Thermal Decomposition of Co-Fe-Cr-Citrate Complex Via Structural and Spectral Study.

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ABSTRACT

A Citrate gel precursor method was employed to prepare $CoFeCrO_4$. The citrate complex of cobalt-iron-chromium was investigated with the help of thermoanalytical technique. Its thermal decomposition study in air by subsequent analysis by FT-IR and XRD were studied to predict the stepwise reaction mechanism at various temperature ranges to get single phase pure spinel compound.

Keywords: Citrate precursor; TG-DTA; FT-IR; Single phase; XRD

INTRODUCTION

Homogenous and fined sized ferrospinels have huge numbers of scientific and technological applications [1-3] due to their physical, chemical and thermal stability. The ferrospinel oxides have general formula AB_2O_4, where A and B are cations with oxidation state 2+ and 3+ respectively. They have been proved as significant materials due to their interesting structural, electrical and magnetic properties [4-6]. These materials can be synthesized by various physical, chemical as well as biological methods [7-10]. Amongst them, simple and economic chemical method, citrate-gel precursor method is mostly employed by various researches to achieve stoichiometry and homogenous particle size in the mixed-metal oxides [11]. This method has great latent in the preparation of fine and uniform sized oxides having potential application as magnetic recording media, microwave devices, catalysis, gas sensors, pigments [12-14] and many more. Thermal decomposition of oxalate solid-solution precursor form fine sized oxides through the formation of various intermenidtae were reported by Schuele et.al. as well as Ravindranathan et.al. [15-16]. Gajbhiye et. al.[17] has been reported the thermal decomposition study of zinc-iron-citrate precursor while Gabal [18] work on oxalate-iron (II) oxalate mixture and Verenkar et.al. worked on thermal decomposition of hydrazinated cobalt zinc ferrous succinate as well as cobalt substituted nickel zinc ferrites from hydrazinated mixed metal fumarates [19-20]. The study on citrate solid-solution precursor and its thermal decomposition/combustion of these metal-precursors, like hydrazinium, metal –hydrazine carboxylate hydrates gives fine-particle sized mixed-metal oxides with versatile physico-chemical properties [21]. It leads to the formation of ultrafine nanoparticles. Hence an attempt had been made to study a systematic thermal decomposition of citrate precursor of Co-Fe-Cr spinel with the possible formation of intermediates which results ultrafine ferrospinel.

Experimental

Simple and economic citrate-gel auto combustion method has been employed to synthesize Cr substituted cobalt ferrite nanoparticles [07]. It offers a significant saving of time and energy consumption over traditional methods and requires less sintering temperature. Physico-chemical investigation of the dry citrate complex of CoFeCr was carried out by formation of spinel structural and thermal analysis. Structural study was followed by XRD while thermal study of in the temperature range of room temperature - 1000°C in static air at the heating rate of 10°C/min. using TG-DTA. FT-IR spectrums were recorded in the range of 400-4000 cm^{-1}.

Result and Discussion

The TG-DTA curve of citrate-precursor heated in air atmosphere is shown in Fig. 1. The above graphs reveal that the reaction steps are in the order of dehydration, decomposition of citrates and carbonates then final formation of Co-Fe-Cr oxide. An endothermic peak corresponds to the dehydration of citrate precursor. The two

close endothermic peaks result the thermal decomposition of citrate to carbonate to then formation of $CoFeCrO_4$ by solid-state diffusion process to get ($2CoO + Fe_2O_3 + Cr_2O_3$) i.e. $2CoFeCrO_4$. The observed results in the loss in masses with respect to their temperature ranges are represented in Table 1. In the Ist step, the water content numbers absorbed by the metal-citrate-precursor could be varied with respect to atmospheric humidity. The extra water molecules can be removed by heating at about 100°C. An endothermic peak at 80 - 110°C reveals the removal of co-ordinated water molecules of 10.31 % which corresponds to the loss of water molecules exclusively. On the basis of molar mass, the loss of 18 coordinated water molecules were predictable.

