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THERMAL BEHAVIOR OF THE Ti(IV), Zr(IV) AND Pb(II) COMPLEXES WITH 5-NITRO-8-HYDROXYQUINOLINE

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Abstract

Ti(IV), Zr(IV) and Pb(II) complexes with 5-nitro-8-hydroxyquinoline (5-NQ) were obtained by precipitation in acetone/ammonium solution medium. The compounds $TiO(C_9H_5N_2O_3)_2 \cdot 0.5H_2O$, $ZrO(C_9H_5N_2O_3)_2 \cdot 2H_2O$ and $Pb(C_9H_5N_2O_3)_2$ were characterized by Elemental Analysis, X-ray Diffratometry and Infrared Absorption Spectrometry and their thermal behavior followed by TG/DTA. This present study intends to show the variations in the thermal behavior of the compounds and in the composition and/or structure of final oxide residues, in different atmospheres and heating rates.

Keywords: complexes, 5-nitro-8-hydroxyquinoline, TG/DTA, thermal behavior

Introduction

The preparation of ceramic oxides from the thermal decomposition of metallic complexes has been reported [1–5] as an alternative to the conventional process of the reaction in the solid state, since it allows changes in the experimental conditions which are temperature [6, 7], precipitation pH [8–10] and starting reactants [11, 12].

This work aims to determine the conditions of the preparation of Ti, Zr and Pb complexes with 5-nitro-8-hydroxyquinoline (5-NQ) so that we can characterize them, study their thermal behavior and, consequently, evaluate their viability to be applied as precursors to obtain mixed oxides.

Experimental

The chelant (5-NQ) was synthesized by nitration of 8-hydroxyquinoline [13]. Metallic cation solutions were prepared from titanium and zirconium oxides and plumb nitrate. The solutions were kept at pH next to zero to avoid the hydrolysis. The complexes were prepared by dissolving the excess of the ligand in acetone and by adding to it the metallic cation solutions. The precipitation was obtained at room temperature, with addition of ammonium hydroxide aqueous solution and the pH being checked by glass electrode attached to the system in order to identify the minimum and the maximum values of the precipitation as soon as the precipitation was complete. The compounds were filtered,

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washed in distilled water, dried for 24 h at 60°C and stored in a desiccator containing anhydrous calcium chloride [14].

The complexes were characterized through elemental analysis (N, C, H) by using CE Instruments equipment, EA 1110-CHNS-O model; by complexometry with EDTA to determine Ti and Zr, and by spectrometry of atomic absorption to determine Pb, by using Intralab (Varian) equipment, AA-1475 model. The coordination models were determined through infrared absorption spectroscopy, by using Nicolet FT 400 spectrophotometer. The complexes and the residues from the thermal decomposition were characterized by X-ray diffractometry, with HGZ/B diffractometer in a Bragg-Bretano assemblage and CuK$_\alpha$ radiation.

The thermal behavior was studied by simultaneous TG/DTA, from TA Instruments, SDT 2960 model, in a dynamic atmosphere of both synthetic air and of nitrogen and at different heating rates of 2.5, 5, 10 and 20°C min^{-1}.

Results and discussion

Table 1 contains the obtained values to determine the stoichiometry of the complexes, their color and the beginning and the end of the pH precipitation.

Table 1 Elemental analysis data

Complex	Elements/%				pH precipitation		Color
	M	N	C	H	initial	end	
Ti	10.37	12.06	47.32	2.56	1.5	6.0	yellow
Zr	17.30	10.91	41.35	3.37	2.1	6.0	green
Pb	35.12	9.45	36.89	1.87	4.3	7.5	yellow

It was observed that the results are close to the expected ones to the following stoichiometry: $TiO(C_9H_5N_2O_3)_2\cdot 0.5H_2O$, $ZrO(C_9H_5N_2O_3)_2\cdot 2H_2O$ and $Pb(C_9H_5N_2O_3)_2$.

Studies about thermal behavior allowed to confirm the stoichiometry proposed on the basis of data from elemental analysis and the quantification of metals, to set the thermal stability order as well as to verify the influence of the heating rate and atmosphere in the thermal decomposition of the complexes.

