

An investigation on the solid state pyrolytic decomposition of bimetallic oxalate precursors of Ca, Sr and Ba with cobalt: A mechanistic approach

Nidhuban Deb*

Department of Chemistry, North Eastern Regional Institute of Science & Technology (Deemed University),
Nirjuli 791109, Itanagar, Arunachal Pradesh, India

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Abstract

The mixed metal oxalate precursors, calcium(II)bis(oxalato)cobaltate(II)hydrate (COC), strontium(II)bis(oxalato)cobaltate(II)pentahydrate (SOC) and barium(II)bis(oxalato)cobaltate(II)octahydrate (BOC) have been synthesized and their thermal stability was investigated. The complexes were characterized by elemental analysis, IR spectral and X-ray powder diffraction studies. Thermal decomposition studies (TG, DTG and DTA) in air showed that the compound COC decomposed mainly to CaC_2O_4 and Co_3O_4 at 340 °C, and a mixture of CaCO_3 and Co_3O_4 identified at 510 °C. A mixture of CaCO_3 and $\text{Ca}_3\text{Co}_2\text{O}_6$ along with the oxides and carbides of both the cobalt and calcium were attributed at 1000 °C as end products. DSC study in nitrogen ascertained the formation of a mixture of CaO and CoO along with a trace of carbon at 550 °C. The mixture species, SrC_2O_4 , CoC_2O_4 and Co_3O_4 were generated at 255 °C in case of SOC in air, which ultimately changed to CoSrO_3 , SrCO_3 and oxides of strontium and cobalt at 1000 °C. The several mixture species also generated as intermediate at 332 and 532 °C. The DSC study in nitrogen indicated the formation of CoSrO_x ($0.5 < x < 1$) as end product. In case of BOC in air, a mixture of BaCoO_2 , BaO, CoO and carbides are identified as end product at 1000 °C through the generation of several intermediate species at 350 and 530 °C. A mixture of BaO and CoO is identified as end product in DSC study in nitrogen. The kinetic parameters have been evaluated for all the dehydration and decomposition steps of all the three compounds using four non-mechanistic equations. Using seven mechanistic equations, the kind of dominance of kinetic control mechanism of the dehydration and decomposition steps are also inferred. The kinetic parameters, ΔH and ΔS of all the steps are explored from the DSC studies. Some of the decomposition products are identified by IR and X-ray powder diffraction studies.

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1. Introduction

Recently we have reported [1] the solid state thermal decomposition of bimetallic oxalate coordination compounds of Mn(II), Fe(II) and Cu(II) with cobalt, where the generation of mixed metal oxides of the type $\text{M}_1\text{M}_2\text{O}_x$ (where $x = 2$ or 3) were observed as main decomposition products in all the precursors. Using mechanistic equations the rate controlling kinetic model of the dehydration and decomposition mechanisms were investigated. As an extension of our work on mixed metal oxalate, and keeping in view of the possibility of formation of

different types of metal oxide and mixed metal oxides, and their possible applicability as prospective materials, we are interested to explore the thermal behaviour of a mixed metal oxalate precursors of calcium, strontium and barium with cobalt. During the extraction of the oxide end products the oxalate precursors generally undergoes several dehydration and decomposition reactions and it is worthwhile to explore the different intermediates and their possible interactions during the degradation process. It is also need to elucidate the mechanism and kinetics of the various steps. Therefore, in continuation with our ongoing work [2–4] in the field of mixed metal oxalates, herein we report the synthesis, characterization and the thermal decomposition of $\text{Ca}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 3.5\text{H}_2\text{O}$, $\text{Sr}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ and $\text{Ba}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 8\text{H}_2\text{O}$. The main purpose of this work is to obtain the route of the growth of

* Tel.: +91 360 2257659.

E-mail address: nidhubandeb@yahoo.com.

the nuclei occurs during the dehydration and decomposition processes using mechanistic approach.

2. Experimental

2.1. Preparation of the complexes

The preparative method is similar to the method adopted earlier [1]. All the reagents used were AR grade. The compounds were prepared from cobalt(II) chloride. The chloride free cobalt hydroxide prepared from cobalt chloride was dissolved in glacial acetic acid and heated on a steam bath. Adding calcium chloride followed by dropwise addition of saturated solution of oxalic acid separated a light pink precipitate of calcium compound. The precipitates were washed several times with distilled water and stored over calcium chloride in a desiccator. Similarly light pink compounds of strontium and barium were obtained by adding their respective chlorides and stored in a desiccator. The water contents of the compounds were determined gravimetrically and thermogravimetrically. The metal contents were estimated using standard methods [5].

