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THERMAL BEHAVIOUR OF SOME POLYHYDROCARBOXYLIC COORDINATION COMPOUNDS WITH NEODIUM

L. Patron, O. Carp, I. Mandru and G. Grasa*

Institute of Physical Chemistry, Splaiul Independentei, Nr. 202, sector 6, Bucharest, Romania

Abstract

New Nd–Co based polynuclear coordination compounds containing as ligand polyhydrocarboxylic acid as tartaric, malic and gluconic acids were prepared, namely: $[NdCo(tart)_3]\cdot 4H_2O$, $(NH_4)[NdCo_{0.5}Cu_{0.5}(tart)_3]\cdot 4H_2O$, $(NH_4)[NdCo(malic)_3]\cdot 4H_2O$, $(NH_4)[NdCo_{0.5}Cu_{0.5}(malic)_3]\cdot 4H_2O$, $[NdCo(gluc)_4]\cdot 4H_2O$ and $[Nd_2CoCu(gluc)_7]\cdot 5H_2O$. A comparison between the thermal behaviour of the studied polynuclear coordination compounds concerning thermal stability and thermal decomposition stoichiometry was inferred. Oxalic and malonic intermediates were identified at about 300°C in the thermal decomposition of tartaric and malic compounds. In all the decomposition processes at about 400°C the presence of oxocarbonate is shown. The residual products are mixed oxides of perovskite type.

Keywords: perovskite precursor, polynuclear coordination compounds, thermal analysis

Introduction

Perovskites type oxides ABO_3 (A^{3+}=Ln, and B^{3+}=Fe, Cr, Ni, Co, Mn) are known to be active catalysts for the gas-phase reactions (CO and hydrocarbon oxidation, NO_x reduction, hydrogenation of CO and hydrocarbons, controlled partial oxidation of hydrocarbons) [1–3]. Perovskites prepared by conventional ceramic and nitrate/acetate decomposition methods have rather small specific area ($\leq 10\ m^2\ g^{-1}$). As a consequence, new strategies were developed in order to obtain fine particles of mixed oxides. Among these, the thermal decomposition of polynuclear coordination compounds precursor method should be mentioned.

The present investigation deals with the thermal analysis of some polynuclear coordination compounds which contain as ligands tartaric, malic and gluconic acids, precursors of the perovskites $CoNdO_3$ and $Co_{0.5}Cu_{0.5}NdO_{2.5}$.

Experimental

The synthesis method of the polynuclear compounds represents a version of the one used by Melson and Pickering [4]. The polynuclear coordination compounds were separated from the reaction medium (a solution containing Co(II)-Nd(III)-

* Author to whom all correspondence should be addressed.

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Kluwer Academic Publishers, Dordrecht

polyhydrocarboxylic acid or Cu(II)-Co(II)-Nd(III)-polyhydrocarboxylic acid) by extraction with ethanol. Complete precipitation required 24 h, and was repeated after adjusting the pH to 5.5–6 by addition of a 20% NH_4OH solution. The separated fine-crystalline products were filtered, washed with ethanol and dried.

Elemental analysis: the metal content was determined by atomic adsorption technique, and the carbon and hydrogen content by using a combustion method coupled with chromatographic techniques.

Spectral measurements: the IR spectra of the polynuclear compounds were obtained by the KBr disc technique in the range 400–4000 cm^{-1} using a BIO-RAD FTIR 125 infrared spectrophotometer type.

Thermal measurements: the thermal decomposition curves have been recorded by a Q-1500 D Paulik-Paulik-Erdey derivatograph in a static air atmosphere, at heating rates in the range 2.5–5 K min^{-1}. The mass of sample was 50 mg.

Results and discussion

Characterization of the polynuclear coordination compounds

The isolated coordination compounds are characterized by the following molecular formula:

$[NdCo(tart)_3]\cdot 4H_2O$ and $(NH_4)[NdCo_{0.5}Cu_{0.5}(tart)_3]\cdot 4H_2O$ with tartaric acid;

$(NH_4)[NdCo(malic)_3]\cdot 4H_2O$ and $(NH_4)[NdCo_{0.5}Cu_{0.5}(malic)_3]\cdot 4H_2O$ with malic acid;

$[NdCo(gluc)_4]\cdot 4H_2O$ and $[Nd_2CoCu(gluc)_7]\cdot 5H_2O$ with gluconic acid.

The results of CHN analysis agree well with the theoretical content corresponding to the above formulae of the coordination compounds.

The IR spectra were used for the investigation of chemical bonding in the synthesized compounds. In order to obtain information about the polyhydrocarboxylic ion function the following absorption regions were analyzed:

a) 1700–1300 cm^{-1}, region which is characterized by the presence of the vibration mode of the carboxilic group. Bands were assigned to $\nu_{OCO\ asym}$ (~1600 cm^{-1}) and $\nu_{OCO\ sym}$ (1390 cm^{-1}). The characteristic bands for free –COOH are present only in the gluconic compounds spectra.

b) 1200–1000 cm^{-1} region is characteristic of the vibration frequency of OH group. The presence of a doublet at ~1100 cm^{-1} and respectively ~1070 cm^{-1} proved that C–OH groups are coordinated dissimilarly, namely to two different metallic ions.

