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COPPER–IRON OXIDES OBTAINED BY THERMAL DECOMPOSITION OF OXALIC COORDINATION COMPOUNDS

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Abstract

The influence of the coordination architecture (materialized by ligand binding mode and content) on the thermal behaviour of coordination compounds containing copper, iron and oxalic anion as ligand was investigated. It was established that the metal–metal connections influence stronger, comparative with ligand content, the stoichiometry of the thermal decompositions.

Keywords: copper ferrite precursor, copper–iron oxalate coordination compound

Introduction

The oxalate precursors thermal decomposition represents an efficient method of various mixed oxides synthesis [1–11]. The use of oxalate species, obtained through different chemical routes (coprecipitation, molten salt synthesis, complexation and sol–gel methods) as precursors in the synthesis of mixed oxides presents some important advantages related to the synthesis reproductibility (a quantitative precipitation due to their water insolubility), accessibility (raw materials with moderate cost), nanosized nature of oxide products (relatively low decomposition temperature with of large amount of gases evolving [12]) and diversity of metallic ions combination ratios (the oxalic anion may form bridged bonds between two metallic ions, binding mode able to generate compounds with polymeric structure in which isomorphic substitutions are possible).

It is known that the nature of the precursor influence the characteristics of the final oxides. On the other hand the thermal decomposition process may be seen as the link between the precursor and final product. So, thermal studies of different precur-

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sors provide besides primary information regarding the temperature range of oxide formation, valuable knowledge concerning the conversion route.

Polynuclear coordination compounds may represent an adaptable synthetic way of obtaining mixed oxides, due to the possibility of changing their molecular architecture by proper synthesis method.

The present paper presents the thermal behaviour of three polynuclear coordination compounds, $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**), $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**II**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**III**), precursors of copper ferrite, which differ among them through ligand content, binding mode and metal–metal connections.

Experimental

For coordination compound synthesis two synthesis methods were utilized, namely precipitative and a hydrolytic decomposition one. All chemicals were of reagent quality. As starting materials in the first synthesis variant, $Fe(NO_3)_2\cdot 9H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$ were used. In the second one, $FeC_2O_4\cdot 2H_2O$ and $Cu(CH_3COO_3)_2\cdot H_2O$ were employed.

Precipitation method: to an aqueous solution that contains the metallic ions, an oxalic acid solution was added in order to obtain the following ratios Fe^{3+}:Cu^{2+}:$nC_2O_4^{2-}$=2:1:2/ or 10. For a complete precipitation (pH~4.5–6) a solution of NH_4OH:H_2O (1:1) was carefully added. The precipitates were filtered, washed with water (or ethanol) and dried on P_4O_{10}.

Hydrolytic decomposition: the aqueous solution containing the starting materials was maintained at ~80°C a period of 4 h. The precipitate was filtered, washed with ethanol and dried on P_4O_{10}.

Elemental analysis: the metal content was determined by the atomic absorption spectrophotometry, C, H and N by microcombustion techniques.

IR spectra (400–4000 cm^{-1}) were recorded with a BIO-RAD FTIR 125 type spectrophotometer in KBr pellets.

The magnetization curves of the encapsulated polynuclear compounds samples were measured as function of temperature at decreasing applied field from 5T using a SQUID magnetometer (MPMS-5S, Quantum Design). The magnetic susceptibilities of the oxides were determined at room temperature using a Faraday balance, with Ni as calibrant.

Thermal measurements: the decomposition curves (TG, DTG, DTA) have been recorded in the temperature range 25–500°C by a Q-1500 Paulik–Paulik–Erdey derivatograph in a static air atmosphere, at heating rates of 2.5–10 K min^{-1} with sample mass about 20 mg. As inert reference material α-Al_2O_3 was used.

About the polynuclear coordination compounds

The pattern of three coordination compounds $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$(**I**), $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**II**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**III**) were obtained by two different synthesis strategies, respective a precipitative [13] compounds (**I**) and (**II**), and a hydrolytic decomposition one [14] compound (**III**). The principal characteristics of the synthesized compounds are summarized in Table 1.

Table 1 Principal characteristics of the three coordination compounds

Coordination compound	Synthesis method	$C_2O_4^{2-}$ binding mode	μ_{exp}*/ M. B.	Fe^{3+}–Fe^{3+} connection
$(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**)	precipitation	tetradentate bridges chelate	7.47	$C_2O_4^{2-}$ bridges
$[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**II**)	precipitation	chelate	4.84	HO^- bridges
$[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**III**)	hydrolytic decomposition	tetradentate bridges	6.33	$C_2O_4^{2-}$ bridges

*$\mu_{theoretic}$ = 8.51 M. B. (by summing the magnetic moments of the paramagnetic metallic ions)

Two very important features are worthy to be mentioned here. Firstly, the differences in $C_2O_4^{2-}$ binding mode and secondly the unusual small magnetic moment of the compound **II**.