Nextly, in the temperature range of citrate decomposition were takes place in the temperature range 275 - 375°C with loss of 38.10 % and two endotherms at 295°C and 330°C respectively. In these two stages, decomposition is a complex reaction which involves dissociation of aconitate along with decarboxylation with the evolution of CO, H_2O, CO_2 as well as oxidation of CO to CO_2. The methylene proton could be oxidizing to water vapors. These results are correlated and are agree well with DTA curve. The sharp peak at 350°C indicates the possibility of decomposition of whole citrate-complex form Co-O with evolution of CO_2 & H_2O [17]. In the same temperature range the ($FeO{\cdot}OH$) and ($CrO{\cdot}OH$) get decompose to form their oxides as Fe_2O_3 & Cr_2O_3 respectively. The notable peak at 520°C gives the formation of $CoFeCrO_4$ phase initiated by solid-state diffusion process, $2CoO + Fe_2O_3 + Cr_2O_3 \qquad 2CoFeCrO_4$.

The IR bands for precursor, metal-precursors and various products of thermal decomposition of citrate precursor are represented in Table 2 & 3. The broad peak in the region of 3000-3600 cm^{-1} & 1600 cm^{-1} could be due to the presence of water which goes to be decrease in the intensity with the heating process. Similar behavior is obtained at 1718, 1559, 1443, & 1255 cm^{-1} which is due to the loss of coordinated water molecules. The band appear at 1254 cm^{-1} is due to formation of metal-hydroxo complex {(δ MOH) $_{\text{bending mode}}$} which is weak and disappear at 420°C. It could be the formation of aconitate-metal complex [18]. Further it goes on decomposition which reveals by the absence of band in the range of 2950 – 2850 cm^{-1} while the formation (δ H-OH) at 1609 cm^{-1} by the formation of $FeO{\cdot}OH$ & $CrO{\cdot}OH$ at 280 - 350°C. Over here citrate group is oxidize totally i.e. disappearance of ν(CH), $\nu_{asym.}$(C=O), ν (CO_3) / $\nu_{asym.}$(CO_3). Some bands at 1511, 1106 and 870 cm^{-1} gives the formation of hrdrocobaltite and carbonates which were not observed after 400°C, result the almost complete decomposition of carbonates to form oxides. A weak band at about 2350 cm^{-1} is due to the free CO_2 after 400°C. X-ray diffraction pattern of sintered sample (500°C) which is decided after thermal study reveals the formation of single phase cubic spinel structure as shown in Fig. 2.

CONCLUSION

The citric acid could be a desired precursor to get ultrafine sized mixed-metal oxide. The decomposition mechanism of the citrate-precursor in air is predicted in various thermal stages. Many of the thermal parameters like decomposition rate, decomposition temperature and heat dissipation with respect to evolution of various gases / vapors to form $CoFeCrO_4$. The FT-IR study is quite well agreeing with thermal decomposition study to decide sintering temperature and get single phase spinel compound.

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Fig. 1 TGA and DTA curve for citrate precursor of CoFeCr (before sintering)

