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ON THE THERMAL DECOMPOSITION OF SOME COBALT HYDROXIDE NITRATES

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ABSTRACT

The thermal decomposition of cobalt hydroxide nitrates of single and double layered lattice type has been studied. It has been shown that both types of compounds decompose to oxide spinels, passing through stages of partial oxidation to intermediate Co(II)–Co(III) oxide hydroxide nitrates. The observed differences in the stoichiometry of the final oxide products have been associated with the lattice type of the initial hydroxide nitrate as well as with the decomposition mechanism.

INTRODUCTION

Thermochemical and thermoanalytical studies on the decomposition reactions of several bivalent metal hydroxides with layered type structures have led to a definite assumption about the mechanism of formation and the morphological characteristics of the corresponding final oxide products [1–4]. Thermally induced transformations of the precursors were described in terms of topotaxy and a shear-collapse mechanism which require no long-range diffusion transport.

As was established more recently, these concepts were valid in the case of hydroxide nitrate precursors with layered structures, derivative of that of brucite, $Mg(OH)_2$. The characteristics of the product, such as crystallite size, shape, structural perfection, etc., were associated with both the structural type of the precursor and the mechanism of its thermal decomposition [5,6].

Our recent studies [7–10] showed that the validity of these assumptions could be extended over precursors representing mixed hydroxide nitrate crystals $Me_xCo_{1-x}(OH)_y(NO_3)_z \cdot nH_2O$ ($0 < x < 0.33$; Me = Cu, Ni, Zn) which, in contrast to the cases already considered, decompose to solid oxide solutions, $Me_xCo_{3-x}O_4$, with a spinel structure. Some similarities in the decomposition processes due to the predominant Co(II) concentrations in the mixed crystals were established. For this reason, it was necessary to elucidate the thermal behaviour of pure cobalt hydroxide nitrates.

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Two cobalt hydroxide nitrates with substantially different structures are known. The single layered $Co_2(OH)_3NO_3$ is isostructural to $Cu_2(OH)_3NO_3$ [11]. The structure of the latter consists of brucite-like $Cu(OH)_2$ layers in which 1/4 of the oxygen atoms belong to nitrate groups [12]. Within such a layer the Me(II) ions occupy octahedral positions alone.

The structure of the double-layered $Co_7(OH)_{12}(NO_3)_2$ has not been determined. It is assumed to contain Co(II) in octahedral and tetrahedral oxygen coordination [13], similar to that of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ [14].

In the present paper the thermal decomposition of both types of hydroxide nitrates is studied, bearing in mind that structural differences may affect the formation processes and characteristics of the final oxide phases.

EXPERIMENTAL

Cobalt hydroxide nitrates were precipitated adding a 0.5 M sodium hydroxide solution to Co(II) solutions at 100°C. The samples with single-layered structures were prepared from 3.5 M Co(II) nitrate solutions, and those with double-layered structures from 0.75 M solutions containing $NaNO_3$ in amounts of 1 g mol l^{-1}. The precipitation proceeded up to a $NaOH/Co(NO_3)_2$ molar ratio of 1.3, a constant suspension volume being maintained by evaporation and regulation of the rate with which the NaOH solution was added. The solid phases obtained were filtered, washed with iced water and ethanol and dried at 60°C. The Co(II), Co(III) and NO_3^- concentrations in the initial and thermally treated precipitates were determined complexometrically, iodometrically [15] and by the method of Dewarda, respectively.

The thermal decomposition was studied by differential thermal (DTA) and thermogravimetric (TG) methods as well as under isothermal conditions. DTA and TG analyses were performed in a steady state air flow (0.05 l min^{-1}) with a heating rate of 10°C min^{-1} at 20–500°C. During decomposition under isothermal conditions the evolution of nitrogen oxides was registered by an IR gas analyser with a convertor for the reduction of NO_2 to NO. Partially decomposed intermediate solid samples were taken out of the reaction vessel periodically and subjected to X-ray diffraction (XRD) and chemical analyses, magnetic and spectral measurements.

The XRD analyses were made with an X-ray powder diffractometer using CoK_α radiation and a scintillation counter. The magnetic susceptibility, κ_{mol}, was determined with a Faraday-type magnetic balance within the temperature range 20–120°C. The upper temperature boundary was limited by the thermal stability of the samples. The κ_{mol} values measured followed the Curie–Weiss law: $\kappa_{mol} = C/(T + \theta)$, whence $\mu_{eff} = (8C)^{1/2}$. Published data [16–18] (Table 1) were used for interpretation of the magnetic measurements.