It was observed that the absorption spectrum of the Ti and Zr compounds present absorption bands at 500 cm^{-1}, which is attributed to the stretching vibrations of the M–N bond and it is strongly depending on the metallic ion in which the chelant is bonded [20]. At 821 and 739 cm^{-1}, the intense bands due to M–O and M–O–M were observed [21]. The absence of an intense band at 900–1000 cm^{-1} region indicate the non-occurence of Ti=O bond [21].

The absorption spectrum in infrared region of the Pb complex presents lower intensity bands at 428, 614 and 567 cm^{-1}, ascribed to see stretching models of the Pb–N and Pb–O bonds, respectively [20]. Around 1090 cm^{-1} it is observed the stretching of C–O bond, from Pb–O–C system [21].

TG/DTA curves, Figs 1a and 1b, respectively, indicate that the thermal behavior of Ti complex at 5 and 10°C min^{-1} in synthetic air atmosphere hasn't shown any change, but just a little displacement occurred when the temperature of the decomposition began to rise and when it reached its end.

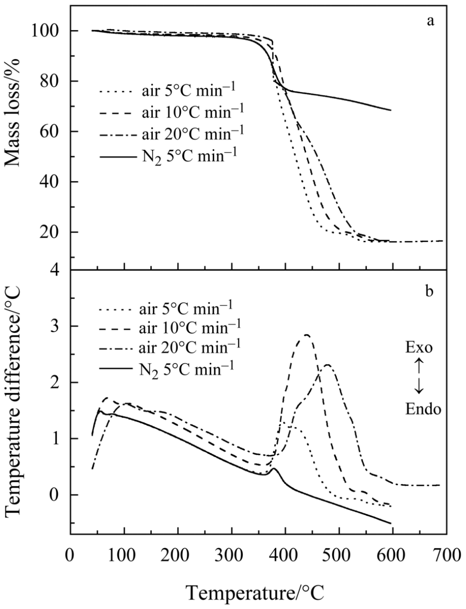

Fig. 1 a – TG and b – DTA curves of the Ti complex, obtained under different atmosphere and heating rate conditions

The first step of mass change is attributed to the dehydration of the complex, with loss of 0.5 water molecule. The second one is ascribed to the partial thermal decomposition of the anhydrous complex, with loss of nitro groups which was followed by the final decomposition of the ligand, producing carbonaceous material, eliminated at 575°C, and with the formation of titanium oxide as a final residue. It is observed that this step occurs in an abrupt form because the temperature of the decomposition rises very fast and, at the same time some energy is released when the loss of the nitro group takes place.

A better definition of the first step of the variation related to the mass with formation of the anhydrous complex can be observed in nitrogen atmosphere, although the thermal decomposition is incomplete up to the final temperature of analysis.

DTA curves present endothermic peaks to the dehydration and exothermic ones to the thermal decomposition steps of the anhydrous complex.

Zr complex presented similar thermal behavior to the Ti, with more defined steps of both dehydration and loss nitro groups, as observed in Fig. 2.

It is verified, however, that the change of mass, Fig. 2a, after the thermal decomposition of the complex, is characteristic depending on the heating rate. The final res-

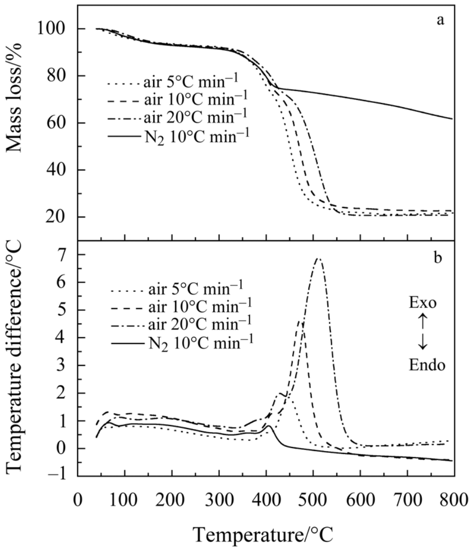

Fig. 2 a – TG and b – DTA curves of the Zr complex, obtained under different atmosphere and heating rate conditions

idue at 5 and 20°C min^{-1} corresponds to a mixture of oxides ZrO and ZrO_2, while at 10°C min^{-1} corresponds only to ZrO_2. These residues were characterized by X-ray diffratometry and indicated just the presence of ZrO_2, Fig. 3, with different structures. The oxide obtained at 10°C min^{-1} presents monoclinic structure [15] and at the other heating rates, 5 and 20°C min^{-1}, present cubic structure [16].

