed oxides (obtained in the temperature range of 300-500°C).⁷²⁻⁸⁶

A next step in the development of the coordination compounds precursor method was made by Brezeanu and coworkers who used polynuclear coordination compounds as precursors for mixed oxides with different structures (spinelic, perovskitic, garnets) and mean crystallite sizes in the range 100-400Å. The synthesis of the mixed oxides requires temperature ranges of 30-400°C (ferrites), 40-600°C (chromites) and 30-625°C (cobaltites). The precursor compounds were obtained by different methods, precipitation^{4,25,26,87-92}

and hydrolytic decomposition^{27,28,93-99} respectively. The former presents the advantage of adjusting and controlling the end oxide product's features through the composition and architecture of the coordination compounds, which depend on the synthesis conditions (nature and ratio of raw materials, pH, temperature and time of reaction, solvent). On the other hand, the latter permits easily the synthesis of mixed oxides with more than two metals, in various ratios. This is possible because in the lattice of the raw insoluble material, respectively ferrous oxalate $\text{Fe}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (α -humboldtine) or Cr_2O_3 , several metallic elements (especially Mg, Mn, Co, Ni, Zn, Cu, etc.) may intrude, replacing partially or totally the iron or chromium cations. As a disadvantage of using oxalates precursors (usually presented as five membered chelate compounds) we can mention the higher decomposition temperature than a chelate with a higher ring size (for example, the malate complex (malic acid, $\text{HOOC-CHOH-CH}_2\text{-COOH}$, which may act in distinct conditions as a seven-membered chelate).^{43,100,101} A decrease of the stability of the chelate complexes with the increasing of the ring size can be explained to a large extent on the basis of the chelate/entropy factor.¹⁰² Another explanation for such a behaviour may be given on the basis of the high-temperature acid-base theory according to which, the weaker the anion base, the higher the temperature of decomposition¹⁰³ (the oxalate is a weaker anion base than the malate). Malates coordination compounds were used to synthesize a large number of spinel ferrites^{5,30,45} and chromites,¹⁰⁴ hexaferrites,^{8,31,105} garnets¹⁰⁶ and perovskites.^{8,32,107} Similar decomposition temperatures with malates complexes were obtained using tartarates (tartaric acid ($\text{HOOC-CHOH-CHOH-COOH}$)). The tartaric acid presents four potentially ionizable H atoms, being characterized by a high coordination versatility and affinity of molecular association due to its polydentate nature. It was used as ligand in polynuclear coordination compounds precursors of ferrites (cubic^{30,33,42,108} and hexagonal structure¹⁰⁹), aluminates,¹¹⁰ chromites,³⁵ perovskites^{9,111} and garnets.¹¹² It is important to mention that tartaric precursors were used with success in the synthesis of pure mixed oxides in some cases where the malates ones failed.¹¹³ This behaviour may be related with the specific coordination geometries of the tartaric acid.

The literature also reveals attempts at obtaining mixed oxides starting from glyoxylates (glyoxylic acid $\text{HC(OH)}_2\text{COOH}$),⁵³ glycolates^{114,115} (glycolic acid $\text{CH}_2(\text{OH})\text{-COOH}$), and malonates²⁹ (malonic acid ($\text{HOOC-CH}_2\text{COOH}$)).

The thermal decompositions of gluconates and citrates (gluconic [$\text{HOOC-(CHOH)}_4\text{-CH}_2\text{OH}$] and citric [$\text{HOOC-C(OH)(COOH)-CH}_2\text{-COOH}$] acids) represents a special route in the synthesis of oxides, the so-called "combustion route". Once initiated (at temperatures $<250^\circ\text{C}$), the reaction is quickly propagated, the organic skeleton is destroyed with evolving of a large amount of gases (specially H_2O and CO_2). The isolation of decomposition intermediates for these decomposition reactions is possible only in few cases.^{49,50}

From gluconate complexes a large variety of mixed oxides were obtained: ferrites (cubic³⁰ and hexagonal,^{8,105} chromite,²⁸ perovskite,^{6,8,9,111} garnets.^{6,112}

The synthesis of oxides through thermal decomposition of citrates precursors can be considered interesting for its simplicity, low cost chemicals, reproducibility and easy scale-up. Temperatures of $500\text{-}600^\circ\text{C}$ are sufficient for the pyrolysis of precursors in synthesis ferrites, while $700\text{-}1000^\circ\text{C}$ are necessary for garnets and aluminates. Thus, a large number of ferrites (cubic^{36,37,116-120} and hexagonal^{49,121,122}), aluminates,^{123,124} garnets¹²⁵ and perovskites^{107,1126,127} were obtained. The applied thermal treatment³⁶ and the amount of organic ligand has an effect on the crystal structure and morphology of the oxide particles.¹²³