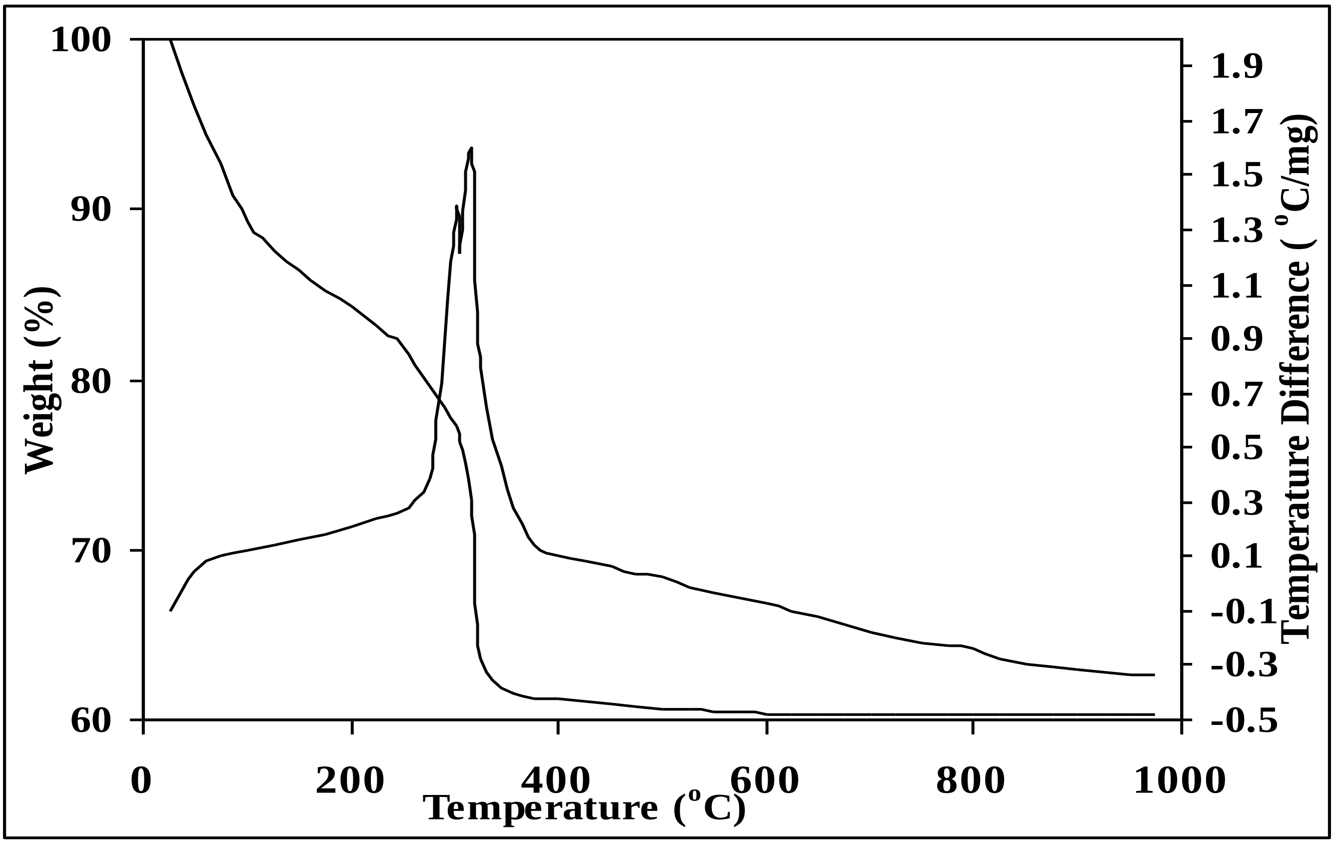

Fig. 2 XRD pattern of $CoFeCrO_4$

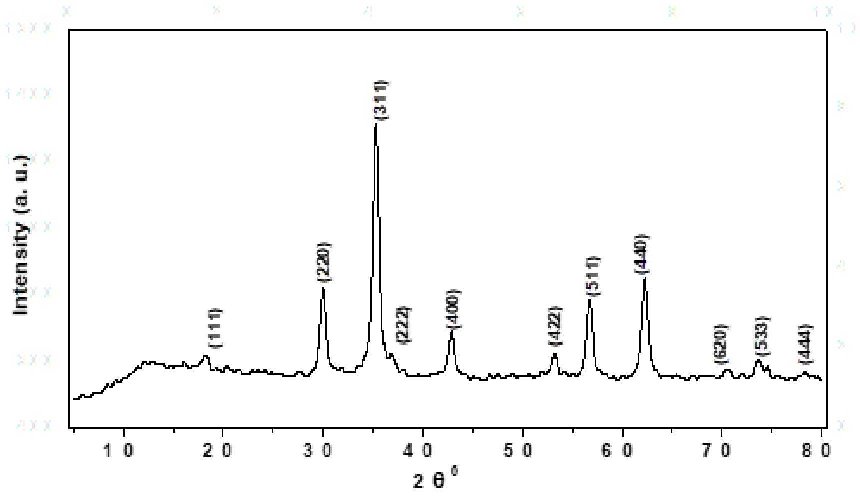

Table 1. Losses in mass in the thermal decomposition of Co-Fe-Cr-Citrate Complex.

