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RARE EARTH TRISOXALATOCOBALTATES(III) - A PRECURSOR FOR RARE EARTH COBALTITES(III)

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ABSTRACT

Rare earth cobaltites, $LnCoO_3$, can be conveniently prepared by the thermal decomposition of the precursors $LnCo(C_2O_4)_3 \cdot nH_2O$ (La, Ce, $n = 9$; Pr, Nd, $n = 8$). $CeCo(C_2O_4)_3 \cdot 8H_2O$, unlike the other oxalato compounds thermally decompose to a mixture of CeO_2 and Co_3O_4. Although $LnCoO_3$ are formed from the precursors at a temperature lower than 800°C, thermal analysis of a mixture of $La_2(C_2O_4)_3 \cdot 10H_2O$ and $CoC_2O_4 \cdot 2H_2O$ at 900°C shows the residue containing mainly La_2O_3 and Co_3O_4 with a small amount of $LaCoO_3$.

INTRODUCTION

Rare earth cobaltites, $LnCoO_3$, manifest interesting electronic and magnetic behavior as evident from the facts that at low temperatures cobalt(III) ions are present mainly in the low-spin state, at higher temperatures they transform to the high-spin state, whereas at high temperatures the cobaltites show localized-itinerant electron transition[1]. Recently, it has been reported[2] that this class of compounds act as active catalysts for the oxidation of carbonmonoxide in auto exhaust at ca. 200°C, and the catalytic performance of $PrCoO_3$ has been found to be better than the commercial PtX catalyst. Further investigations on the catalytic activity of rare earth cobaltites have been made more recently[3–5] and one such study showed[3] that $NdCoO_3$ and $HoCoO_3$ are superior catalysts than $LaCoO_3$ which has been related with the spin-state properties in the cobaltites. In $NdCoO_3$ and $HoCoO_3$, the relative proportion of high-spin Co^{3+} reaches unity at a fairly low temperature. Rare earth cobaltites are commonly prepared by prolonged heating (ca. 96 h) of a mixture of the individual oxides or the carbonates at high temperature (ca. 1100°C)[6]. It appears to us that to be commercially useful as catalysts for automotive emissions a simpler and expedient route for $LnCoO_3$ formation is needed. Moreover, the catalysts should have a large surface area since oxidations occur, for the most part, at the surface of the catalysts. In this respect metal oxalates are extensively used for preparing oxides having a large surface area. $LnCoO_3$ could be generated in principle by thermally decomposing a precursor which contains Ln(III) and Co(III) ions in the ratio 1:1. Here we wish to report that $LnCo(C_2O_4)_3 \cdot nH_2O$ ideally serves as the precursor for $LnCoO_3$.

EXPERIMENTAL

$LnCo(C_2O_4)_3 \cdot nH_2O$

The procedure for preparing different rare earth compounds is similar. The La(III), Ce(III), Pr(III) and Nd(III) compounds are described here. The preparations were performed in the dark as much as possible, since the compounds are photosensitive. 1.5 g of hydrated potassium trisoxalatocobaltate(III) and 2 g of the hydrated rare earth nitrate were dissolved separately in 5 and 3 ml of 1.2M nitric acid. The solutions were cooled to about 10°C and then mixed together with stirring. After stirring the mixture vigorously for 2–3 min, the slurry was filtered, washed with small portions of chilled 1.2M nitric acid, and finally with acetone. The compound was dried at room temperature over calcium chloride in the absence of light.

Analysis

Rare earths were estimated as oxide after double precipitation of their oxalates. Cobalt was determined in the form of $CoSO_4$ after precipitating with α-nitrose β-naphthol. Oxalate was determined volumetrically by permanganate.

Physical measurements

Thermal analyses were carried out in a MOM derivatograph in an air atmosphere using a platinum crucible. X-ray powder patterns were obtained using a 11.48 cm diameter Debye-Scherrer camera with nickel filtered CuK_α radiation.

RESULTS AND DISCUSSION

The rare earth trisoxalatocobaltates(III) are of composition $LnCo(C_2O_4)_3 \cdot nH_2O$. The La(III) and the Ce(III) compounds contain nine water molecules but in the Pr(III) and the Nd(III) compounds eight water molecules are present. In table 1 the analytical data of the compounds are shown.