Another class of complexes precursors of oxides are complexes with nitrogen containing ligands which were used in the self-propagated synthesis reaction of very fine, crystalline unagglomerated oxides (single and mixed). This method uses an exothermic, redox reaction, usually very rapid and self-sustained. The key feature is that the heat required to drive the chemical reactions is provided by the reaction itself and not by an external source. A first group of precursors compounds is represented by hydrazine (N_2H_4) and its derivative complexes such as hydrazine carboxylate ($\text{N}_2\text{H}_3\text{COO}^-$).¹²⁸ Hydrazine complexes have low ignition temperature ($<300^\circ\text{C}$) and once ignited decompose autocatalytically to yield fine particles oxides. This low temperature decomposition has been attributed to the endothermic nature of the N-N bond, which releases an enormous amount of heat energy during its thermal cleavage. This energy is in fact responsible for the decomposition of other parts of the complex to simple¹²⁸⁻¹³⁴ and mixed metal oxides (ferrites and cobaltite).¹³⁴⁻¹³⁸ A disadvantage of such compounds is the high instability of metal hydrazines, which could be partially controlled through replacement of the oxidizing anions (nitrate and perchlorate) in the complex by the reducing groups such as formate, acetate and oxalate. Noteworthy are hydrazine carboxylate

precursors too. These complexes also have low ignition temperatures (120-300°C) and decompose autocatalytically with evolution of a large amount of gases (NH₃, H₂O, CO₂) which help to dissipate the heat, thereby preventing the oxide sintering. Simple metal oxides such as γ -Fe₂O₃,¹³⁹ mixed oxides such as ferrites,^{137,140,141} cobaltites¹⁴² and manganites¹⁴³ with specific area values in the range 4-140 m²/g and narrow size distribution (average agglomerate particle sizes range 0.5-5 μ m) have been obtained. The synthesis method has some limitations. Firstly, it takes days to prepare metal hydrazine carboxylate precursors. Secondly, not all metals form complexes and therefore it was not possible to prepare oxides such as aluminates and chromites. Another group of coordination compounds precursors consists of compounds with urea as ligand and NO₃⁻ the as other sphere ion. Simple oxides¹⁴⁴⁻¹⁴⁶ and mixed oxides such as cubic^{147,148} and hexagonal¹⁴⁹ ferrites and perovskites¹²⁷ were obtained using the thermal decomposition of urea containing precursors. The presence of an amino acid ligand and in other sphere of NO₃²⁻ leads also to a self-propagated decomposition. The first representative of this class, glycine, (aminoacetic acid, NH₂CH₂COOH) was used with success in synthesising nanosized ferrites.^{150,151}

The difference between the carboxylate (citrate or gluconate) and nitrogen ligand combustion route is the nature of the auto-ignition (combustion) of the precursors. In the first route the auto-ignition is gentle, having tiny glowing flints propagating within the compound until the reactions completes. Instead, in the nitrogen ligand route, due to the strong exothermic redox reaction, the precursors turns to a vigorous fire, which lasts until the combustion process completes. For the last class of compounds the ratio oxidand/reductant plays a crucial role in avoiding sintering (through generation of high temperatures).

Finally we have to mention, the cyano complexes. Their thermal decomposition was used to a lesser extent, in order to obtain some cobalt perovskites.¹⁵²⁻¹⁵⁴

2. Sulfides synthesis

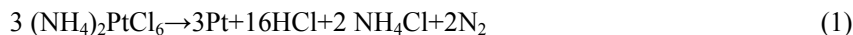
Recently there has been substantial interest in the preparation and characterization of nanocrystalline materials of chalcogenide, specially sulfide.^{155,156} As a promising method for the preparation of nanocrystallites of sulfides, the decomposition of complex precursors containing metal-sulfur would be regarded as an efficient synthetic route.¹⁵⁷ Some examples are given in the following.

