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THERMAL BEHAVIOUR AND NON-ISOTHERMAL DECOMPOSITION KINETICS OF SOME Nd(III) COORDINATION COMPOUNDS

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Abstract

The authors present the results concerning the thermal behaviour of three polynuclear coordination compounds of Nd(III) and Co(II) or Fe(III) with triptophan. For the dehydration steps the values of the non-isothermal kinetic parameters have been determined.

Keywords: decomposition, kinetics, non-isothermal

Introduction

Following our research on the thermal behaviour and non-isothermal decomposition kinetics of rare earth coordination compounds yielding mixed oxides [1–5], we present in this paper the results concerning the thermal stability of three coordination compounds: $[CoNd(Trp)_4(OH)]\cdot 4H_2O$, $[FeNd(Trp)_2(OH)_4]\cdot 3H_2O$ and $[Fe_2Nd(Trp)_2(OH)_7]\cdot 3H_2O$ where Trp is the anion of triptophan.

Experimental

Powders of the following compounds: $[CoNd(Trp)_4(OH)]\cdot 4H_2O$, $[FeNd(Trp)_2(OH)_4]\cdot 3H_2O$ and $[Fe_2Nd(Trp)_2(OH)_7]\cdot 3H_2O$ where Trp is the triptophan anion were used. The coordination compounds were synthesized and analysed according to methods described elsewhere [6].

The thermal curves of the samples in air at atmospheric pressure were recorded from ambient temperature up to 1000°C by means of a Q-1500 type Paulik-Paulik-Erdey derivatograph (MOM, Budapest, Hungary) at various heating rates β between 2.3 and 10.8 K min^{-1}, with α-Al_2O_3 as inert reference compound.

The crystalline states of the powdered compounds were determined with a Philips PW 1140 X-ray diffractometer using CuK_{α} radiation. The crystallite

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mean sizes l were calculated for the most intense diffraction lines using Scherrer's formula [7].

The TG data were used in order to evaluate the decomposition non-isothermal kinetic parameters by three integral methods after Coats-Redfern [8], Flynn-Wall (for constant heating rate) [9] and Urbanovici-Segal [10] who modified the Coats-Redfern method.

For automatic processing of the data a program written in BASIC by Dragoe and Segal [11] were used. Besides the optimal values of the non-isothermal kinetic parameters, this program regenerates, by using the values obtained by means of the Coats-Redfern method, the TG curve in coordinates (α, T/°C), then the experimental points are placed on the same curve.

Taking into account that the procedures applied to evaluate the non-isothermal kinetic parameters are based on various approximations of the temperature integral [12], the correspondence between the regenerated (α, T/°C) curves and the experimental points indicates both the accuracy of the experimental measurements and the correctness of the description of the experimental data by these approximations.

Results and discussion

As shown by X-ray diffractograms, $[FeNd(Trp)_2(OH)_4]\cdot 3H_2O$ and $[Fe_2Nd(Trp)_2(OH)_7]\cdot 3H_2O$ exhibit a crystalline state while $[CoNd(Trp)_4(OH)]\cdot 4H_2O$ is an amorphous material. The interplanar distances d, relative intensities I/I_0 and mean crystallite sizes l for the most intense diffraction lines given by $[FeNd(Trp)_2(OH)_4]\cdot 3H_2O$ and $[Fe_2Nd(Trp)_2(OH)_7]\cdot 3H_2O$ are listed in Table 1.

Table 1 X-ray powder diffraction data for crystalline compounds

Compound	d/Å	I/I_0	l/Å
	9.30	15	
$[FeNd(tript)_2(OH)_4]\cdot 3H_2O$	6.30	75	
	5.25	100	140
	9.30	7	
$[Fe_2Nd(tript)_2(OH)_7]\cdot 3H_2O$	6.35	57	
	5.28	100	146
	4.82	7	

Thermal behaviour of $[CoNd(Trp)_4(OH)]\cdot 4H_2O$

The decomposition curves obtained for $[CoNd(Trp)_4(OH)]\cdot 4H_2O$ are shown in Fig. 1. According to the TG, DTG and DTA data obtained for β=8.3 K min^{-1} the first thermal decomposition step occurs through the reaction described by the following equation:

$$[\mathrm{CoNd(Trp)_4(OH)}]\cdot 4\mathrm{H_2O}(s) \xrightarrow{100^{\circ}\mathrm{C}} [\mathrm{CoNd(Trp)_4(OH)}](s) + 4\mathrm{H_2O}(g) \qquad (1)$$