TABLE 1

Magnetic moments, μ_{eff}, of Co ions with different valences and coordinations (BM)

Ion	Co_o^{2+}	Co_t^{2+}	LS Co_t^{3+}	HS Co_t^{3+}	LS Co_o^{3+}
μ_{eff}	5.1	4.88	3.6	5.1	0.0

o, t = octa- and tetrahedral coordinations, respectively; LS, HS = low and high spin states, respectively.

The magnetic moment $\mu_{eff}(Co_t^{2+})$ was determined from measurements of κ_{mol} at 20–300°C on stoichiometric Co_3O_4 prepared by thermal decomposition of $Co_2(OH)_3NO_3$ in air at 800°C. The value obtained agrees with that found in ref. 18.

Diffuse reflectance (DR) spectra were recorded with a Beckman spectrophotometer in the range 250–2500 nm using $BaSO_4$ as a standard.

RESULTS

Single-layered cobalt hydroxide nitrate

The synthesized single-layered cobalt hydroxide nitrate corresponded to the composition $Co_2(OH)_{3.3}(NO_3)_{0.78}(H_2O)_{0.24}$ (relative Co(II) amount Co(II)/ΣCo = 0.96). The XRD pattern was indexed on the basis of a hexagonal unit cell with parameters $a_0 = 3.17$ and $c_0 = 6.95$ Å (Fig. 1a), which are in good agreement with the data published elsewhere [19]. The broadening of the lines with mixed diffraction indices (*hkl*) was ascribed to turbostratic disordering of the layers stacking, which is typical of Co(II) hydroxide nitrates not subjected to prolonged ageing in the mother solution. The value of 5.1 BM was obtained for the effective magnetic moment μ_{eff}(Co). The DR spectrum showed bands at 510, 535 and 1180 nm, which are characteristic of Co(II) in octahedral coordination alone [20] (Fig. 2a).

According to TG and DTA analysis data the salt decomposed endothermally in one step (Fig. 3a). During isothermal treatment (180°C) the process began with elimination of water accompanied by weight losses of up to 2.27%. Chemical analysis data on intermediate samples showed that prior to the appearance of nitrogen oxide traces in the gas phase the relative amount of Co(II) decreased from 0.96 in the initial salt to 0.86. At this stage no substantial changes were observed in the XRD pattern. However, the oxidation process produced alterations of the DR spectrum. Broad bands appeared at 350–450 and 600–700 nm (Fig. 2b) which are characteristic of Co(III) in octahedral coordination [21]. With advancing decomposition accompanied by intense evolution of nitrogen oxides, lines of a spinel phase whose intensities gradually increased were also observed in the XRD pat-

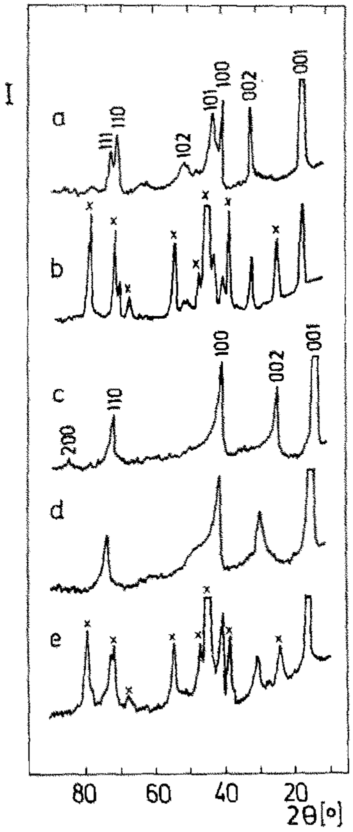


Fig. 1. XRD patterns of initial cobalt hydroxide nitrates and intermediate products of thermal decomposition: (a, b) single-layered type; (c, d, e) double-layered type; (×) spinel phase.

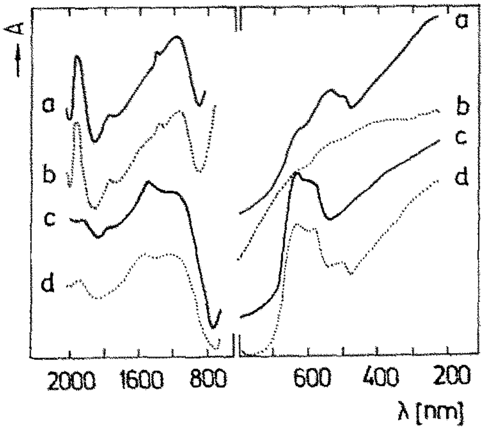


Fig. 2. DR spectra: (a, b) single-layered cobalt hydroxide nitrate and intermediate product of thermal decomposition, respectively; (c, d) double-layered cobalt hydroxide nitrate and intermediate product of thermal decomposition, respectively.

