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A COMPARATIVE STUDY ON THE THERMAL DECOMPOSITION OF LANTHANIDE BISCITRATO CHROMATE(III) HYDRATES, $Ln[Cr(C_6H_5O_7)_2]\cdot nH_2O$

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Abstract

The thermal decomposition of lanthanide biscitrato chromate (III) hydrates, $[Ln(Cr(C_6H_5O_7)_2]\cdot nH_2O$ where *Ln* = Pr, Nd, Dy and Ho have been carried out in static air and flowing argon atmospheres and thereby compared the decomposition nature with that of the lanthanum biscitrato chromate(III) dihydrate reported earlier. The precursor complexes decompose in four major steps. Stable oxycarbonates and chromates(V) have been isolated as intermediates. It has been found that for heavier lanthanide complexes all the decomposition steps are pushed to 'higher temperature' ranges. Moreover, the thermal stability range of chromates(V) is much lesser compared to that of $LaCrO_4$. Based on the observed experimental results a general scheme for the decomposition of lanthanide biscitrato chromate(III) hydrates is proposed.

Keywords: complexes, lanthanide biscitrato chromate(III) hydrates

Introduction

Lanthanum biscitrato chromate(III) dihydrate (LCC), has been shown [1] to be a very good precursor for the low-temperature preparation of chemically pure and stoichiometric lanthanum chromite. The thermal decomposition of LCC was also studied in static air and dynamic argon atmospheres [1]. Further, the thermal decomposition behavior of a few lighter lanthanide chromium citrato complexes have also been studied [2]. For the preparation of heavier chromites, except an oxalato complex, no other carboxylate complexes have been described [3]. Hence, the citrate gel process has been exploited as a low-temperature route for the preparation of lanthanide chromites in general [4]. This paper describes a comparative study of the thermal decomposition behaviour of chromium citrato complexes of a few lighter and heavier lanthanides.

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Experimental

Reagents

All the reagents used were of Analar grade. 99.90% pure lanthanide oxide of AAS standard from Alfa products, Merck guaranteed citric acid and BDH Analar chromium nitrate were used.

Preparation

Lanthanide biscitrato chromate(III) hydrates (LnCC), $Ln[Cr(C_6H_5O_7)_2]\cdot nH_2O$, where *Ln*=Pr, Nd, Dy and Ho were prepared by adopting the procedure reported earlier [1] for the preparation of lanthanum biscitrato chromate(III) dihydrate.

Chemical and physical studies

Lanthanide contents were estimated gravimetrically after double precipitation of their oxalates. Chromium content and citrate content in the complex was determined as reported earlier [1]. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the precursors were recorded using an Ulvac TA-1500 automatic thermal analyzer in static air and flowing argon atmospheres with a flow rate of 25 ml min^{-1}. Platinum cups were used as sample holders. A heating rate of 20°C min^{-1} and a sample weight of 3–4 mg were used for all the measurements. Infrared (IR) spectra were recorded in alkali halide pellets using a Perkin-Elmer 597 spectrometer. X-ray diffractograms were recorded on Philips PW 1050/70 diffractometer using CuK_∞ radiation at a scan rate of 2° min^{-1}.

Results and discussion

The analytical data for a few lanthanide biscitrato chromate(III) hydrates are shown in Table 1. It is clear from the results that the extent of hydration decreases as we go to higher lanthanide complexes. All the complexes were bluish-black non-hygroscopic solids. They were insoluble in water and common organic solvents. They, however, readily decomposed in presence of mineral acids.