The temperature written above the arrow corresponds to the maximum decomposition rate as shown by the DTG curve. After dehydration, a further temperature increase in the range 180–550°C leads to some overlapping exothermic reactions probably due to an oxidative degradation of the ligand. These are described by the overall reaction:

$$[\mathrm{CoNd(Trp)_4(OH)}](s) + \mathrm{O_2}(g) \xrightarrow{400^{\circ}\mathrm{C}} \mathrm{CoNdO_3}(s) + \text{gaseous products} \qquad (2)$$

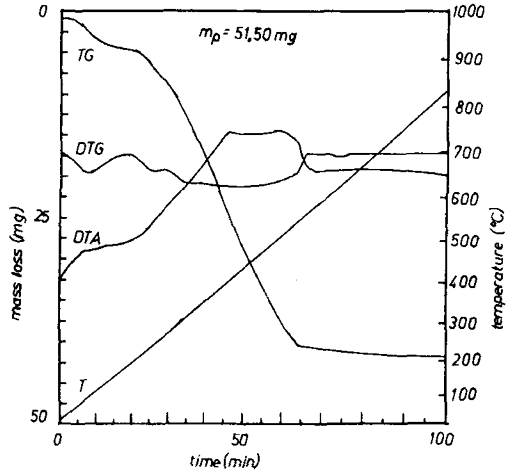

Fig. 1 TG, DTG and DTA curves of $[\mathrm{CoNd(Trp)_4(OH)}]\cdot 4\mathrm{H_2O}$ for $\beta = 8.3$ K min^{-1}. m_p is the weight of the powdered material before heating

Table 2 Values of non-isothermal kinetic parameters for the dehydration step of the investigated compounds

Reaction	Method	n	E/kJ mol^{-1}	A/s^{-1}	r*
	Coats-Redfern	1.8	57.8	$3.12\cdot 10^5$	–0.9987
(1)	Flynn-Wall	1.8	60.7	$1.20\cdot 10^6$	–0.9990
$\beta = 2.30$ K min^{-1}	Modified Coats-Redfern	1.8	59.3	$5.78\cdot 10^5$	–0.9980
	Coats-Redfern	1.8	60.4	$7.60\cdot 10^5$	–0.9983
(3)	Flynn-Wall	1.8	63.1	$2.67\cdot 10^6$	–0.9987
$\beta = 2.30$ K min^{-1}	Modified Coats-Redfern	1.8	61.2	$1.10\cdot 10^6$	–0.9984
	Coats-Redfern	1.8	62.2	$1.94\cdot 10^6$	–0.9989
(5)	Flynn-Wall	1.8	64.8	$6.18\cdot 10^6$	–0.9991
$\beta = 2.46$ K min^{-1}	Modified Coats-Redfern	1.8	63.0	$2.80\cdot 10^6$	–0.9990

*r is the correlation coefficient of the corresponding linear regression

The oxide product resulted from the decomposition was analysed by X-ray diffraction; the diffractogram of this oxide residue showed that the perovskitic phase has been obtain.

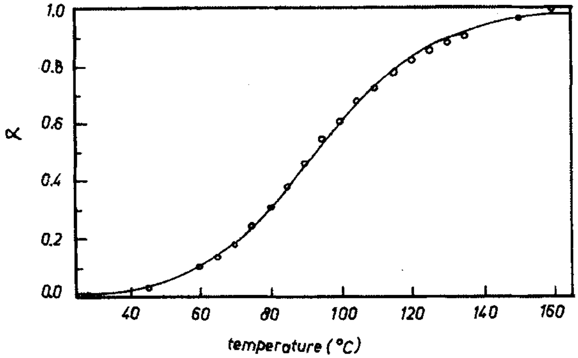

Fig. 2 Regenerated (α, T/°C) curve for reaction (1) at $\beta=2.30$ K $\min^{-1}$: (—) calculated curve; (o) experimental points

Only reaction (1) is kinetically workable, the values of the non-isothermal kinetic parameters, reaction order n, preexponential factor A and activation energy E for this reaction being listed in Table 2. Inspection of these results shows a quite satisfactory agreement among the non-isothermal kinetic parameter values obtained by means of the applied methods. The regenerated TG curve for reaction (1) and the corresponding experimental points are given Fig. 2. As seen in this figure, the experimental points lie practically on the curve.