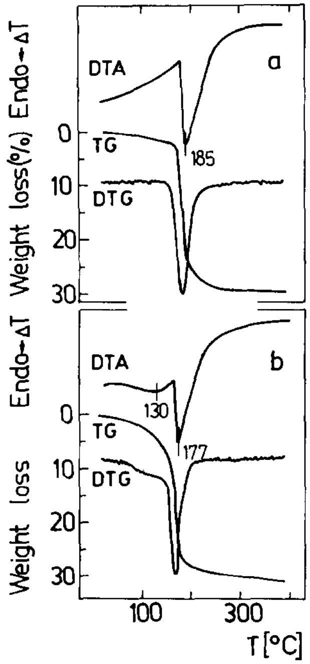


Fig. 3. DTA, TG and DTG curves of: (a) single-layered and (b) double-layered cobalt hydroxide nitrates.

terns (Fig. 1b). The lines of the undecomposed intermediate phase become more diffuse but no change in the interplanar spacings was observed. The final product of thermal decomposition at 280°C was a cobalt oxide spinel with lattice parameter $a_0 = 8.085$ Å.

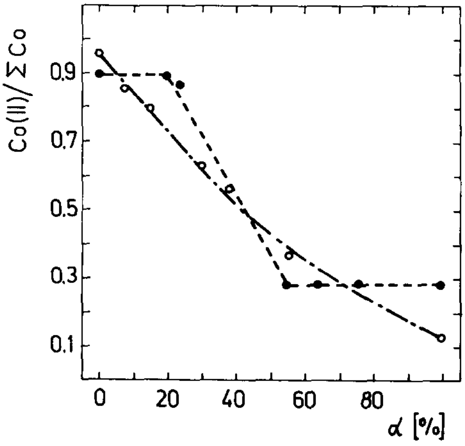


Fig. 4. Dependence of Co(II)/ΣCo ratio on relative weight losses α[%]: (○, ●) single- and double layered cobalt hydroxide nitrates, respectively.

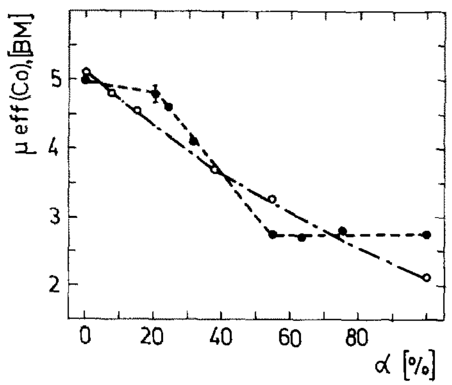


Fig. 5. Dependence of $\mu_{\text{eff}}(\text{Co})$ on relative weight losses $\alpha[\%]$: (○, ●) single- and double-layered cobalt hydroxide nitrates, respectively.

The decomposition process under isothermal conditions is characterized by a monotonous decrease in the relative amount of Co(II) and in $\mu_{\text{eff}}(\text{Co})$ with increasing weight losses, $\alpha\%$ (Figs. 4 and 5). The Co(II)/ΣCo ratio changes from 0.96 in the initial salt to 0.13 (0/ΣCo = 1.43) in the final spinel product. The last two values considerably differ from those of stoichiometric Co_3O_4: Co(II)/ΣCo = 0.33 and 0/ΣCo = 1.33. The difference between μ_{eff} of Co_3O_4 (2.82 BM) and that of the nonstoichiometric product (2.1 BM) is also significant.

On the basis of previous studies of nonstoichiometric cobalt oxide spinels, the following model describing the cation distribution is proposed as the most probable [22]:

$$\left(\text{Co}^{2+}_{1-3x}\Delta_x\text{Co}^{3+}_{2x}\right)\left[\text{Co}^{3+}_{2}\right]\text{O}_4$$

Δ = vacant tetrahedral site.

