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Thermo gravimetric Investigations of Mixed Metal Tartrates leading to Oxidic Spinels

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Abstract

The present investigationconsistsof study of the thermal decompositions of mixed metal tartrates obtained by co-precipitation method forming cobaltites as final products.The solutions of M_2SO_4 (M=Cd, Ni, Cu) and cobalt sulphate, heptahydrate are used. The mixed tartrates of Cd-Co, NI-Co and Cu-Co are synthesized by the addition of 10% disodium tartrate. These tartrate compounds are characterized by the elemental analysis, metal analysis and infrared spectra. They are decomposed thermally and decomposition reactions are recorded on Sieko instrument under static air atmosphere. In these tartrate compounds, the dehydration takes place in a single stage within the temperature range of 35-210^{0}C. The DTG and DTA curves of these tartrate compounds show the broad exothermic peaks. Further the decompositions of intermediate carbonate compounds are observed within the temperature range of 410-600^{0}C leading to corresponding cobaltites. The cobaltites, thus obtained,are characterized by the chemical analysis, infrared spectra and powdered XRD techniques.

1. Keywords

Mixed Metal Tartrates, Thermo gravimetric Analysis, Cadmium cobaltite, Nickel cobaltite, and Coppercobaltite.

2. Introduction

The cobaltites of zinc, nickel, and copper were synthesized for the first time by Holgerson and Karlsson by using metal nitrate solutions. Binary metal cobaltites (M=Ni, Zn, Cu) were synthesized by thermal treatment of mixed hydroxides [1, 2]and alsoby usingoxalates [3], hydroxide nitrates [4] malonatehydrazines[5],hydroxycarbonates[6], hydrazinium compounds [7]hydrazine carboxylates [8] hydrothermal and precipitation method.[9] The synthesis of various types of cobaltites were reported by many scientists[10, 11, 12] . From the literature survey, it is apparent that inspite of its long history, the studies on these compounds are still presenting useful information. The present investigation has been undertaken to study the thermal decompositions of tartrates of Cd-Co, Ni-Co, and Cu-Co leading to corresponding cobaltites.

3.Materials and Methods

A solution of mixture of Cadmium sulphate, octahydrate and cobalt sulphate, heptahyrate was used .Disodium tartrate (10%) was added with constant stirring till a permanent precipitate occured. Equal amount of distilled acetone was added to get homogenous co-precipitate. The light pink precipitate of Cadium-cobalt tartarate [$CdCo_2(C_4H_4O_6)_3$ 0.5 H_2O]was filtered, washed with distilled water and air-dried at ambient temperature. Similarly,Nickel-cobalt tartrate[$NiCo_2(C_4H_4O_6)_3.H_2O$] and Copper-cobalt tartrate [$CuCo_2(C_4H_4O_6)_3$ .H_2O] were prepared by using Nickel sulphate, hexahydrate and copper sulphate, pentahydrate respectively.

The elemental analyses of carbon and hydrogen for all three tartrate compounds were done by micro analytical technique ,The metal analyses of these tartrate compounds were carried out by using the Perlein Elmer Model 3110 Atomic Absorption Spectrophotometer (AAS) employing an air acetylene flame and a hollow cathode lamp as the light source. The infrared spectra of these tartrate compounds were recorded in the region of 4000-400 cm^{-1} on the Perkin-Elmer 783 spectrophotometer using nujol mull . Thermal decompositions of tartrate compounds of each sample were recorded on Sieko instruments under static air atmosphere with 5mg sample weight using platinum crucible at the temperature range of 30-700^0 C with the heating rate of 10^{0}C. The x-ray diffraction patterns were determined on Rigaku miniflex diffractometer using CuKα radiatio (λ =1.5405 A^0.Nickel filter)

4. Results& Discussion

It is observed from the analytical data of $[CdCo_2(C_4H_4O_6)_3 0.5H_2O]$,$[NiCo_2(C_4H_4O_6)_3.H_2O]$ and $[CuCo_2(C_4H_4O_6)_3 .H_2O]$ that the elemental analysis made in weight percent for these tartrate compounds are very well matched with calculated values (Table 1). The infrared spectra of tartarate compounds of Cd-Co, Ni-Co & Cu-Co show a band at 3445cm^{-1} corresponding to the weakly bonded water of crystallization and intense band at 1604cm^{-1} due to ν_{asym} (C=0) and bonds at 1452cm^{-1} and 1375cm^{-1} due ν_{sym} (C=C) and coordinate carboxylate group [13]. In addition to this, strong bands at 1085cm^{-1} and 1045cm^{-1} indicates the presence of secondry –OH group tartrate. From these results, it can be suggested that there was no bonding with free –OH group to that metal in solid state [14]. The bidentate linkages of the carboxylate group with the metal was confirmed on the basis of difference between the unsymmetric and symmetric stretching frequencies. Hence these tartarate compounds show a chain-like polymeric octahedral structure [15].

The thermal analysis measurements confirm the presence of water of hydration for these tatrate compounds. The TG, DTG and DTA curves of these tatrate compounds under oxygen atmosphere are shown in Fig.1**.** The complete data for the observed and calculated mass losses for different stages of decomposition of compounds and the corresponding temperature ranges are shown in (Table 2).