Thermal behaviour of [FeNd(Trp)$_2$(OH)$_4$]·3H$_2$O

The TG, DTG and DTA curves recorded at a programmed heating rate of $\beta=10.6$ K $\min^{-1}$ allows to detect the following decomposition steps:

$$[\mathrm{FeNd(Trp)_2(OH)_4}]\cdot 3\mathrm{H_2O}(s) \xrightarrow{110^\circ\mathrm{C}} [\mathrm{FeNd(Trp)_2(OH)_4}](s) + 3\mathrm{H_2O}(g) \qquad (3)$$

$$[\mathrm{FeNd(Trp)_2(OH)_4}](s) + \mathrm{O_2}(g) \xrightarrow{380^\circ\mathrm{C}} \mathrm{FeNdO_3}(s) + \text{gaseousproducts} \qquad (4)$$

The values of the non-isothermal kinetic parameters for reaction (3) are listed in Table 2. These results show a quite satisfactory agreement among the non-isothermal kinetic parameter values obtained by means of the three methods applied.

The regenerated TG curves for reaction (3) in coordinates (α, T/°C) using the non-isothermal kinetic parameters obtained by means of the Coats-Redfern method are given in Fig. 3. As one can notice from the figure, the experimental points lie practically on the calculated curve, thus showing the reliability of the method applied to evaluate the non-isothermal kinetic parameters as well as of their determined values.

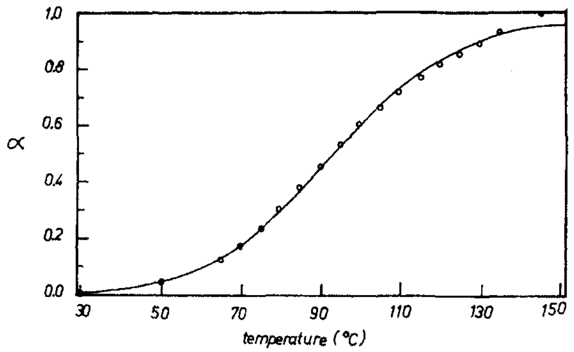

Fig. 3 Regenerated (α, T/°C) curve for reaction (3) at β=2.30 K min^{-1}: (—) calculated curve; (o) experimental points

Thermal behaviour of [$Fe_2Nd(Trp)_2(OH)_7$]$\cdot 3H_2O$

The thermal decomposition steps described by the following equations have been derived from the TG, DTG and DTA curves recorded at β=10.8 K min^{-1} in the temperature range 20–1000°C:

$$[Fe_2Nd(Trp)_2(OH)_7]\cdot 3H_2O(s) \xrightarrow{115^\circ C} [Fe_2Nd(Trp)_2(OH)_7](s) + 3H_2O(g) \quad (5)$$

$$[Fe_2Nd(Trp)_2(OH)_7](s) + O_2(g) \xrightarrow{375^\circ C}$$

$$[FeNdO_3(s) + 1/2Fe_2O_3(s) + \text{gaseous products} \quad (6)$$

Only reaction (5) proved to be kinetically workable. The values of the non-isothermal kinetic parameters for this reaction are also listed in Table 2. A satisfactory agreement among these values can be observed for this case too. The TG curve regenerated for reaction (5) in the coordinates (α, T/°C) is given in Fig. 4.

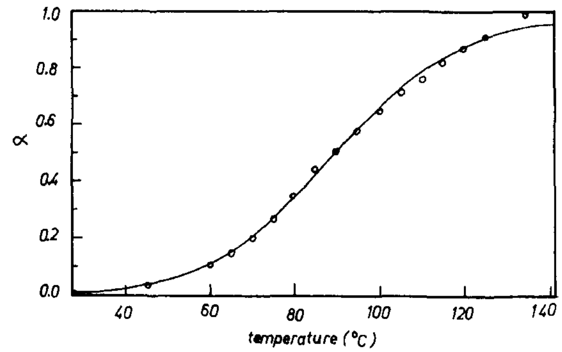

Fig. 4 Regenerated (α, T/°C) curve for reaction (5) at β=2.46 K min^{-1}: (—) calculated curve; (o) experimental points

The experimental points lie on the curve, thus indicating the validity of the applied method as well as the accuracy of the results.

The fractional and higher than unity value of the reaction order for reaction (5) as well as for reactions (1) and (3) can be assigned to the decomposition of structural units consisting of more than one molecule which coexist in variable ratios in the investigated system. Comparison between the results listed in Table 2 shows that the values of the non-isothermal kinetic parameters for the investigated reactions are very close, this fact suggesting a possible unique mechanism for all of them.

Conclusions

1. The thermal behaviour of three polynuclear coordination compounds of Nd(III) and Co(II) or Fe(III) with triptophan was investigated.
2. The decomposition process of these compounds led to a mixed oxide with perovskitic structure as residue.
3. The values of the non-isothermal kinetic parameters for the dehydration steps were determined.
4. The values of the non-isothermal kinetic parameters obtained by three integral methods are in satisfactory agreement.

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