The effective magnetic moment, $\mu^{\text{mod}}_{\text{eff}}(\text{Co})$, corresponding to this model is calculated by the formula:

$$\left(\mu^{\text{mod}}_{\text{eff}}\right)^2 = (1-3x)\mu_{\text{eff}}\left(\text{Co}^{2+}_{\text{t}}\right)^2 + 2x\mu_{\text{eff}}\left(\text{Co}^{3+}_{\text{t}}\right)^2$$

In the case under consideration the experimental value of the coefficient x is 0.21. Assuming Co^{3+} to be in a low-spin state in tetrahedral and octahedral sites we obtained for $\mu^{\text{mod}}_{\text{eff}}(\text{Co})$ the value 2.18 BM, which is in good agreement with the experimentally found one (~2.1 BM).

Double-layered cobalt hydroxide nitrate

The precipitated sample had the composition $Co_7(OH)_{13.44}(NO_3)_{1.40}(H_2O)_{4.97}$. Its XRD pattern (Fig. 1c) was indexed on the basis of a hexagonal unit cell ($a_0 = 3.13$, $c_0 = 9.18$ Å) and indicated the presence of (001) and ($hk0$) reflections only, which is characteristic of hydroxide nitrates with a disordered layer structure [19]. The effective magnetic moment was found to be 5.0 BM. The DR spectrum (Fig. 2c) contained bands at 500, 1180 and 590, 635, 1520 nm which corresponded to Co(II) in octahedral and tetrahedral coordinations, respectively. These data confirm the assumption about the structure type of the double layered hydroxide nitrate. This structural type is very tolerant with respect to stacking faults and deviations from stoichiometry, which explains the observed difference between the real and ideal sample composition [23].

TG and DT analyses indicate that the sample decomposes in two steps (Fig. 3b). Weight losses of 7.8 correspond to the first endo-effect within the range 80–140°C. Chemical analyses of the sample treated under isothermal conditions at 180°C show that the weight losses at this step are due to the elimination of water. The initial Co(II)/ΣCo ratio (0.89) does not change. The XRD pattern of the intermediate product corresponds to a hexagonal unit cell with parameters $a_0 = 3.13$ and $c_0 = 7.91$ Å, i.e. changes have occurred in the interlayer spacing only (Fig. 1d). The DR spectrum (Fig. 2d) exhibits no noticeable changes, therefore the coordination of cobalt ions is preserved.

An endo-effect at 170–250°C corresponds to the second step of decomposition. Intense evolution of nitrogen oxides accompanies the process. With advancing decomposition, the XRD patterns (Fig. 1e) show that the interlayer spacing in the intermediate phase decreases from 7.9 to 7.39 Å, the a_0 value remaining practically constant. The final product of thermal decomposition obtained at 280°C is a spinel oxide with $a_0 = 8.086$ Å.

The oxidation processes accompanying the decomposition was illustrated by the dependences of the Co(II)/ΣCo ratio and $\mu_{\text{eff}}(\text{Co})$ on the relative weight losses (Figs. 4 and 5). Contrary to the single-layered type hydroxide nitrate, oxidation in this case stops before complete decomposition of the intermediate phase. The values $0/\Sigma\text{Co} = 1.36$, $\text{Co(II)}/\Sigma\text{Co} = 0.28$ and $\mu_{\text{eff}}(\text{Co}) = 2.76$ for the spinel phase show that the oxide obtained is close in composition and cationic distribution to stoichiometric Co_3O_4. Here, application of the model describing the cationic distribution and spin states, which has been used in the previous case, again leads to a good agreement between the experimental and model effective moments: $\mu_{\text{eff}}^{\text{mod}}(\text{Co}) = 2.67$, $\mu_{\text{eff}}^{\text{exp}}(\text{Co}) = 2.76$ BM ($x = 0.05$).

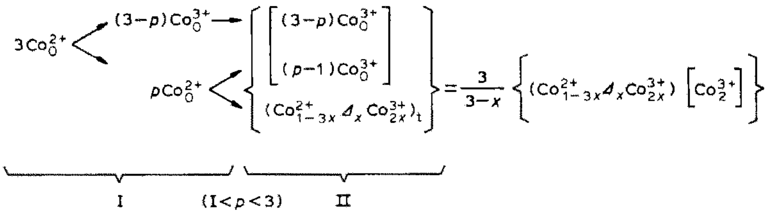
DISCUSSION

The investigation of the thermal decomposition of cobalt hydroxide nitrates revealed a characteristic of the process inherent to both structural types. Similar to the initial phases, the intermediate phases have layered-type structures irrespective of the changes in chemical composition and valence state of the cobalt ions. In addition, the Co(II)/Co(III) ratio can probably vary over a wide homogeneity range depending on the degree of conversion, as is found, for instance, with the hydroxide salts of a pyroaurite type:

$Me(II)_{1-x}Me(III)_x(OH)_2A_x \cdot nH_2O$ ($A = X$, NO_3, OH, $1/2CO_3$, $1/2SO_4$) [13]. This was checked by additional experiments, i.e. oxidation of the hydroxide nitrates with a NaClO solution. It was established that in the oxidized single-layered hydroxide nitrate, double-layered hydroxide nitrate and its intermediate product (with $a_0 = 3.13$ and $c_0 = 7.91$ Å) the Co(II)/ΣCo ratio attained the values of 0.86, 0.84 and 0.73, respectively, the initial Me/NO_3 ratio remaining unchanged. The double-layered hydroxide nitrates (initial and intermediate) correspond in their oxidation degrees and lattice parameters to the known compounds $16Co(OH)_2Co_5(OH_{1-x}O_x)_4$-$(NO_3)_6$ and $5Co(OH)_2Co(OH_{1-x}O_x)NO_3$ [24,25]. Therefore, it can be assumed that the intermediate products of thermal treatment are oxide hydroxide nitrates with layered structures similar to the samples oxidized with NaClO. Obviously, during decomposition the geometrical conditions necessary for a collective topotactic transformation are preserved.

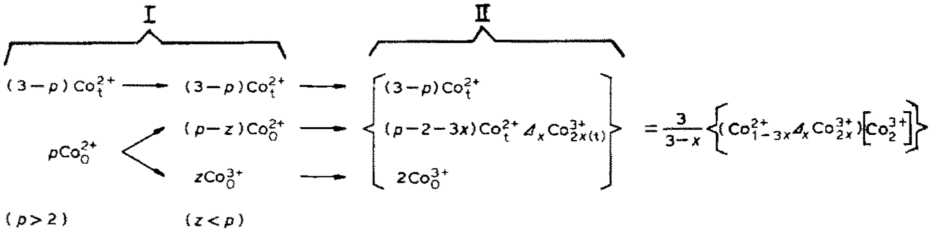
The experimental data obtained on the composition, structure and cation coordination allow a generalized representation of the successive changes in valency and coordination of Co ions during the decomposition according to the following model schemes.

Single-layered cobalt hydroxide nitrate



Stage I corresponds to the transformation of cobalt hydroxide nitrate to oxide hydroxide nitrate. It is characterized by partial oxidation of Co^{2+} ions, their initial coordination remaining the same. During stage II the intermediate oxide hydroxide nitrate is decomposed to a spinel oxide: the evolution of gaseous products is accompanied by further oxidation of Co^{2+} and lattice collapse. During the latter the available Co^{2+} ions and part of the Co^{3+} ions change their coordination to a tetrahedral one with the formation of the spinel lattice.

Double-layered cobalt hydroxide nitrate



The formation of the Co(II)–Co(III) oxide hydroxide nitrate during stage I is accompanied by partial oxidation of Co^{2+} to Co^{3+}. The second stage, i.e. the decomposition of the intermediate phase to a spinel, also proceeds with further oxidation of Co^{2+}. The lattice collapse in this case leads to a change in coordination of the Co^{2+} ions and part of the Co^{3+} ions, similar to the process observed with the single layered oxide hydroxide. However, in this case the amount of Co^{3+} ions changing their coordination is negligible and only complements the number initially occupying tetrahedral positions to give the number needed for formation of the spinel lattice. This explains the smaller cation deficiency in the spinel phase compared to that with the decomposition product of the single-layered hydroxide nitrate.

Similar schemes are used to describe the final stage of thermal decomposition of Co(II) oxalate, nitrate, hydroxide carbonate and CoOOH at temperatures below 400°C when cation-deficient cobalt oxide spinels are formed [26].

CONCLUSIONS

The thermal decomposition of both hydroxide nitrates results in the formation of cobalt oxide spinels. The stoichiometry of the final product is predetermined by the structural type of the precursor, a fact which supports the concept of collective, diffusionless mechanism of formation of the solid product. Indeed, the more pronounced similarity of the cobalt oxide polyhedral type and packing in the double-layered hydroxide nitrate, on the one hand, and the spinel, on the other, leads to the formation of a spinel with much fewer defects than in the case of the single-layered hydroxide nitrate.

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