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ON THE THERMAL STABILITY OF SOME POLYNUCLEAR COORDINATION COMPOUNDS GENERATING MIXED OXIDES WITH PEROVSKITIC STRUCTURE

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INTRODUCTION

Following our research concerning thermal stability of coordination compounds [1] this note deals with nonisothermal kinetics concerning the solid state decomposition of some mononuclear coordination compounds (m.c.c.) of lanthanum and cobalt and almost polynuclear coordination compounds(p.c.c.) of the pairs La-Co and Nd-Co with salicylic acid and chloromandelic acid. The final product of the thermal decomposition for all the p.c.c. consists of a mixture of oxides, which by a proper subsequent treatament leads to a mixed oxide with perovskitic structure and the general formula ABO_3 , where A=La or Nd and B=Co; such compounds exhibit catalytic properties for oxido-reduction reaction [2], dehydrogenation[3] as well as for depolution processes which are similar to those exhibited by platinum catalysts.

MEASURING METHODS

The following powdered compounds have been used : $[La(Sal)_3]\cdot 3H_2O$; $[Co(Sal)(OH)]\cdot 4H_2O$; $[CoLa(Sal)_4(OH)]\cdot 4H_2O$; $[CoLa(ClMand)_5]\cdot 4H_2O$; $[CoNd(Sal)_4(OH)]\cdot 4H_2O$, where Sal and ClMand means the salicylic and chloromandelic anions respectively; the heating curves were recorded by help of a MOM Budapest Q1500 derivatograph type Paulik-Paulik-Erdey, at heating rate between 2.5K/min and 10K/min. The cristaline state of the solid compounds has been investigated with a Philips P.W.1400 X-Ray diffractometer using the chromium Kα radiation. The values of the kinetic parameters have been obtained by working the derivatographic date using the Coats-Redfern method[4].

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RESULTS AND DISSCUSION

The X-Ray diffractograms of all the coordination compounds whith La-Co showed an amorpheous structure;the p.c.c. which contains Nd-Co exhibits a crystaline structure-the main of crystallits calculated according to Scherrer's formula is d= 160 Å.The X-Ray diffraction analyssis of the decomposition products of $[La(Sal)_3]\cdot 3H_2O$ between 650°C and 850°C alowed to identify the lanthanum carbonate as well as the lanthanum oxide.The only decomposition product at 950°C is La_2O_3.Taking account these results,the derivatographic data and the literature information[5],the following sequence of decomposition for $[La(Sal)_3]\cdot 3H_2O$ should be considered:

$$[La(Sal)_3]\cdot 3H_2O_{(s)} \xrightarrow[(I)]{90^\circ C} [La(Sal)_3]_{(s)} \xrightarrow[(II)]{310^\circ C} [La_2(Sal)_3(HCOO)_3]_{(S)} \longrightarrow$$

$$\xrightarrow[(III)]{530^\circ C} [La_2(CO_3)_3]_{(s)} \xrightarrow[(IV)]{560^\circ C} La_2O_3\ (s)$$

where the temperature above the arrows correspound to the maximum decomposi--tion rates.

The values of the nonisothermal kinetic parameters for reactions (I), (II),(III) are the following:

REACTION (I)	REACTION (II)	REACTION (III)
$n= 1$	$n = 1$	$n = 1$
$E= 10.7$ kcal/mol	$E = 15.0$ kcal/mol	$E = 3.6$ kcal/mol
$A= 1.6\cdot 10^4\ s^{-1}$	$A = 1.7\cdot 10^5 s^{-1}$	$A = 4.3\cdot 10^3 s^{-1}$

The dehydratation of the m.c.c. $[Co(Sal)(OH)]\cdot 4H_2O$ occurs in the following two steps :

$$2[Co(Sal)(OH)]\cdot 4H_2O_{(s)} \xrightarrow{130^\circ C} [Co_2(Sal)_2(OH)_2]\cdot 7H_2O_{(s)} + H_2O_{(g)} \qquad (V)$$

$$[Co_2(Sal)_2(OH)_2]\cdot 7H_2O_{(s)} \xrightarrow{250^\circ C} 2[Co(Sal)(OH)]\cdot 2H_2O_{(s)} + 3H_2O_{(g)} \qquad (VI)$$

Subsequent heating of the dehydrated compound leads to overlapping decomposition steps which can not be resolved in suitable forms for kinetic analysis as well as to the decomposition of Co_3O_4 to CoO. The following values of the kinetic parameters have been obtained for reaction (V) and(VI) :

REACTION (V)	REACTION (VI)
$n = 1$	$n = 1$
$E = 1400$ cal/mol	$E = 66$ kcal/mol
$A = 1.3\cdot 10^3 s^{-1}$	$A = 1.6\cdot 10^6 s^{-1}$

Thelow value of the activation energy corresponding to reaction (V) can be assigned to the decomposition of a metastable surface intermediate.

