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THERMAL STABILITY AND NON-ISOTHERMAL DECOMPOSITION KINETICS OF SOME COMPOUNDS OF LANTHANOIDS WITH CHROMIUM AND GLUCONIC ACID

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ABSTRACT

The results of an investigation concerning the thermal stability as well as the non-isothermal decomposition kinetic analysis of three solid compounds of lanthanoides with chromium and gluconic acid are presented.

INTRODUCTION

This paper deals with the thermal stability and non-isothermal decomposition kinetics of three compounds with the general formula $LnCrGluc_4 \cdot nH_2O$ where Ln is La, Pr or Nd, and Gluc is the gluconate ion.

EXPERIMENTAL

The compounds were synthesized according to a method described elsewhere [1]. The heating curves (TG, T, DTG, DTA) in static air atmosphere were recorded using a MOM Budapest derivatograph Q-1500 D type Paulik, Paulik, Erdey, at heating rates between 2.5 and 16 K min^{-1} in the temperature range 20–1500 °C. The X-ray diffractograms were recorded on a Philips PW 1400 diffractometer using Cr $K\alpha$ radiation.

For evaluation of the non-isothermal kinetic parameters, the Coats–Redfern [2] method and, in some cases, the Ozawa [3] method were applied. For

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automatic data processing the original programs were written [4] and run on a HC-85 PC.

RESULTS AND DISCUSSION

The X-ray diffractograms of all the powdered solid compounds used in this work indicated an amorphous state.

All the investigated compounds were initially synthesized with three molecules of water. During the time elapsed before the present investigation, more water was taken up and the initial composition of the compounds was: $LaCr(Gluc)_4 \cdot 7.5H_2O$, $PrCr(Gluc)_4 \cdot 9H_2O$ and $NdCr(Gluc)_4 \cdot 6H_2O$.

In the first decomposition step, all the compounds lost water according to the reactions

$$LaCr(Gluc)_4 \cdot 7.5H_2O(s) \xrightarrow{345\ K} LaCr(Gluc)_4(s) + 7.5H_2O(g) \quad (1)$$

$$PrCr(Gluc)_4 \cdot 9H_2O(s) \xrightarrow{342\ K} PrCr(Gluc)_4(s) + 9H_2O(g) \quad (2)$$

$$NdCr(Gluc)_4 \cdot 6H_2O(s) \xrightarrow{357\ K} NdCr(Gluc)_4(s) + 6H_2O(g) \quad (3)$$

The temperatures above the arrows correspond to the maximum dehydration rates at 2.5 K min^{-1}.

After dehydration, a further temperature increase in the range 150–370 °C leads to some overlapping exothermic reactions probably due to the oxidative degradation of the ligand. These are described by the overall reaction

$$LnCr(Gluc)_4(s) + O_2(g) \rightarrow LnCr(CO_3)_3(s) + CO_2(g) + H_2O(g) \quad (4)$$

The following three reactions occur at temperatures in the range 370–580 °C

$$LnCr(CO_3)_3(s) \rightarrow LnCrO(CO_3)_2(s) + CO_2(g) \quad (5)$$

$$LnCrO(CO_3)_2(s) \rightarrow LnCrO_2(CO_3)(s) + CO_2(g) \quad (6)$$

$$LnCrO_2(CO_3)(s) \rightarrow LnCrO_4(s) + CO(g) \quad (7)$$

The presence of $LnCrO_4$ was demonstrated by chemical gravimetric analysis as well as by X-ray diffractometric analysis.

At temperatures near 1000 K, the $LnCrO_4$ compounds undergo the following reactions

$$2LaCrO_4(s) \xrightarrow{1028\ K} 2LaCrO_3(s) + O_2(g) \quad (8)$$

$$2PrCrO_4(s) \xrightarrow{983\ K} 2PrCrO_3(s) + O_2(g) \quad (9)$$

$$2NdCrO_4 \xrightarrow{990\ K} 2NdCrO_3(s) + O_2(g) \quad (10)$$

For each of these three reactions, the temperature corresponding to the maximum decomposition rate has been recorded at 10 K min^{-1}.

TABLE 1

Non-isothermal kinetic parameters for reactions (1)–(3) evaluated using the Coats–Redfern method for various heating rates