The IR spectra of carboxylate complex compounds are usually dominated by two strong bands in 1650–1550 and 1400–1300 cm^{-1} range, arising from the C–O stretching vibrations (ν_{asym} and ν_{sym}). On the basis of spectroscopic criteria, function of the value of the magnitude of separation $\Delta\nu$ ($\Delta\nu=\nu_{asym}-\nu_{sym}$), [15] the binding mode of the group may be evaluated (Fig. 1).

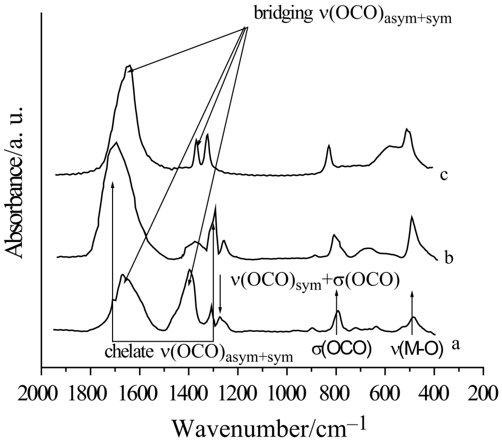

Fig. 1 IR spectra of the three coordination compounds; a – $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**); b – $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (precipitative metod) (**II**); c – $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (hydrolytic decomposition) (**III**)

From the magnetic point of the compounds are paramagnetic. While for compounds (**I**) and (**III**) the magnetic moment values are closed with the theoretical one, the unexpected small value obtained for compound (**II**) could be understood only if the coordination compound exists in a dimer structure:

Fe–Fe–Cu–Cu–Fe–Fe

where the bulk unit (with smaller font sizes) is diamagnetic and iron ions are bonded via HO^- groups. The susceptibility's variation with temperature supports this assumption [13].

Thermal decomposition investigations

Figures 2–4 present comparative the registered TG, DTG and DTA curves of the three coordination compounds. Table 2 summarized the thermoanalytical data obtained for the compounds at a heating rate of 2.5°C min^{-1}.

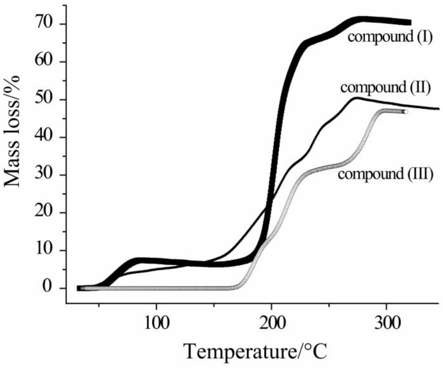

Fig. 2 TG curves of the three coordination compounds: $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**), $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (precipitative method) (**II**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (hydrolytic decomposition) (**III**)

The thermal decomposition of the first compound $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$, starts with an endothermic evolving of $0.5(NH_4)_2C_2O_4$ molecule. A small mass gain occurs in the following temperature range (97.5–166.1°C), due probably to the reversibility in a certain extent of the first reaction. On further heating, besides the evolving of the rest of $(NH_4)_2C_2O_4$, the thermal degradation of three oxalate anions occurs. The occurrence of two different processes is evidenced by the two maxima of the DTA curve. The last $C_2O_4^{2-}$ is decomposed in the temperature range 239.5–285.4°C. The subsequent process consists in a mass gain assigned to metallic ions oxidation. The values of the mass variations registered for the last two reaction steps are heating rate dependent, their magnitudes increasing with heating rate decreasing. This finding may be explained as follows: during the oxalate degradation, a reducing reaction atmosphere is formed due to the presence of CO. In these conditions, Fe^{3+} ions are par-

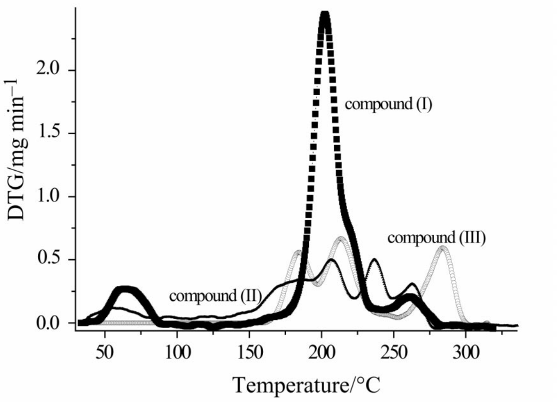

Fig. 3 DTG curves of the three coordination compounds: $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**), $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (precipitative method) (**II**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (hydrolytic decomposition) (**III**)