For the other p.c.c. the decomposition sequence and the associated kinetic parameters are given below :

Decomposition of $[CoLa(Sal)_4(OH)]\cdot 6H_2O$

$$[CoLa(Sal)_4(OH)]\cdot 4H_2O_{(s)} \xrightarrow{150^\circ C} [CoLa(Sal)_4(OH)]_{(s)} + 4H_2O_{(G)} \qquad (VII)$$

$$[CoLa(Sal)_4(OH)]_{(s)} \xrightarrow[(VIII)]{250^\circ C} [CoLa(Sal)_2O(OH)]_{(s)} \xrightarrow[(IX)]{410^\circ C} Co_2O_{3(s)} + La_2O_{3(s)}$$

REACTION (VII)	REACTION (VIII)	REACTION (IX)
$n = 1$	$n = 1$	$n = 2$
$E = 7.78$ kcal/mol	$E = 30.1$ kcal/mol	$E = 52$ kcal/mol
$A = 3\cdot 10^3 s^{-1}$	$A = 4.52\cdot 10^3 s^{-1}$	$A = 6.06\cdot 10^{13} s^{-1}$

Decomposition of $[LaCo(ClMand)_5]\cdot 4H_2O$:

$$[LaCo(ClMand)_5]\cdot 4H_2O_{(s)} \xrightarrow[(X)]{90^\circ C} [LaCo(ClMand)_5]_{(s)} \xrightarrow[(XI)]{270^\circ C}$$
$$\longrightarrow [LaCo(ClMand)_3(OH)_2]_{(s)} \xrightarrow[(XII)]{420^\circ C} [LaCo(ClMand)_2(OH)_3CO]_{(s)} \longrightarrow$$
$$\xrightarrow[(XIII)]{690^\circ C} La_2O_{3(s)} + Co_2O_{3(s)}$$

REACTION (X)	REACTION (XI)	REACTION (XII)	REACTION (XIII)
$n = 1$	$n = 1$	$n = 1$	$n = 1$
$E = 8.07$ kcal/mol	$E = 22.43$ kcal/mol	$E=25.4$ kcal/mol	$E = 18.4$ kcal/mol
$A = 1.12\cdot 10^2 s^{-1}$	$A = 3.66\cdot 10^6 s^{-1}$	$A = 3.6\cdot 10^5 s^{-1}$	$A = 6.8\cdot 10^3 s^{-1}$

Decomposition of $[NdCo(Sal)_4(OH)]\cdot 4H_2O$

$$[NdCo(Sal)_4(OH)].4H_2O_{(s)} \xrightarrow[(XIV)]{110^\circ C} [NdCo(Sal)_4(OH)]_{(S)} \xrightarrow[(XV)]{240^\circ C}$$

$$\longrightarrow [NdCo(Sal)_2(OH)]_{(s)} \xrightarrow[(XVI)]{390^\circ C} Nd_2O_{3(s)} + Co_2O_{3(s)}$$

REACTION (XIV)	REACTION (XV)	REACTION (XVI)
$n = 1$	$n = 1$	$n = 1$
$E = 11.7$ kcal/mol	$E = 24.1$ kcal/mol	$E = 29.4$ kcal/mol
$A = 4.6\cdot 10^6 s^{-1}$	$A = 2.8\cdot 10^{11} s^{-1}$	$A = 8.9\cdot 10^{11} s^{-1}$

CONCLUSIONS

An analysis of the reported data shows that in almost all the cases the values of the reaction order equal unity. Taking into account the relatively low values of the preexponential factors compared with those predicted by the tranzition state theory [6] one conclude that reaction order value is an aparent one. Actually a kinetic equation corresponding to a reaction order value which equals unity, is a particular form of the

JMAYK eqn. for instantaneous nucleation and unidimensional growth of the nuclei[7]. For reactions (XV) and (XVI) , the value of the preexponential factor being close to that predicted by the t.s.t., one can suspect a true reaction order n = 1. As far as the value n = 2 (for reaction IX) is concerned, this could be eventualy assigned to the decomposition of two structural units in the elementary step of thermoanalysis.

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