In order to prepare the precursor compound of the proper stoichiometry, concentrated solutions of both the reactants need to be used, since the use of more dilute solution yields a product that is contaminated with rare earth oxalates. Moreo-

TABLE 1

Compound	*% Ln*	*% Co*	*% C_2O_4*
$LaCo(C_2O_4)_3 \cdot 9H_2O$	22.4	9.4	42.4
	(22.3)[a]	(9.4)	(42.3)
$CeCo(C_2O_4)_3 \cdot 9H_2O$	22.2	9.3	42.4
	(22.4)	(9.4)	(42.2)
$PrCo(C_2O_4)_3 \cdot 8H_2O$	23.1	9.5	43.6
	(23.2)	(9.7)	(43.4)
$NdCo(C_2O_4)_3 \cdot 8H_2O$	23.4	9.5	43.4
	(23.6)	(9.7)	(43.2)

[a] Figures in parentheses are the calculated values.

ver, it is found that an optimum concentration of nitric acid (1.2M) in the reaction medium is needed; while in acid of lower concentration, there is a chance of formation of a minor amount of rare earth oxalates, in higher acid concentration the yield is reduced. The ease of formation of these compounds and their yields are apparently related with the ionic radii of the lanthanide ions, the Nd(III) complex is obtained in a lower yield. An aqueous suspension of these compounds is readily decomposed to their individual oxalates.

In general, all trisoxalatocobaltates are photosensitive but the rare earth compounds are found to be more photosensitive. On exposure to light the bright green compounds become pink. The compounds may be preserved unchanged in composition for about a week by keeping them in a dark vial in a refrigerator. A sample of the lanthanum compound was kept for about a month in light (occasionally crushed during this period) which on analysis gave a composition $LaCo(C_2O_4)_{2.5}\cdot 7H_2O$. The presence of Co(II) in this product was confirmed from its visible spectrum (mulled with Nujol) and magnetic moment measurement. The photoreduced product is actually a mixture of $La_2(C_2O_4)_3\cdot 10H_2O$ and $CoC_2O_4\cdot 2H_2O$ in the molar ratio 1:2. This was proved by thermal analysis. The product is identical to that of a mechanical mixture of the two components combined in 1:2 molar proportion. The thermal decomposition of the above mixture takes place in the following manner:

$$LaCo(C_2O_4)_{2.5}\cdot 7H_2O\ [La_2(C_2O_4)_3\cdot 10H_2O+2CoC_2O_4\cdot 2H_2O] \xrightarrow{60-180\ ^\circ C}$$
$$La_2(C_2O_4)_3\cdot nH_2O+CoC_2O_4 \xrightarrow{180-280\ ^\circ C} La_2(C_2O_4)_3\cdot nH_2O+Co_3O_4$$
$$\xrightarrow{290-380\ ^\circ C} La_2(C_2O_4)_3+Co_3O_4 \xrightarrow{400-430\ ^\circ C} La_2O_3\cdot 2CO_2+Co_3O_4$$
$$\xrightarrow{430-500\ ^\circ C} La_2O_3\cdot CO_2+Co_3O_4 \xrightarrow{640-780\ ^\circ C} La_2O_3+Co_3O_4 \xrightarrow{850\ ^\circ C} LaCoO_3$$

The above decomposition scheme is consistent with the decomposition behavior reported for $La_2(C_2O_4)_3\cdot 10H_2O$[7,8] and $CoC_2O_4\cdot 2H_2O$[9]. The X-ray powder pattern of the thermolysis product at 920°C showed the presence of lines mainly due to La_2O_3 and Co_3O_4, and some lines due to $LaCoO_3$ formation. In addition there are several more lines which could not be identified.

Figure 1 shows the thermal decomposition of $LaCo(C_2O_4)_3\cdot 9H_2O$ and $CeCo(C_2O_4)_3\cdot 9H_2O$. It may be seen that the decomposition behavior of these two compounds is entirely different. The Ce(III) compound decomposes in an ill-defined way, the final decomposition of the compound takes place at 420°C and the composition of the residue remains unchanged till 900°C. The residue has been identified from X-ray data to be a mixture of CeO_2 and Co_3O_4. The lanthanum compound on the other hand decomposes in a stepwise manner. The first stage of decomposition takes place between 60–300°C. The observed weight loss 31% is quite near to the calculated weight loss 33% for the reaction

$$LaCo(C_2O_4)_3\cdot 9H_2O \rightarrow \tfrac{1}{2}La_2Co_2^{II}(C_2O_4)_5+CO_2+9H_2O$$

It is well known that during thermolysis Co(III) in $K_3Co(C_2O_4)_3$ also undergoes reduction to a Co(II) complex accompanied by the loss of carbondioxide[10]. It will