	Heating rate (K min^{-1})	E (kcal mol^{-1})	n	A (s^{-1})	r [a]	T_{max} [b] (K)	k_{360} (s^{-1})
Reaction (1)	3.12	14.8	2.31	5.28×10^{6}	0.9992	345	4.91×10^{-3}
	4.92	18.6	1.97	2.23×10^{9}	0.9997	355	1.20×10^{-2}
	6.20	14.9	2.18	5.27×10^{6}	0.9993	359	4.69×10^{-3}
	7.40	14.9	1.94	5.74×10^{6}	0.9998	373	4.95×10^{-3}
	9.38	15.3	1.82	1.42×10^{7}	0.9978	362	7.10×10^{-3}
	9.62	18.6	2.30	1.41×10^{9}	0.9998	363	6.89×10^{-3}
	15.02	16.4	2.12	5.75×10^{7}	0.9995	374	5.53×10^{-3}
Average values		16.2	2.09	5.32×10^{8}			6.58×10^{-3}
Reaction (2)	3.37	14.2	2.22	2.51×10^{6}	0.9986	342	6.30×10^{-3}
	5.08	22.5	2.89	3.96×10^{11}	0.9989	349	8.06×10^{-3}
	6.25	14.8	2.21	5.18×10^{6}	0.9995	355	5.63×10^{-3}
	6.30	14.0	2.21	1.38×10^{6}	0.9999	368	3.89×10^{-3}
	8.54	18.0	2.20	2.20×10^{9}	0.9996	343	2.54×10^{-2}
	10.71	15.6	2.21	2.82×10^{7}	0.9995	363	9.11×10^{-3}
	15.62	12.6	1.59	1.26×10^{5}	0.9992	375	2.93×10^{-3}
Average values		16.0	2.21	5.69×10^{10}			8.76×10^{-3}
Reaction (3)	3.30	12.8	1.16	1.59×10^{5}	0.9998	357	2.66×10^{-3}
	4.80	20.8	2.31	1.84×10^{10}	0.9991	363	4.08×10^{-3}
	6.42	13.6	1.72	4.85×10^{5}	0.9999	370	2.67×10^{-3}
	6.38	13.1	1.79	2.69×10^{5}	0.9991	373	3.15×10^{-3}
	9.09	19.6	2.28	4.68×10^{9}	0.9994	371	5.63×10^{-3}
	14.63	12.5	1.97	2.11×10^{5}	0.9998	374	5.41×10^{-3}
Average values		15.4	1.95	3.85×10^{9}			3.88×10^{-3}

[a] r is the correlation coefficient of the linear regression.
[b] T_{max} is the temperature corresponding to the maximum decomposition rate.

TABLE 2

Non-isothermal kinetic parameters for reactions (8) and (9) evaluated using the Coats–Redfern method

Reaction number	Heating rate (K min^{-1})	E (kcal mol^{-1})	n	A (s^{-1})	r [a]	T_{max} [b] (K)	k_{1000} (s^{-1})
8	10.2	178	1.88	8.82×10^{35}	0.9951	1036	9.02×10^{-4}
9	5.08	219	1.98	3.56×10^{46}	0.9995	983	4.72×10^{-2}

[a] r is the correlation coefficient of the linear regression.
[b] T_{max} is the temperature corresponding to the maximum decomposition rate.

TABLE 3

Non-isothermal kinetic parameters for reaction (10) evaluated using the Coats–Redfern method for various heating rates

	Heating rate (K min^{-1})	E (kcal mol^{-1})	n	A (s^{-1})	r [a]	T_{max} [b] (K)	k_{1000} (s^{-1})
	4.80	188	2.18	1.62×10^{39}	0.9974	992	1.53×10^{-2}
	9.06	199	2.80	1.23×10^{42}	0.9993	982	4.63×10^{-2}
	9.80	153	1.90	4.86×10^{31}	0.9975	988	1.78×10^{-2}
Average values		180	2.29	7.12×10^{45}			2.65×10^{-2}

[a] r is the correlation coefficient of the linear regression.
[b] T_{max} is the temperature corresponding to the maximum decomposition rate.

Of the above reactions, only (1), (2), (3) and (8), (9), (10) are kinetically viable: the values of their non-isothermal kinetic parameters are given in Tables 1–4.

Although the values of the pre-exponential coefficient, A, and the activation energy, E, change with the heating rate, the rate constant evaluated at the same temperature (360 K) is fairly constant thus indicating a compensation effect. The lack of influence of the heating rate on the values of the rate constant shows that the reactions are not limited by heat transfer. These considerations are valid for reactions (1), (3) and (4). The closeness of the average values of the non-isothermal kinetic parameters for these three reactions is noticeable.

TABLE 4

Non-isothermal kinetic parameters for reactions (1), (2) and (3) calculated using Ozawa's method

Degree of conversion	Reaction number					
	1		2		3	
	E (kcal mol^{-1})	r	E (kcal mol^{-1})	r	E (kcal mol^{-1})	r
0.2	15.1	0.9848	–		18.8	0.8592
0.3	15.6	0.9902	11.9	0.9854	18.2	0.8759
0.4	16.5	0.9993	14.4	0.9948	19.4	0.9244
0.5	17.8	0.9996	14.8	0.9956	18.9	0.9331
0.6	18.5	0.9967	14.8	0.9944	19.2	0.9650
0.7	19.9	0.9964	15.6	0.9936	18.6	0.9795
0.8	22.1	0.9932	17.3	0.9917	17.2	0.9900
Average values	17.9		17.8		18.6	

For the activation energy values obtained using Ozawa's method, there is a quite satisfactory agreement with those values calculated according to the Coats–Redfern method for reactions (1) and (2). The Ozawa-method value of the activation energy for reaction (3) is considerably higher than the corresponding value calculated by the Coats–Redfern method.

Fairly high values for the pre-exponential factors and activation energies of reactions (8), (9) and (10) are noticeable. Nevertheless, the values of k_{1000} are quite close for the three reactions investigated.

Concerning the reaction order for all the investigated reactions a value close to 2 can be assigned to the decomposition of two structural units in an elementary step.

CONCLUSIONS

A non-isothermal kinetic analysis of some reactions which occur in the thermal decomposition of compounds with the general formula $LnCr(Gluc)_4 \cdot nH_2O$ has been performed. The kinetic parameters showed a compensation effect when the heating rate was changed. The values of the rate constants for the same kinds of reactions of different compounds are quite close.

REFERENCES

1 L. Patron, S. Ploştinaru and A. Conţescu, unpublished work.
2 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
3 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
4 P.G. Schullerus and E. Segal, unpublished work.