The TG curves showed continuous mass losses between 35-190^o C in Cd-Co tartrate, 35-210^{o}C in Ni-Co tartrate and 35-240^o C in Cu-Co tartrate, indicating that the anhydrous tartrates formed at these temperatures were unstable. The decompositions of anhydrous tartrates took place in two stages with very strong exothermic peaks on DTA and DTG curves at the same temperatures. The exothermic peaks were attributed to the oxidation of Co^{2+} to $Co^{3+}$by oxygen atmosphere.

The intermediate carbonates in each compounds decomposed between 410^{0}C to 600^{o}C with the evolution of CO_2forming corresponding cobaltites. The observed mass losses were in good agreement with calculated values. The changes occured in DTA curves are at about 440^o C in Cd-Co tartrate, 370^o C in Ni-Co tartrate and 360^{o}C in Cu-Co tartrate. The gaseous products such as Ethylene CO_2 and CO obtained by thermal decompositions of tartrate compounds under oxygen atmosphere were analyzed by qualitative gas detection method. Carbon-dioxide was detected by precipitation as $CaCO_3$ from the solution of $Ca(OH)_2$ while CO is detected by reduction of iodine-pentoxide to Iodine. Ethylene gas was detected by the decolorization of bromine water (2 % Br_2 in CCl_4) or $KMnO_4$ solution.

On the basis of TG. DTG and DTA studies, the following tentative scheme is proposed for the thermal decomposition of tartrate compounds in oxygen atmosphere.

$$MCo_2(C_4H_4O_6)_3.0.5H_2O \xrightarrow{35\text{-}190^oC} MCo_2(C_4H_4O_6)_3\uparrow + 0.5H_2O$$

$$MCo_2(C_4H_4O_6)_3.MCo_2 \xrightarrow{190\text{-}340^oC} (CO_3)_3 + 2C_2H_4\uparrow + 2H_2O\uparrow + 2CO_2\uparrow + 3CO\uparrow$$

$$MCo_2(CO_3)_3 \xrightarrow{340\text{-}450^oC} MCo_2O_4 + 2CO_2\uparrow + CO\uparrow$$

Where M = Cd, Ni, Cu

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Thus, the mixed metal tartrates on thermal decomposition formed respective cobaltites as the final products. The formation of CdCo2O4 , $NiCo_2O_4$ and $CuCo_2O_4$ were confirmed by the chemical analysis , infrared spectra and X-ray diffraction studies. The experimentally observed d-spacing values and relative intensities of these cobaltites formed are shown in Table 3and were found to be well- matched with those reported in literature [16, 17, 18]. This clearly revealed the formation of desired cobaltites [19].

Table 1 : Analytical data of Cd-Co and Ni-Co Tartarate precursors.

Tartrate Compounds	Formula Weight	Elemental analysis in wt %+0.5											
		C		H		Co		Cd		Ni		Cu	
		Cald	Obsd	Cald	Obsd	Cald	Obsd	Cald	Obsd	Cald	Obsd	Cald	Obsd
$CdCo_2(C_4H_4O_6)_3.0.5H_2O$	683.27	21.07	21.49	1.90	2.34	16.18	16.69	15.40	14.98			---	----
$NicO_2(C_4H_4O_6)_3.H_2O$	638.58	22.55	22.16	2.19	2.33	17.00	17.50	---	---	8.47	9.51		
$CuCo_2(C_4H_4O_6)_3.H_2O$	643.41	22.38	21.67	2.02	1.96	17.81	16.77	--	--			9.60	9.12

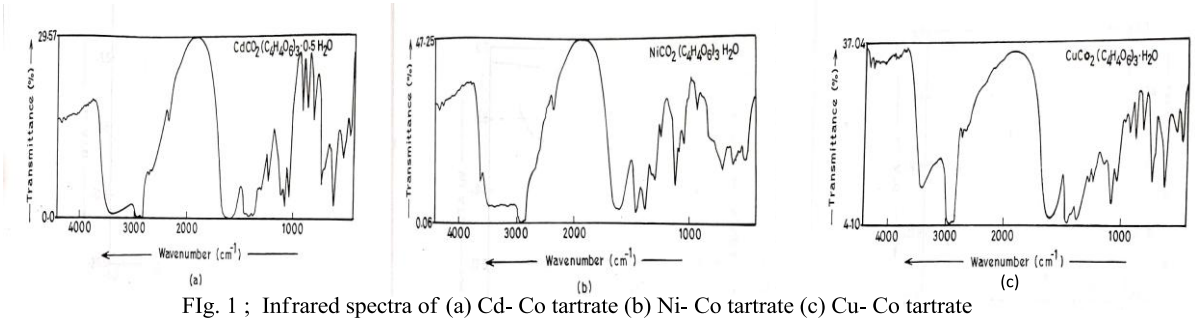

FIg. 1 ; Infrared spectra of (a) Cd- Co tartrate (b) Ni- Co tartrate (c) Cu- Co tartrate