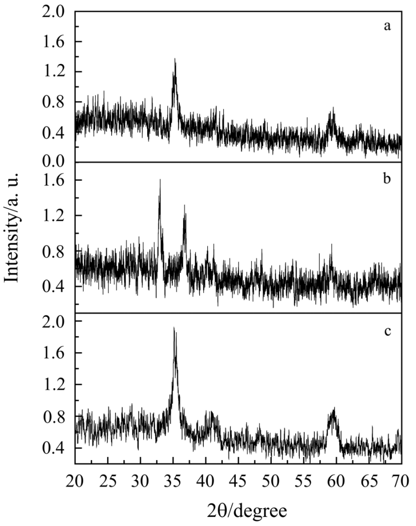

Fig. 3 XRD of the residues of the Zr complex, obtained under dynamic synthetic air atmosphere and heating rate of a – 5, b – 10 and c – 20°C min^{-1}

The residues obtained at 5 and 20°C min^{-1} heating rate s are formed by the oxidation of ZrO during the cooling period.

The thermal decomposition is also incomplete in N_2 atmosphere as it was in Ti complex.

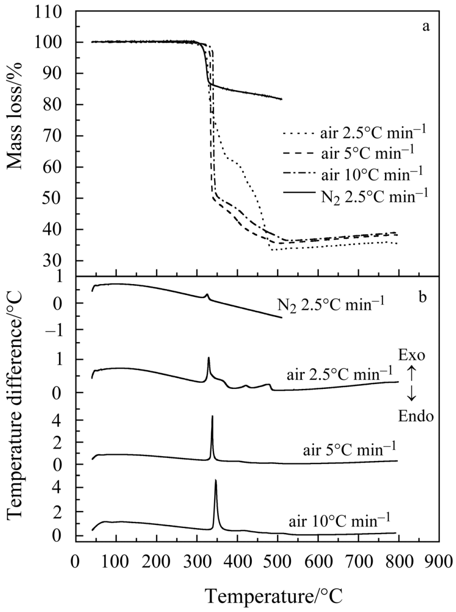

Fig. 4 a – TG and b – DTA curves of the Pb complex, obtained under different atmosphere and heating rate conditions

Pb complex presented changes during the steps of decomposition, as verified in TG/DTA curves, Figs 4a and 4b, respectively.

In N_2 atmosphere, the behavior is similar to the two anhydrous complexes of Ti and Zr. The first mass change is due to the loss of nitro group and the thermal decomposition shows itself incomplete up to the final temperature of analysis. In synthetic air and at 2.5°C min^{-1} heating rate, the first step of mass loss is similar to the observed one in N_2, with loss of nitro group. The following steps are similar to those presented by the Pb complex with 8-hydroxyquinoline [17, 18] and are attributed to the decomposition/oxidation of the remaining part of the chelant. A gain of mass after 490°C can be observed, which is ascribed to the oxidation of non-stoichiometry plumb oxide, (PbO_{1-x}) resulting from the thermal decomposition of the complex, without formation of metallic plumb. The final residue, PbO, was characterized by X-ray diffractometry.

To 5 and 10°C min^{-1}, the first step of abrupt mass loss is due to the elimination of nitro groups followed by a partial thermal decomposition of the ligand that occurs up to 350°C, producing carbonaceous material, which is eliminated at 520°C. A gain of mass related to the oxidation of the residue at 2.5°C min^{-1} could, also be noticed. The final residue was characterized as PbO by X-ray diffractometry.