Thermal analysis data

The thermal decomposition of Praseodymium biscitrato chromate(III) hydrate (PCC) and Neodymium biscitrato chromate(III) hydrate (NCC) as representatives of lighter lanthanide complexes and Dysprosium biscitrato chromate(III) hydrate (DCC) and Holmium biscitrato chromate(III) hydrate (HCC) as representatives of heavier lanthanide complexes have been carried out in static air and flowing argon atmospheres. The decomposition was found to proceed through various steps which were similar to those observed during the thermal decomposition of LCC and interestingly all the citrate precursors follow a similar decomposition mechanism yielding the corresponding lanthanide chromites. One-to-one correlation exists, between the

Table 1 Analytical data for $LnCr(C_6H_5O_7)_2 \cdot nH_2O$

Compound	% Ln		% Cr		% Citrate		% H_2O	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
$PrCr(C_6H_5O_7)_2 \cdot 3.5H_2O$	22.22	22.20	8.20	8.19	59.63	59.65	9.91	9.94
$NdCr(C_6H_5O_7)_2 \cdot 3H_2O$	23.03	22.94	8.30	8.25	60.39	60.30	8.62	8.59
$DyCr(C_6H_5O_7)_2 \cdot 2.5H_2O$	25.38	25.48	8.12	8.15	59.07	59.30	7.42	7.07
$HoCr(C_6H_5O_7)_2 \cdot H_2O$	26.76	26.90	8.43	8.48	61.38	61.70	3.43	2.93

Table 2 Data on the thermal decomposition of LnCC in air

Decomposition step	PCC			NCC			DCC			HCC		
	Mass loss/%		T_{range}/ K	Mass loss/%		T_{range}/ K	Mass loss/%		T_{range}/ K	Mass loss/%		T_{range}/ K
	obs.	calc.		obs.	calc.		obs.	calc.		obs.	calc.	
Dehydration	10.50	10.05	323– 423	8.00	8.57	323– 423	7.42	7.07	353– 473	3.43	2.93	353– 483
Decomppsition of anhydrous citrate	50.52	48.00	423– 753	52.54	54.00	423– 763	47.00	51.00	473– 783	47.00	53.00	483– 783
Decomposition of oxycarbonate	56.50	59.40	753– 953	58.00	58.45	763– 968	51.00	56.00	783– 983	48.50	51.50	783– 993
Decomposition of chromate (V)	62.00	62.00	953–1073	61.00	61.00	968–1143	59.00	59.05	983–1183	57.00	57.20	993–1210

DTA and TG results, indicating thermal effects are accompanied by mass losses. Four mass loss steps and the corresponding thermal effects could be identified on the thermograms. The probable reactions are: (i) dehydration, (ii) decomposition of the anhydrous citrate to an oxycarbonate, (iii) decomposition of the oxycarbonate to lanthanide chromate(V) and (iv) decomposition of chromate(V) to chromite(III). A typical TG/DTG/DTA curve for a representative member is shown in Fig. 1.

Dehydration of the hydrates

Dehydration of both PCC and NCC takes place in a single step between 333–463 K and the corresponding mass loss are given in Table 2. In both cases the observed mass loss agrees well with the calculated mass loss for the removal of water.

Dehydration of DCC and HCC takes place at comparatively higher temperatures than those of PCC and NCC. In both cases, dehydration is found to be complete around 473 K. The observed mass loss of 3.43% is slightly more for HCC. In either case, anhydrous citrates could not be isolated by isothermal heating as the citrate de-