Thermal behaviour of polynuclear coordination compounds

In the following paragraphs the thermal stabilities and behaviour of the compounds tested during heating in air (heating rate 5°C min^{-1}) are described on the basis of the thermal analysis and IR spectra of the intermediates.

Polynuclear coordination compounds with tartaric acid as ligand

Thermal decomposition data obtained for the two coordination compounds are listed in Table 1. It is worth mentioning that, the presence of copper ion in the coordination compound led to a decrease of the final decomposition temperature by approximately 80°C.

Table 1 Thermoanalytical data for the coordination compounds, $[NdCo(tart)_3]\cdot 4H_2O$ and $(NH_4)[NdCo_{0.5}Cu_{0.5}(tart)_3]\cdot 4H_2O$

T_i–T_f/°C	T_{max} (DTG)/°C	Mass loss/%	Thermal effect	Suggested intermediates
		$[NdCo(tart)_3]\cdot 4H_2O$		
93–180	107	10.34	weak endo	$[NdCo(tart)_3]$
207–316	280	4.32	weak exo	$[NdCo(ox)_3]$
316–383	326	22.24	strong exo	$NdCo(Co_3)_3O$
383–530	452	6.02	medium exo	$NdCo(CO_3)_{0.5}O_{2.5}$
570–680	641	2.95	medium exo	$NdCoO_3$
		Total: 65.96		
		$(NH_4)[NdCo_{0.5}Cu_{0.5}(tart)_3]\cdot 4H_2O$		
90–179	108	9.17	weak endo	$[NdCo_{0.5}Cu_{0.5}(tart)_3]$
179–250	228	15.03	weak exo	$[NdCo_{0.5}Cu_{0.5}(tart)(ox)_2]$
250–322		10.93	medium exo	$[NdCo_{0.5}Cu_{0.5}(ox)_3]$
322–343		1.56	strong exo	
343–470	399	21.42	strong exo	$NdCo_{0.5}Cu_{0.5}(CO_3)_{1.5}O$
470–608		8.78	weak exo	$NdCo_{0.5}Cu_{0.5}O_{2.5}$
		Total: 66.64		

The prepared compounds are thermally stable up to 90–95°C. Due to the gradual heating the compounds lose water and ammonia in a single endothermic step up to 180°C. The following one/two decomposition steps correspond to the transformation of tartaric anions to oxalate ones. The intermediates obtained are unstable, being converted to oxocarbonates. Such oxocarbonate intermediates have already been reported in the thermal decomposition of polynuclear coordination compounds which contain tartaric acid as ligands [5, 6]. These intermediates undergo a further decomposition (two or one steps) into oxocarbonates with lower content of carbonate anion. The final stage of the thermal decomposition is the total transformation of oxocarbonates intermediates.

Besides the stoichiometric calculations based on the thermoanalytical curves, the above mechanism was confirmed by IR investigations of the intermediates. The disappearance with increasing temperature of the bands characteristic for the presence

of tartaric ligands, assigned to ν_{C-OH} (1120 and 1050 cm^{-1}) and ν_{C-H} (900 cm^{-1}) and the conservation until ~300°C of the bands specific for carboxylic anion, indicate the formation of oxalic anion. The appearance at higher temperature of the absorption bands assigned to CO_3^{2-} vibrations (1420–1410 cm^{-1} and 820–810 cm^{-1}) and the increasing intensities of the bands assigned to the metal–oxygen bond proved the proposed reaction stoichiometry.

Polynuclear coordination compounds with malic acid as ligand

Table 2 summarizes the thermogravimetric data for the two synthesized coordination compounds. It is worth emphasising that the presence of copper ions affects only the reactions stoichiometry with no influence on the temperature range of decomposition occurrence.

Table 2 Thermoanalytical data for the coordination compounds, $(NH_4)[NdCo(malic)_3]\cdot 4H_2O$ and $(NH_4)[NdCo_{0.5}Cu_{0.5}(malic)_3]\cdot 4H_2O$