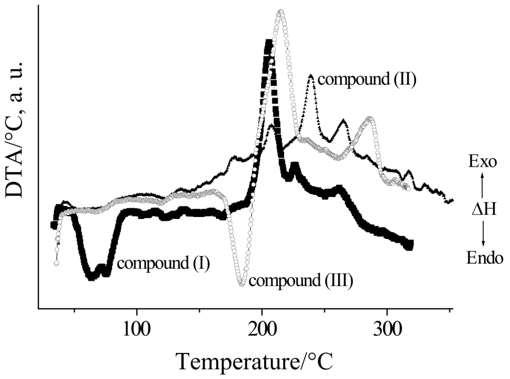

Fig. 4 DTA curves of the three coordination compounds: $(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**), $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (precipitative method) (**II**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (hydrolytic decomposition) (**III**)

tially reduced to Fe^{2+}. The reduction is more pronounced at low heating rates, owing to the smaller diffusion rate of the reaction gaseous products.

The thermal curves of the $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**II**) compound reveal six decomposition steps. A first endothermic process (39.4–135.2°C) is associated with the breakdown of the dimer structure due to the evolving of two water molecules. The next four processes characterized by relatively small exothermic effects (comparative to the other two compounds) may be attributed to a multistep oxalate degradation came together with gradual dehydration processes. At temperatures higher than 274.5°C a continuous oxidation of the metallic ions takes place. As in the case of the first compound, the mass variations of the last two processes are heating rate dependent.

The thermal decomposition of the third compound, $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**III**), begins with a strong endotherm process (158.6–196.1°C), assigned the evolv-

Table 2 Thermoanalytical data of the three coordination compounds (heating rate 2.5°C min^{-1})

Compound	Reaction step	T_I–T_f/°C	T_{min}/°C	$T_{min/max}$/°C	Mass loss/%	Assignation
$(NH_4)_4[Fe_2Cu(C_2O_4)_6]$ (**I**)	1	39.7–97.5	63.4	64.0 76.7	7.11	–0.5$(NH_4)C_2O_4$
	2*	97.5–166.1	–	–	1.05	
	3	166.1–238.5	202.3	205.5 226.7	54.88	–1.5$(NH_4)C_2O_4$ 3$C_2O_4^{2-}$ degradation
	4	238.5–285.4	261.4	261.8	7.68	$C_2O_4^{2-}$ degradation
	5*	>285.5	–	–	0.80	metallic ions oxidation
$[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**II**)	1	39.4–135.2	54.9	56.7	6.86	–H_2O
	2	135.2–193.0	185.9	177.9	15.13	oxalate degradation and dehydration
	3	193.0–224.4	206.6	207.6	14.05	
	4	224.4–249.1	236.7	238.9	10.66	
	5	249.1–274.5	262.9	265.1	6.72	
	6*	>274.5	–	–	6.04	metallic ions oxidation
$[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 2H_2O$ (**III**)	1	158.6–196.1	184.5	184.6	121.32	–2H_2O
	2	196.1–250.2	213.9	215.2	19.77	$C_2O_4^{2-}$ degradation
	3	250.2–303.6	284.0	285.3	14.94	$C_2O_4^{2-}$ degradation
	4*	>303.6	–	–	0.28	metallic ions oxidation

*mass gain process

ing of the two water molecules. The high temperature range of this reaction step occurrence sustains the assumption that the water molecules are coordinated. The next two steps, assigned to $C_2O_4^{2-}$ degradation (196.1–250.2 and 250.2–303.6°C) are followed by a small oxidation process, in this case heating rate independent.

The values of the magnetic moments of the oxides obtained from compounds **II** and **III** are close with the theoretical one (16.60, 26.89 and 27.42 μB for **I**, **II** and **III**, respectively) [16]. The smaller one obtained for the oxides generated from compound I denote the presence of α-Fe_2O_3 as impurity into the final decomposition product.

Discussion

On the basis of nonisothermal analysis the following outcomes concerning the thermal degradation of the three coordination compounds may be pointed out:

– the thermal decompositions occur in the range ~40–500°C in 3–5 mass losses steps followed by a mass gain process;

– the first endothermic process may be attributed to the $(NH_4)_2C_2O_4$ (**I**) or water molecules (**II** and **III**) respectively, release. The different temperature ranges of reactions occurrence registered for compounds (**II**) and (**III**) may be attributed to the different structures of these compounds.

– the evolving coupled with degradation of the oxalate anion occurs in 2–4 steps, producing a reducing reaction environment which lead to a partial reducing of the metallic ions;

– at temperatures higher than 300°C, a mass gain process assigned to metallic ion oxidation occurs. Its values which varies in the following order

compound (**II**)>compound (**I**)>compound (**III**)

may constitute a criterion in estimation the reduction underwent by Fe^{3+} and probable Cu^{2+} during the decomposition processes. The special structure of compound (**II**) favors the reduction more than an increase of $C_2O_4^{2-}$ ligand content from two to six anions.

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