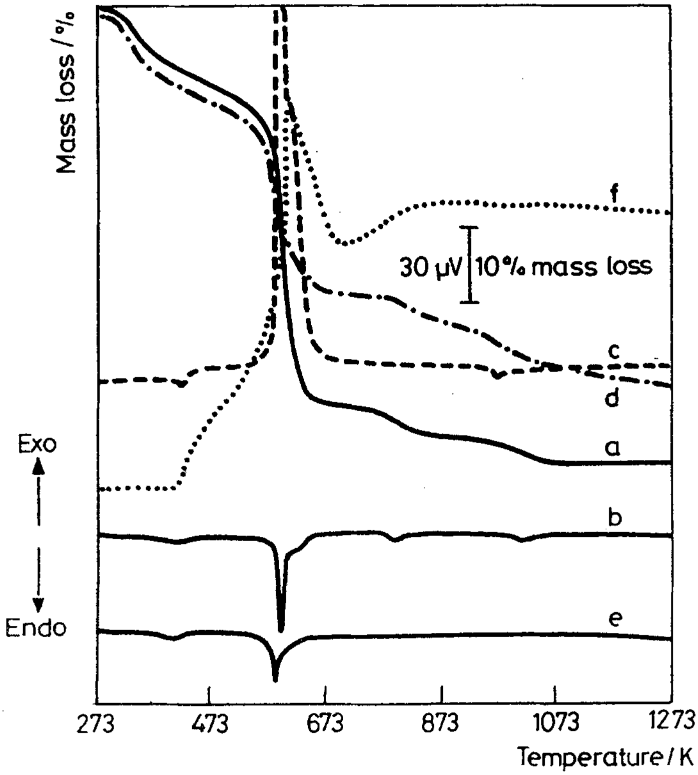

Fig. 1 TG, DTG and DTA of NCC: a), b) and c) in static air; d), e) and f) in flowing argon atmospheres

composition immediately follows dehydration. The dehydration steps are not affected significantly in flowing argon atmosphere as observed from the thermograms.

Decomposition of anhydrous citrate

This is found to be the most important and at the same time the most complex stage of decomposition. The actual decomposition might be more complex than observed and it is assumed that the citrate is probably converted to aconitate and then subjected to decarboxylation with the evolution of gases like CO, CO_2 and water vapour [5]. The process is found to be highly exothermic in air while less so in argon and considerable foaming is observed in both cases. The asymmetric nature of the DTA peak confirms that the decomposition of the complex as well as the burning of carbonaceous matter occurs simultaneously. In all cases, at the end of the citrate decomposition step, the black residue has been identified as an oxycarbonate $LnCrO_{3-x}(CO_3)_x$, Ln=Pr, Nd, Dy and Ho. Isothermal heating of PCC in air at 673 K for 6 h resulted in a mass loss of 49% and the chemical analysis of the residue gave the following results: Pr=50.31%, Cr=18.56% and CO_2=11.99%. This corresponds to an oxycarbonate with $x=0.9$. Calculated mass loss for this decomposition is 48%. A residue with $x=0.8$ could be isolated by isothermal heating in air of NCC at 693 K for 6 h. Isothermal heating of DCC and HCC at 723 K for 6 h resulted in the formation of residues with $x=0.8$.

The isolated oxycarbonates were amorphous to X-rays as well as electron diffraction. The oxycarbonates were further identified by their IR spectra shown in Fig. 2a–d. The spectra are comparable to the type I spectrum of rare earth oxycarbonates and also the spectrum of the lanthanum oxycarbonate $La_2O_2CO_3$ identified by us [6]. The spectra of Fig. 2 shows two fold splitting of the ν_2, ν_3 and ν_4 modes which is characteristic of a Type I spectrum [7]. The additional absorption peak at 1100°C, observed in the case of heavier rare earth oxycarbonates could be due to the OH bending band of the absorbed water. We did not observe any IR band ($\sim$2350 cm^{-1}) corresponding to trapped CO_2, which indicates that gas evolution ceased soon after the decomposition.

In the argon atmosphere, the citrate decomposition step was less exothermic with DTA peaks shifted to slightly higher temperature. The observed mass losses were significantly less than in static air, which might be due to the presence of unburnt carbon in the residue.

Decomposition of oxycarbonates

The oxycarbonate $PrCrO_{3-x}(CO_3)_x$ decomposes in the temperature range 743–863 K which is shown up as a small endotherm in the DTA around 783 K. The dark green powder collected at the end of this decomposition is analyzed to be the composition $PrCrO_4$. The total mass loss observed upto this stage of decomposition is around 56.4% which, however, is less than the calculated value of 59.4% for the formation of $PrCrO_4$. The differences in weight might be again due to partial carbonization of the sample. Isothermal heating of PCC in air at 773 K for 6 h has