- Decomposition of thiourea and its derivate complexes:
 - ZnS obtained from the thermal decomposition of Zn(tu)₂Cl₂¹⁵⁷ (tu=thiourea);
 - NiS, CoS and FeS obtained through the thermal decomposition of N,N-diethyl-N'-benzoylthiourea¹⁵⁸ under dynamic nitrogen atmosphere.
- Decomposition of thiocyanate complexes: MgS was obtained by decomposition of Mg(SCN)₂(Py)₃·2H₂O (Py=pyridine) at 625°C.¹⁵⁹
- Decomposition of thiocarbamate and its derivatives:
 - MnS produced from the thermal decomposition of manganese pyrrolidinethiocarbamate in nitrogen atmosphere at 700°C;¹⁶⁰
 - CdS through the thermal decomposition of dialkyldithiocarbamate (Cd(S₂CNR₂)₂ where R=C₂H₅, *n*-C₃H₇, *n*-C₄H₉ and *i*-C₄H₉) in nitrogen atmosphere;¹⁶¹
 - Ba and M=Co²⁺ and Ni²⁺ sulfide from the thermal decomposition of mixed ligand complexes Ba[M(ox)₄glydte] where *Hox*=8-hydroxyquinoline and *glydte*=glycinyldithiocarbamate.¹⁶²
- Decomposition of thiohydrazide and thioamides complexes: SnS₂ was produced from the thermal decomposition of tribenzyl tin(IV) complexes with thiohydrazides and thiodiamides in nitrogen atmosphere at 700°C.¹⁶³
- Mixed sulfide CuMS₂ where M=Mn(II), Co(II), Ni(II) and Zn(II) are obtained as intermediates during the thermal decomposition of [CuML(CH₃COO)₃] heteropolynuclear coordination compounds with *LH*= 2-amino-5-mercapto-1,3,4-thiadiazole (C₂H₂N₃S₂) in air. The sulfide intermediate is stable on a range of 30-40°C and consequently can be isolated.¹⁶⁴

3. Metal synthesis

The thermal degradation of diammoniumhexachloroplatinate (NH₄)₂PtCl₆¹⁶⁵ is used on a technical scale for production of pure platinum metal.

One of the first reports on this topic was given by Wöhler who translated a manuscript of Berzelius,¹⁶⁶ where platinum, HCl, NH₄Cl and H₂O were found as thermal degradation products. When inert atmosphere is used, the following degradation mechanism was advanced.¹⁶⁷



Formation of NH₄·HCl as well as inconsistencies within the quantification of the degradation products was later reported.^{168,169}

A mechanism for the degradation in reducing atmosphere (hydrogen) was also proposed.¹⁷⁰



Recent investigation has confirmed the degradation processes reported more than one century ago. Nevertheless, in inert atmosphere minor degradation pathway leading to the evolution of volatile platinum species was detected.¹⁷¹ Another compound from which Pt depositions are obtained (500°C in inert atmosphere) is diethyldithiocarbamate, Pt((C₂H₅)₂NCS₂)₂.¹⁷²

Hydrazine containing complexes were also used in the synthesis of various metals.^{173,174}

Also Bi and Sb were obtained (~560°C) from the thermal decomposition of some hexamethylenetetramine complexes.¹⁷⁵

4. Nitrides synthesis

Nanocrystalline uniform CrN particles with an average size of 7 nm can be obtained by reaction for 1 h at 600°C from Cr[OC(NH₂)₂]₆Cl₃ in NH₃ atmosphere.¹⁷⁶ As a possible mechanism, CrN particles may form by nucleation and growth processes, *via* intermediate solid compounds, CrCl₃·xNH₃ and or (ClCrCrNH)_n.

5. Composite materials synthesis

The thermal decomposition of carboxylic complexes with double and aromatic carbon-carbon bonds (like maleates and *ortho/tere* phthalates,¹⁷⁷ acrylates¹⁷⁸) in inert atmosphere may lead to the synthesis of ‘metal-polymer’ composites with most diversified properties. It is possible to synthesize ultra dispersed particle and simultaneously chemically passivate them by *in situ* formation of polymer matrix during the thermal decomposition of metal containing monomers.

The decomposition of the coordination compounds occurs *via* three main processes: dehydration, solid state polymerization (with formation of a polymeric matrix) of the initial ligand which may be considered as monomer, decarboxylation of metallocarboxylate groups in metal polymer followed by formation of metal or metal-oxide ultra dispersed particles. A catalytic polymerization on the surface of metal is not excluded.¹⁷⁷ Possible reactions are:



The formation of metal nuclei, their growth according to complex topochemical laws, merging of metal particles and simultaneous outgrowth of polymer layer on them, leads, as is possible to assume, to spherical form of metal-polymer conglomerates.

6. New complexes synthesis

Some thermal reactions are used allowing the preparation of complexes which cannot be synthesized in aqueous solutions.

As example we mention the preparation of the Cr(en)₂Y₂]Y type complex through the reaction:^{179,180}



Another example of the pyrolytic synthesis method is the synthesis of monodiamine species with squarate anion MLC₄O₄ (M=Cd²⁺ and Ni²⁺, L= N-methylethane-1,2-diamine, N-ethylethane-1,2-diamine, N-propylethane-1,2-diamine, propane-1,2-diamine, N-methylpropane-1,2-diamine).¹⁸¹⁻¹⁸³

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