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Note

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

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Following our research concerning the thermal stability of coordination compounds generating mixed oxides [1], this paper deals with the non-isothermal kinetics of solid-state decompositions of some mononuclear coordination compounds (MCC) of La and Co, and a polynuclear coordination compound (PCC) of the pair La–Co with salicylic acid. The paper is part of a research series looking to obtain some mixed oxides with general formula ABO_3, specific to perovskitic structure, where A is a rare earth ion, and B is a transition metal ion, by thermal decomposition of some polynuclear coordination compounds. The importance of mixed oxides of La with perovskitic structure [2–4] is due to their catalytic properties for oxidation–reduction reactions [5], dehydrogenation [6] and depollution processes, which are similar to those exhibited by platinum catalysts.

EXPERIMENTAL

The following powdered compounds have been used: $[La(Sal)_3] \cdot 3H_2O$, $[Co(Sal)(OH)] \cdot 4H_2O$, $[CoLa(Sal)_4(OH)] \cdot 4H_2O$ (Sal = salicylic anion), which were synthesised and analysed according to methods described elsewhere [7]. The crystalline state of the solid compounds has been investigated with a Philips (PW 1400) X-ray diffractometer using chromium $K\alpha$ radiation. The heating curves were recorded with a Paulik–Paulik–Erdey type MOM derivatograph (Q-1500) at heating rates between 2.5 and 10 K min^{-1}.

The values of the kinetic parameters have been obtained by working the derivatographic data using the Coats–Redfern method [8].

RESULTS AND DISCUSSION

The X-ray diffractograms of all the coordination compounds showed an amorphous structure at ambient temperature. The X-ray diffraction pattern and chemical analysis of the decomposition products of $[La(Sal)_3] \cdot 3H_2O$ between 650 and 850°C allowed the lanthanum carbonate and the lanthanum oxide to be identified. The only decomposition product at 950°C is La_2O_3. By working the derivatographic data concerning the decomposition of $[La(Sal)_3] \cdot 3H_2O$, and taking into account the results of the chemical analysis and the literature information concerning the presence of phenol in the decomposition products of salicylic compounds [9], we consider the following sequence for $[La(Sal)_3] \cdot 3H_2O$ decomposition

$$[La(Sal)_3] \cdot 3H_2O_{(s)} \xrightarrow{90°C} [La(Sal)_3]_{(s)} + 3H_2O_{(g)} \qquad (I)$$

$$2[La(Sal)_3]_{(s)} + 3H_2O_{(g)} \xrightarrow{310°C} [La_2(Sal)_3(HCOO)_3]_{(s)} + 3C_6H_5OH_{(g)} + \tfrac{3}{2}O_{2(g)} \qquad (II)$$

$$[La_2(Sal)_3(HCOO)_3]_{(s)} + \tfrac{3}{2}O_{2(g)} \xrightarrow{530°C} [La_2(CO_3)_3]_{(s)} + 3C_6H_5OH_{(g)} + 3CO_{2(g)} \qquad (III)$$

$$La_2(CO_3)_{3(s)} \xrightarrow{560°C} La_2O_{3(s)} + 3CO_{2(g)} \qquad (IV)$$

where the temperatures above the arrows correspond to the maximum decomposition rates given by the DTG curves. Since, during heating we had a static air atmosphere, a part of the water eliminated in the first reaction, in contact with the solid dehydrated product, reacted in the second reaction.

The values of the non-isothermal kinetic parameters for reactions (I), (II) and (III) (reaction order, *n*; activation energy, *E*; pre-exponential factor, *A*) are as follows.

	Reaction (I)	Reaction (II)	Reaction (III)
n	1	1	1
E (kcal mol^{-1})	10.7	15.0	3.6
A (s^{-1})	1.6×10^4	1.7×10^5	4.3×10^3

According to the derivatographic data, the decomposition of the $[Co(Sal)(OH)] \cdot 4H_2O$ occurs in the following two steps

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

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

Subsequent heating of the dehydrated compounds leads to overlapping decomposition steps, which cannot be resolved in suitable forms for kinetic analysis and to the decomposition of Co_3O_4 to CoO (880–980°C).

$$Co_3O_{4(s)} \rightarrow 3CoO_{(s)} + 1/2O_{2(g)}$$

The values of the kinetic parameters obtained for reactions (V) and (VI) are as follows.

	Reaction (V)	Reaction (VI)
n	1	1
E (kcal mol^{-1})	1.4	33.6
A (s^{-1})	1.3×10^{3}	1.29×10^{10}

The activation energy value of reaction (V) is evidently lower than the vaporisation energy of water. Reaction (V) can be assigned to the decomposition of a metastable [10] surface intermediate. One can equally consider that the reaction order ($n = 1$) is an apparent value.

The decomposition of $[\mathrm{CoLa(Sal)_4(OH)}]\cdot 4\mathrm{H_2O}$ occurs in the following three steps

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

$$[\mathrm{CoLa(Sal)_4(OH)}]_{(s)} + \mathrm{H_2O_{(g)}} \xrightarrow{250^\circ\mathrm{C}} [\mathrm{CoLa(Sal)_2O(OH)}]_{(s)} + 2\mathrm{C_6H_5OH_{(g)}} + 2\mathrm{CO_{2(g)}} \qquad \text{(VIII)}$$

$$[\mathrm{CoLa(Sal)_2O(OH)}]_{(s)} + 2\mathrm{H_2O_{(g)}} \xrightarrow{410^\circ\mathrm{C}} \mathrm{Co_2O_{3(s)}} + \mathrm{La_2O_{3(s)}} + 4\mathrm{C_6H_5OH_{(g)}} = 4\mathrm{CO_{2(g)}} + \tfrac{1}{2}\mathrm{H_{2(g)}} \qquad \text{(IX)}$$

By working the heating curves, we obtained the following values for the non-isothermal kinetic parameters of reactions (VII), (VIII) and (IX).

	Reaction (VII)	Reaction (VIII)	Reaction (IX)
n	1	1	2
E (kcal mol^{-1})	7.78	30.1	52
A (s^{-1})	3×10^{3}	4.52×10^{3}	6.06×10^{13}

Analysis of the kinetic parameters of the nine thermolysis reactions studied shows that for the first eight reactions the reaction order equals unity. The activation energy of reactions (I)–(VIII) varies within large limits. Taking into account the relatively low values of the pre-exponential factors compared with those predicted by the transition state theory [11], one can conclude that the reaction order value is an apparent one. Actually, a kinetic equation corresponding to a reaction order equal to unity is a particular form of the JMAYK equation [12–16] for instantaneous nucleation and unidimensional growth of the nuclei [17], the activation energy determined experimentally being equal to that of the nuclei growth. Perhaps this is the case for reaction (V) whose energy has a very low value. As far as the value $n = 2$ (for reaction IX) is concerned, this could be eventually assigned to the decomposition of two structural units in the elementary step of decomposition.

CONCLUSIONS

(1) An investigation concerning the thermal stability of two coordination compounds of lanthanum and cobalt with salycylic acid as well as a polynuclear coordination compound of lanthanum and cobalt with the same ligand has been performed.

(2) The non-isothermal kinetic data concerning the thermal decomposition of the coordination compounds suggest a model for the nucleation and growth of nuclei.

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