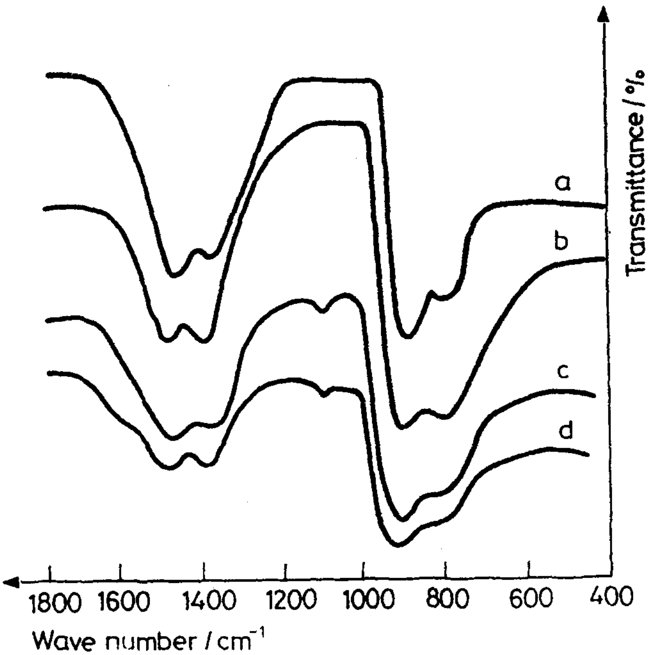

Fig. 2 IR spectra of $LnCrO_{3-x}(CO_3)_x$: a) Pr b) Nd c) Dy and d) Ho

shown a mass loss of 59%, which agrees very well with the calculated value of 59.4%. The oxycarbonate $NdCrO_{3-x}(CO_3)_x$ decomposes at a slightly higher temperature of 753–883 K. The total mass loss of 58% that is observed at the end of this decomposition compares very well with the calculated value of 58.4% for the formation of $NdCrO_4$. Isothermal heating of NCC at 773 K for 6 h gave rise to the dark green powder of $NdCrO_4$. The oxycarbonates of DCC and HCC started decomposing at a higher temperature of 783 K. The total mass loss observed in TG upto the formation of the chromates(V) was 51% for DCC and 48.5% for HCC. These mass losses are considerably lesser than the values calculated for the formation of $LnCrO_4$ (V). A comparison of the TG curves in air and argon shows that, the step corresponding to the formation of $LnCrO_4$ is not so evident in argon and the isothermal experiments confirmed that the formation of $LnCrO_4$ requires either air or oxygen. The green powders of chromates(V) collected by isothermal heating of the precursors have been characterized by XRD and IR spectroscopy, the details of which have been reported elsewhere [8].

Decomposition of chromate(V)

In the final stage of decomposition, $LnCrO_4$ gives rise to $LnCrO_3$ by the loss of oxygen and is evident by a small exotherm on the DTA in air. Beyond 1123–1173 K, the weight of the residue remains constant. The total mass loss observed in static air was 62 and 61% for PCC and NCC respectively. The mass losses agree very well with the calculated values for the formation of $PrCrO_3$ and $NdCrO_3$. The total mass loss recorded in TG are 59% for DCC and 57% for HCC. These are comparable to the theoretical values for the formation of $DyCrO_3$ and $HoCrO_3$ from DCC and HCC respectively.

Minimum thermal treatment required for the formation of phase pure crystalline $PrCrO_3$ and $NdCrO_3$ are 873 and 893 K, where as for $DyCrO_3$ and $HoCrO_3$ a higher minimum temperature of 1023 K is required. The identity of the residues were confirmed by XRD, IR etc. All of them were found to have the orthorhombic structures as evident from XRD patterns shown in Fig.3.

From the results of thermal analysis of the citrato complexes PCC, NCC, DCC and HCC and their similarity to the thermal decomposition behavior of lanthanum biscitrato chromate(III) dihydrate (LCC), a general scheme can be proposed for the thermal decomposition of these lanthanide biscitrato chromate(III) hydrates (LnCC) in air.