Table 2 Thermogravimetry and differential thermal analysis data

Complex	Initial mass/ mg	β/ °C min^{-1}	TG			DTA	
			Δm/mg	T/°C	Residue/%	Endo/°C	Exo/°C
Ti	1.8546	5	–0.0386	45–102	97.92	69	
			–0.3764	277–400	77.62		395
			–1.0754	400–497	19.64		421
			–0.0636	498–561	16.21		535
	2.4535	10	–0.0527	44–111	97.85	93	
			–0.4964	290–404	77.62		
			–1.4264	404–515	19.48		439
			–0.0708	516–576	16.60		547
	1.3892	20	–0.0297	50–138	97.86	137	
			–0.2821	329–378	77.56		425
			–0.8055	378–427	19.57		480
			–0.0426	428–595	16.51		577
Zr	2.7640	5	–0.1911	45–156	93.09	66	
			–0.4878	287–411	75.44		399
			–1.4524	411–543	22.89		450
			–0.0205	543–636	22.14		534
	3.8228	10	–0.2647	46–194	93.08	84	
			–0.6739	293–424	75.45		416
			–1.9739	425–569	23.81		473
			–0.0202	569–671	23.28		642
	4.0521	20	–0.2806	46–223	93.08	121	384
			–0.7126	303–442	75.49		430
			–2.1635	442–605	22.09		512
Pb	1.1924	2.5	–0.1874	296–330	84.28		330
			–0.2615	330–387	62.35		359
			–0.3441	387–491	33.50		421
			0.0263	504–726	35.70		479
	1.2038	5	–0.5905	299–340	50.95		338
			–0.1854	340–502	35.55		403
			0.0323	510–759	38.23		492
	1.1280	10	–0.5551	306–349	50.79		347
			–0.1621	349–526	36.42		416–470
			0.0275	528–781	38.86		510

At 2.5°C $\min^{-1}$ it is verified a difference in the residue can be seen when compared to those obtained at 5 and 10°C $\min^{-1}$; this difference can be attributed to the partial volatilization of the complex after the loss of the nitro group. This thermal behavior occurs similarly to Pb complex with 8-hydroxyquinoline [17].

The volatilization was verified by the amount of metal in the final residue, through atomic absorption spectrometry: 30.6, 34.5 and 35% to 2.5, 5 and 10°C $\min^{-1}$, respectively. So, it can be observed that the lower the heating rate, the higher amount of metal loss (Table 1).

Table 2 contains both the variation of mass and of the temperature in TG and DTA curves of the complexes obtained at different heating rates.

According to the values observed in the Table 2, the increasing order of thermal stability at 5°C $\min^{-1}$ can be described this way:

$$TiO(C_9H_5N_2O_3)_2\cdot 0.5H_2O<ZrO(C_9H_5N_2O_3)_2\cdot 2H_2O<Pb(C_9H_5N_2O_3)_2$$

It is verified a decrease in the final temperature of thermal decomposition to Ti and Pb complex when compared with those obtained with 8-hydroxyquinoline as a ligand [17], which emphasizes the influence of the nitro groups in the structure. The mixed oxides formed from the thermal decomposition of the complexes with 5NQ can be obtained at lower temperatures.

A kinetic study of the thermal decomposition of the complexes by Kissinger method [19] using the peak temperatures observed in DTA curves at different heating rates was carried out with the objective to determine the Activation Energy, E_a, values.

Just the first step of the thermal decomposition of the anhydrous complexes was analyzed because their steps occur in a consecutive and/or simultaneous way making it difficult to determine the influence of one step over the other. The values of the E_a are indicated in Table 3.

Table 3 Results obtained from the graphics of $\ln(\beta/T_p^2)\times 1000/T$

Complex	T_p/K from DTA curves				b/K^{-1}	E_a/kJ mol^{-1}
	2.5°C $\min^{-1}$	5°C $\min^{-1}$	10°C $\min^{-1}$	20°C $\min^{-1}$		
Ti	–	611.55	618.45	626.95	–33.2500	276.44
Zr	–	568.05	572.65	579.65	–33.7500	280.60
Pb	602.85	611.45	618.85	–	–33.2500	276.44

It is possible to propose two considerations once E_a values are very close to each other:

1 – the elimination of nitro groups at the beginning of the thermal decomposition as described previously;

2 – nitro groups show the same influence in the complexes studied, indicating that they are coordinated in a similar way in their structures.

Conclusions

The complexes were prepared, characterized and studied regarding their thermal behavior with the objective to establish under which conditions they can be used as precursors to obtain ceramic oxides.

The precipitation pH, the coordination of the metals to the chelant, the crystallinity and the stoichiometry of the complexes were determined. The thermal behavior showed that different heating rates and different atmospheres affect the steps of the thermal decomposition as well as the formation of the final residues.

The thermal stability order was proposed to the complexes and the E_a=278 kJ mol^{-1} determined to the beginning of the thermal decomposition of the anhydrous complexes.

The released heat from the nitro groups could be responsible by the lower temperatures in which the formation of the ceramic oxide occurs.

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