Table 2: **TG-DTG-DTA data of tartrates of Cd-Co, Ni-Co and Cu-Co under Oxygen atmosphere.**

Compounds	TGA			DTG Peak Temp .(^OC)	DTA Peak Temp .(^OC)
	% mass loss		Temp range (^oC)		
	Obsd.	Cald.			
Cadmium-cobalt Tartrate, half hydrate $CdCo_2(C_4H_4O_6)_3.0.5H_2O$	1.79 41.81 25.29	1.32 42.12 24.60	35 -190 190-340 340-450	155 320 380	170 315 400
Nickel- cobalt Tartrate, monohydrate $Ni Co_2(C_4H_4O_6)_3.H_2O$	2.91 36.81 39.03	2.82 37.18 38.28	35- 210 210-320 320 -334	170 341 400	190 345 420
Copper-cobalt Tartrate,monohydrate $CuCo_2(C_4H_4O_6)_3.H_2O$	1.79 46.23 29.02	1.55 45.41 28.12	35 -240 240 -360 360 -460	165 318 385	180 320 390

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Table 3 : XRD Data of Cobaltites of Cd, Ni and Cu

hkl	$CdCo_2O_4$		$NiCo_2O_4$		$CuCo_2O_4$	
	Reported [16]	Obsd.	Reported [17]	Obsd.	Reported[18]	Obsd.
111	4.667(10)[a]	4.668 (15)	4.690 (14)[a]	4.669 (16)	4.460 (10)	4.691(13)
220	2.863(35)	2.873 (23)	2.869 (25)	2.838 (33)	2.855(30)	2.873(33)
311	2.440(100)	2.447 (100)	2.447 (100)	2.440(100)	2.434(100)	2.447(100)
222	2.337 (09)	2.354 (07)	2.342 (10)	2.378 (11)	2.331(10)	2.336(33)
400	2.024 (18)	2.030 (15)	2.029 (25)	2.021 (22)	2.018(20)	2.027(26)
331	1.858 (01)	1.850 (05)	1.656 (08)	1.660 (11)	1.848(15)	1.840(20)
422	1.652 (12)	1.663 (16)	1.562 (30)	1.552 (27)	1.648(10)	1.640(03)
511	1.558 (35)	1.550(30)	1.434 (45)	1.439 (41)	1.554(35)	1.559(30)

Note :- The figures in parentheses are intensities to the linewidth intensity (100).

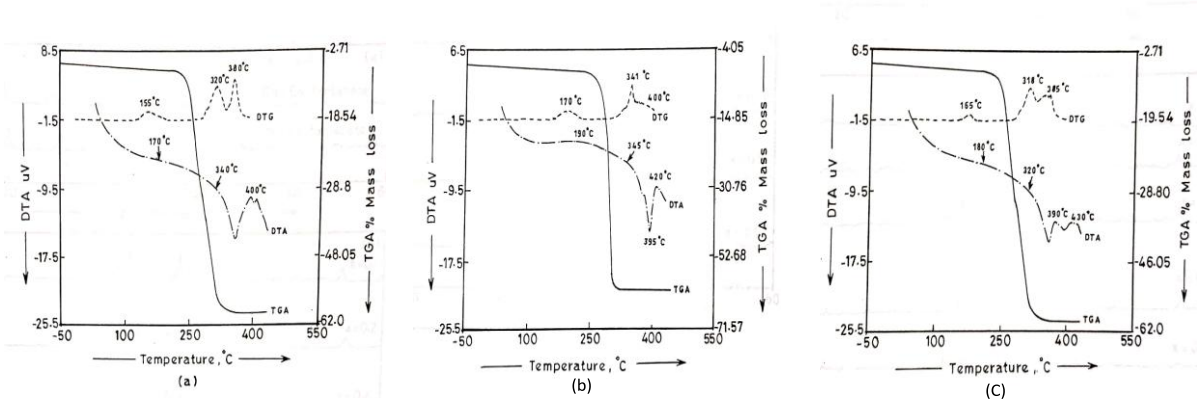

Fig. 2 ; TGA, DTG, and DTA curves for (a) Cd- Co tartrate (b) Ni- Co tartrate (c) Cu-Co tartrate

5.Conclusion:-

The tartarate compounds of Cd-Co, Ni-Co and Cu-Co were prepared by the co-precipitation method. They were characterized by the elemental analysis, metal analysis, infrared spectra. The infrared spectra of these tartrate compounds showed a chain-like polymeric octahedral structure. These tartrate compounds were thermally decomposed and decomposition reactions were studied under static air atmosphere. The dehydration was is found to be in a single stage within the temperature range 35^0-210^0C .The broad exothermic peaks were found from DTG and DTA curves. Further , the decomposition of intermediate carbonate compounds were found within the temperature range of 410^0-600^0C, which finally formed corresponding metal cobaltites. Thus, $CdCo_2O_4$, $NiCo_2O_4$ and $CuCo_2O_4$ were prepared by the thermal decomposition of corresponding tartrate compounds. The formation of these cobaltites were confirmed from metal analysis, infrared spectra, and powdered XRD. The Cobaltite's are used as catalysts [22], supercapacitors [23], and gas sensors [24].

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