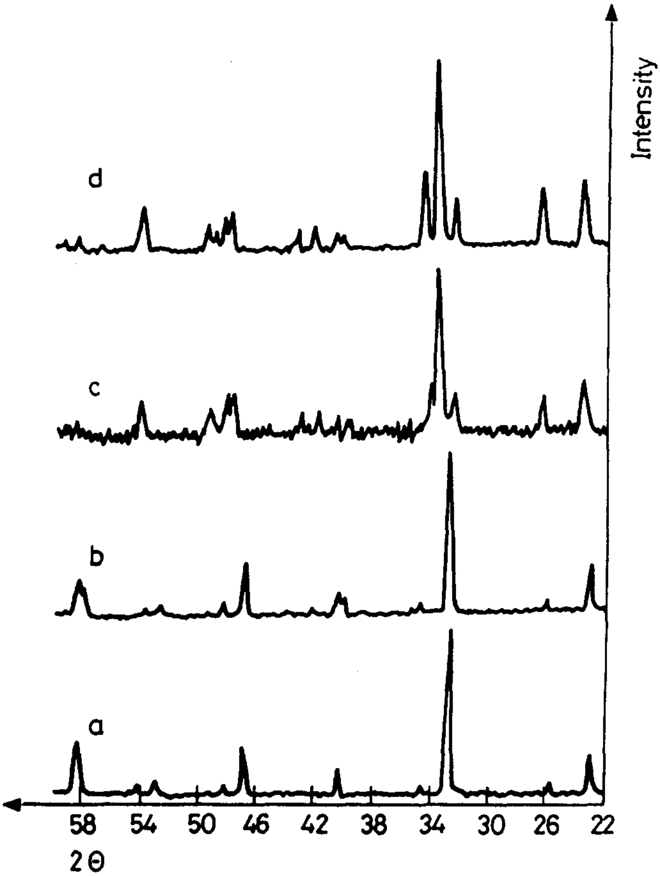

Fig. 3 XRD of a) $PrCrO_3$ b) $NdCrO_3$ c) $DyCrO_3$ and d) $HoCrO_3$

$$Ln[Cr(C_6H_5O_7)_2]\cdot nH_2O \rightarrow Ln[Cr(C_6H_5O_7)_2]+nH_2O \quad (1)$$

$$Ln[Cr(C_6H_5O_7)_2] \rightarrow Ln[Cr(C_6H_3O_6)_2]+2H_2O \quad (2)$$

$$Ln[Cr(C_6H_3O_6)_2]+9O_2 \rightarrow LnCrO_{3-x}(CO_3)_x+3H_2O+(12-x)CO_2 \quad (3)$$

$$LnCrO_{3-x}(CO_3)_x+0.5O_2 \rightarrow LnCrO_4+xCO_2 \quad (4)$$

$$LnCrO_4 \rightarrow LnCrO_3+0.5O_2 \quad (5)$$

where, Ln=Pr, Nd, Dy, Ho or any other lanthanide and $n=3.5H_2O$ for PCC, $3H_2O$ for NCC, $2.5H_2O$ for DCC and $1H_2O$ for HCC respectively.

The significant differences compared to the thermal decomposition of LCC are (i) anhydrous citrates could not be isolated by isothermal heating, as citrate decomposition immediately follows dehydration (ii) the thermal stability range of chromates(V) is much less than that of $LaCrO_4$ (V) (iii) the formation of chromites of heavier lanthanides requires a considerably higher temperature than that for the lighter lanthanide chromites and (iv) for heavier lanthanide complexes all the decomposition steps are pushed to 'higher' temperature ranges.

Conclusions

A comparative study on the thermal decomposition of lanthanide biscitrato chromate(III) hydrates, where the lanthanide is Pr, Nd, Dy and Ho to La have been carried out in static air and flowing argon atmospheres. During thermal decomposition of precursor, large amounts of gases like CO, CO_2 and water vapour are evolved and result in light green coloured fine particles of lanthanide chromites. In addition, stable oxycarbonates and chromates(V) have also been isolated as intermediates. Based on the experimental observations a general scheme is proposed for the thermal decomposition of these citrato complexes.

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