T_i–T_f/°C	T_{max} (DTG)/°C	Mass loss/%	Thermal effect	Suggested intermediates
		$(NH_4)[NdCo(malic)_3]\ 4H_2O$		
90–192	110	13.39	weak endo	$[NdCo(malic)_3]$
192–300	265	15.49	weak exo	$[NdCo(malonic)_3]$
300–357	307	19.04	strong exo	$NdCo(CO_3)$
357–560		11.9	weak exo	$NdCo(CO_3)_{0.33}O_{2.66}$
560–660	588	2.38	weak exo	$NdCoO_3$
		Total: 61.87		
		$(NH_4)[NdCo_{0.5}Cu_{0.5}(malic)_3]\cdot 4H_2O$		
82–180	101	11.67	weak endo	$[NdCo_{0.5}Cu_{0.5}(malic)_3]$
216–275	253	14.38	weak exo	$[NdCo_{0.5}Cu_{0.5}(malonic)_3]$
275–328	299	12.72	strong exo	$[NdCo_{0.5}Cu_{0.5}(malonic)_2(CO_3)]$
328–520	438	20.75	strong exo	$[NdCo_{0.5}Cu_{0.5}(CO_3)_{1/2}O_2]$
550–658	547	3.38	weak exo	$NdCo_{0.5}Cu_{0.5}O_{2.5}$
		Total: 62.90		

The five-step decompositions start with the evolution of water and ammonia in an endothermic step. The following decomposition step may be assigned to the transformation of malic ions to malonic ones, which are subsequently converted, totally or partially, to carbonates compounds. These intermediates are turned into mixed oxides as final products via oxocarbonates intermediates. The presence of malonic intermediates during the thermal decomposition of malic compounds was mentioned in earlier studies [7].

The IR spectrum of the intermediates isolated at about 270°C exhibits two very strong bands assigned to carboxylate group at ~1400 cm^{-1} ($\nu_{OCO\ sym}$) and ~1570 cm^{-1} ($\nu_{OCO\ asym}$). The band at 1090 cm^{-1} assigned to the frequency ν_{C-OH} disappeared, which supports the reaction mechanism mentioned above. The IR spectrum of the reaction intermediate isolated at about 400°C exhibits some bands assigned to the carbonate group: a very strong band at ~1400 cm^{-1} which replaces the band assigned to the carboxylate groups, a strong band ~880 cm^{-1} (δ_{CO_3} out of plane) and a medium one at ~700 cm^{-1} (δ_{CO_3} in plane).

Polynuclear coordination compounds with gluconic acid

As shown in Table 3, the thermal decomposition of these compounds is similar. The presence of copper ions has no influence upon the temperature of occurrence of the multistep decomposition.

Table 3 Thermoanalytical data for the coordination compounds, $[NdCo(gluc)_4]\cdot 4H_2O$ and $[Nd_2CoCu(gluc)_7]\cdot 5H_2O$

T_i–T_f/°C	T_{max} (DTG)/°C	Mass loss/%	Thermal effect	Assignation
		$[NdCo(gluc)_4]\cdot 4H_2O$		
98–150	107	7.58	weak endo	dehydration
150–238	204	21.66	weak endo	internal dehydration release –COOH
238–282	262	16.68	medium exo	thermal degradation of
282–333		4.11	strong exo	the ligand molecules
333–561	379	28.38	strong exo	
600–641	618	1.29	weak exo	$NdCoO_3$
		Total: 74.39		
		$[Nd_2CoCu(gluc)_7]\cdot 5H_2O$		
102–170	111	5.1	endo	dehydration
170–283	201, 217	32.58	weak endo turns in weak exo	internal dehydration release COOH
283–348		16.59	strong exo	thermal degradation of the ligand molecules
348–650	386	16.39	strong exo	$NdCo_{0.5}Cu_{0.5}O_{2.5}$
		Total: 70.66		

It was not possible to establish a reaction stoichiometry for the whole decomposition process due to the complexity of the ligand molecule.

The release of water starts at about 100°C and is finished at about 150°C, four and five molecules of water respectively being released in one endothermic step. A sec-

ond endothermic reaction was isolated in the decomposition of $[NdCo(gluc)_4]\cdot 4H_2O$ compound, assigned to an internal dehydration and the release of free acid moiety –COOH. The second decomposition step of $[Nd_2CoCu(gluc)_7]\cdot 5H_2O$ compound is accompanied only in the beginning by an endothermic effect. The decomposition turns rapidly into an exothermic one, because of the thermal degradation of polyhydroxocarboxylic acid molecules. An oxocarbonate intermediate was isolated at about 500°C for the first coordination compound.

Characterization of the final products of the thermal decomposition

A thermal treatment performed at 700°C–5 h, leads to clean perovskite phase. Further studies will be made to correlate the precursors' nature with specific area. Preliminary investigations identified the optimal conditions for high specific area mixed oxides obtained from malic polynuclear coordination compounds as precursors.

Conclusions

1. The thermal behaviour of six polynuclear coordination compounds of Nd and Co with tartaric, malic and gluconic acid as ligands was investigated.

2. The decomposition process of the compounds with tartaric and malic acid led to oxalic and malonic compounds respectively in an intermediate stage.

3. In the thermal decomposition of the compounds with gluconic acid, an internal dehydration was identified.

4. At temperatures higher than 350°C oxocarbonates intermediates were isolated.

5. The end products are mixed oxides of perovskite type.

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