Peak Temp. (°C)	Temperature Range (°C)	Loss of mass (%)	Molecular Formula
	25 - 800	-	$(CoFeCr)_3(C_6H_5O_7)_8.18H_2O$
85	80 – 200	10.31	$(CoFeCr)_3(C_6H_5O_7)_8$ [M-aconitate]
295	220 – 300	6.58	$Co_6(CO_3)_2.6(OH)+6(CrO.OH)+ 6(FeO.OH)$
330	300 – 400	31.50	$Co_6CO_2 + (Cr_2O_3)\ CO_2 + (Fe_2O_3)\ CO_2$
430	450 – 500	0.86	$(CoFeCrO_4)_6.CO_2$
510	500 – 600	1.20	$CoFeCrO_4$

Table 2 FT-IR spectral frequency assignments of various compounds (cm^{-1})

Citric Acid	**Precursor**	**Fe-Citrate**	**Assignment**
$3497_{(vs)}$	$3412_{(s)}$	$3412_{(s)}$	ν (OH) hydroxyl
$3291_{(vs)}$	$3236_{(br)}$	$3239_{(br)}$	ν (OH) water
2910 - $2880_{(br)}$	$2951_{(s)}$	2950-$2850_{(br)}$	ν (CH)
$1744_{(vs)}$, $1705_{(vs)}$	$1718_{(vs)}$, $1611_{(vs)}$, $1561_{(vs)}$	$1718_{(vs)}$, $1611_{(vs)}$, $1561_{(vs)}$	$\nu_{asym.}$(C=O) δ(H-OH) ν_{asym} (COO) Carboxylate
$1426_{(s)}$, $1309_{(s)}$	$1440_{(s)}$, $1390_{(s)}$	$1440_{(s)}$, $1390_{(s)}$	ν_{asym} (COO)
1239 - 1140 $_{(s)}$	1260-$1195_{(br)}$	1255 $_{(m)}$	δ(M-OH)

1086 - 1065 $_{(sh)}$	1081$_{(m)}$	1116$_{(m)}$	Citrate
942$_{(s)}$	987$_{(s)}$	978-956$_{(m)}$	
775$_{(vs)}$	851$_{(vs),}$ 804$_{(m)}$	804$_{(m)}$	
640$_{(m)}$	652$_{(sh)}$	673$_{(sh)}$	
597$_{(m)}$	609$_{(s)}$	565$_{(sh)}$	

Table 3 FT-IR spectral assignments for metal-citrate complex and decomposition products (cm^{-1})

Assignment	85°C	295°C	330°C	430°C	510°C
ν (OH) hydroxyl	3412$_{(s)}$	3412$_{(s)}$	3412$_{\mathbf{(br)}}$	3412$_{\mathbf{(br)}}$	-
δ(H-OH) water	1609$_{(s)}$	1609$_{(s)}$	1609$_{(w)}$	1609$_{(w)}$	1609$_{(w)}$
ν $_{asym.}$(C=O)	1718 $_{(s)}$	1718 $_{(w)}$	1718 $_{(w)}$	-	-
ν $_{asym}$ (COO) Carboxylate	1559 $_{(s)}$	1559 $_{(m)}$	1559 $_{(m)}$	-	-
ν $_{asym}$ (COO)	1443 $_{(m)}$	1443 $_{(vw)}$	-	-	-
δ(M-OH)	1252 $_{(m)}$	1252 $_{(w)}$	1252 $_{(vw)}$	-	-
ν (CO_3)	-	870 $_{(m)}$	-	-	-
ν (CO_2)	-	-	-	2350$_{(w)}$	2350$_{(w)}$
ν (CH)	2950-2850 $_{\mathbf{(br)}}$	2950-2850 $_{\mathbf{(w)}}$	-	-	-
ν $_{asym.}$(CO)	1718$_{(s)}$	1718$_{(s)}$	-	-	-
δ(M-OH)	1252$_{(m)}$	1252$_{(m)}$	-	-	-
ν (Fe-O) / (Cr-O)	614$_{(m)}$	614$_{(m)}$	614$_{(m)}$	614$_{(m)}$	614$_{(m)}$
	480$_{(m)}$	480$_{(m)}$	480$_{(m)}$	480$_{(m)}$	480$_{(m)}$

Abbreviations: s – strong, br-broad, m – medium, w – weak, vw – very weak, sh-shoulder