2.2. Instrumentation

Elemental analysis, IR spectra, DTA, TG and DTG in air, DSC in nitrogen and X-ray powder diffraction patterns were recorded as described earlier [1]. The amount of sample taken was 6.69 mg in TG and 10.5 mg in DTA in case of compound COC. The samples taken for SOC were 7.34 and 10.3 mg in respective TG and DTA, and for the compound BOC the respective amounts were 5.74 and 10.4 mg. The sample mass taken for the respective compounds, COC, SOC and BOC in DSC study were 4.03, 6.70 and 6.80 mg. The powder XRD of the pyrolytic decomposition products at different temperatures as well as the end products of all the compounds were recorded using Seifert XRD 3003 TT. The Ni filter and Cu target were used in the unit.

2.3. The kinetics of decomposition

Different non-mechanistic equations, such as, Freeman and Carroll [6], Coats and Redfern [7], Flynn and Wall [8], and MacCallum and Tanner [9] were used to calculate the kinetic parameters, such as, activation energy (E^*), pre-exponential factor (A) and the order of reaction (n) of all the dehydration and decomposition steps for all the precursors from non-isothermal TG curves.

The evaluations of the mechanism of reaction using mechanistic equations have been discussed by several authors [10–13]. We have used the following kinetic expression [13]:

$$\frac{\Delta \ln \alpha'}{\Delta \ln(1 - \alpha)} = -\frac{E^*}{R} \cdot \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} + \frac{\Delta \ln f(\alpha)}{\Delta \ln(1 - \alpha)} \quad (1)$$

where the terms have their usual meaning and $f(\alpha)$ is a function depending on the actual mechanism of the process. A series of seven forms of $f(\alpha)$ are proposed [13] out of the possible

mechanisms [11] of thermal decomposition. Thus a plot of $\Delta \ln \alpha - \Delta \ln f(\alpha)/\Delta \ln(1 - \alpha)$ against $\Delta(1/T)/\Delta \ln(1 - \alpha)$ is a straight line whose slope is $-E^*/R$, irrespective of the form of $f(\alpha)$ employed. One can select the $f(\alpha)$ that best fits the actual mechanism of reaction corresponding to the intercept value close to zero. The actual mechanisms and forms of $f(\alpha)$ are as follows:

Mechanism	Form of $f(\alpha)$	Rate-controlling process
D1	$1/2\alpha$	One-dimensional diffusion
D2	$[-\ln(1 - \alpha)]^{-1}$	Two-dimensional diffusion
D3	$3/2(1 - \alpha)^{2/3} \cdot [1 - (1 - \alpha)^{1/3}]$	Three-dimensional diffusion; Jander equation
D4	$[3/2 \cdot (1 - \alpha)^{-1/3}]^{-1}$	Three-dimensional diffusion; Ginstling–Brounshtein equation.
F1	$(1 - \alpha)$	Random nucleation
R2	$2(1 - \alpha)^{1/2}$	Phase-boundary reaction (cylindrical symmetry)
R3	$3(1 - \alpha)^{2/3}$	Phase-boundary reaction (spherical symmetry)

Further, to test the correctness and validity of the above conclusion regarding the identification of the actual mechanism of the process, the Arrhenius equation of the following type is used:

$$\ln \alpha' - \ln f(\alpha) = \ln \left(\frac{A}{\beta} \right) - \frac{E^*}{RT} \quad (2)$$

where the terms have their usual meaning. The slope, $-E^*/R$, and intercept, $\ln(A/\beta)$, can be obtained from the plot of $\ln \alpha' - \ln f(\alpha)$ against $1/T$ which is a straight line. It now follows that the mechanism proposed on the basis of the kinetic Eq. (1) is correct provided the E^* value obtained from the above plot of Eq. (2) turns out to be same.

Thus, we have evaluated the E^* from TG curves employing the kinetic Eqs. (1) and (2) for seven forms of $f(\alpha)$ and thus ascertained the rate controlling process for the dehydration and decomposition steps as described above. The details of the kinetic parameters calculated are available as [supplementary material](#) in the online publication of the paper.

3. Results and discussion

The complexes, $\text{Ca}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 3.5\text{H}_2\text{O}$ (COC), $\text{Sr}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ (SOC) and $\text{Ba}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 8\text{H}_2\text{O}$ (BOC) were isolated as light pink powders and were insoluble in water. These are also insoluble in common organic solvents. However, they decomposed in the presence of strong acid or alkali. The estimated metal contents and microanalytical results (Table 1) show good agreement for the proposed formula of the complexes. The chelating character of the oxalate groups as well as the presence of coordinated and water of crystallization have been concluded on the similar way of earlier studies [1–4,14]. The assignments of the bands are shown in Table 2. Powder XRD pattern of the complexes are given in Fig. 1 and that are differed from one other. This suggested that they are not isomorphous. But these are crystalline in nature.

Thermal decomposition of the precursor calcium(II)bis(oxalato)cobaltate(II)hydrate, $\text{Ca}[\text{Co}(\text{C}_2\text{O}_4)_2] \cdot 3.5\text{H}_2\text{O}$ (COC) and

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