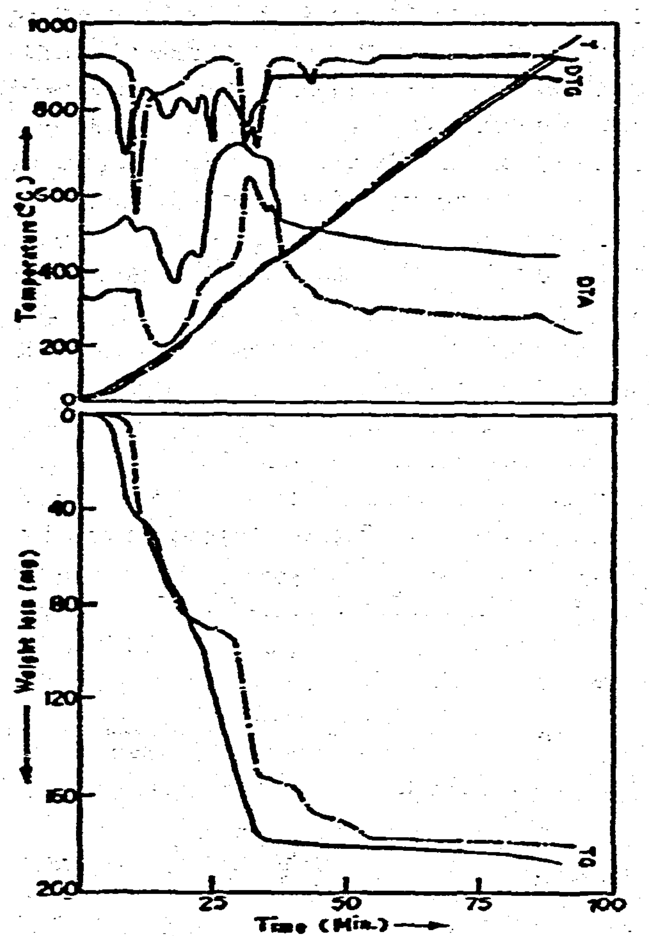

Fig. 1. Thermal decomposition of: —·—·—, $LaCo(C_2O_4)_3 \cdot 9H_2O$; and ————, $CeCo(C_2O_4)_3 \cdot 9H_2O$. Weight of sample: 300 mg; sensitivity of DTA and DTG: 1/15 of the full scale.

be evident from subsequent discussion that the thermally reduced lanthanum complex is different from the photoreduced products. From slightly above 300°C two consecutive exothermic reactions take place (also evident from the DTG curve) with a total loss is weight of 51.5%. The product at this stage agrees well with the formation of a compound having the empirical formula $LaCoO_3 \cdot 2CO$. The calculated weight loss for the formation of this supposed compound from the precursor compound is 51.6%. From 480–540°C this compound suffers further change in mass and the total weight loss at the end of this reaction is 56% which is in good agreement with the calculated weight loss 56.1% for the formation of $LaCoO_3 \cdot CO$. Another decomposition reaction between 560–640°C leads to the formation of $LaCoO_3$ (total weight loss, calc.: 60.5%, obs: 60.2%). It may be noted that during the last two decomposition reactions two small endothermic changes occur which should be the case if there is really the evolution of carbonmoxide. However, we have not been able to characterize the products formed in these two stages in detail. The powder pattern of the residue at 800 °C showed the absence of any line due to La_2O_3 or Co_3O_4 and the d spacings are in excellent agreement with those reported in literature[11]. The Pr(III) and the Nd(III) trisoxalatocobaltates decompose almost in a similar way as the La(III) compound. In these cases also the final decomposition products have been identified to be pure $PrCoO_3$ and $NdCoO_3$ by comparing the d spacings reported in literature[6]. Table 2 compares the X-ray diffraction data of $LaCoO_3$ and $NdCoO_3$ obtained by calcination of the oxalato precursors at 800 °C for 2 h in air with those reported in literature.

TABLE 2

X-RAY POWDER DATA OF $LaCoO_3$ AND $NdCoO_3$

$LaCoO_3$		*$NdCoO_3$*	
$d_{(obs)}$	$d_{(reported)}$[11]	$d_{(obs)}$	$d_{(reported)}$[6]
3.832(m)	3.82(m)	2.65(vs)	2.67(vs)
2.721(vs)	2.711(vs)		2.64(vs)
2.693(vs)	2.679(vs)	2.163(w)	2.172(w)
2.222(m)	2.213(m)	1.872(s)	1.884(s)
2.182(w)	2.173(w)	1.686(w)	
1.916(s)	1.909(s)	1.534(m)	1.540(m)
1.711(w)	1.719(vvw)	1.328(m)	1.333(m)
1.706(vw)	1.701(vvw)	1.188(m)	1.193(m)
1.567(s)	1.563(s)		1.179(m)
1.547(m)	1.542(m)		
1.363(m)	1.356(m)		
1.346(m)	1.340(m)		
1.284(vw)	1.275(vvw)		
1.277(w)			
1.216(m)	1.213(m)		
1.207(m)	1.203(m)		
1.162(vw)			
1.157(vvw)			
1.146(vw)	1.143(vw)		

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