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Thermal decomposition and structural elucidation of Cobalt-Iron-Chromium citrate precursor.

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Abstract:

Citrate precursor sample of CoFeCr metal ions was under investigation for thermogravametric analysis (TG-DTA). The scanned TG-DTA curve provides different kinds of kinetic as well as thermodynamic parameters. A well-known Coat-Redfern and Piloyan - Novicova method was employed for the said study. These thermal study helps to elect the desired sintering temperature to get anticipated compound. Pure and single phase formation of the compound was evaluated by powder X-ray diffraction (XRD) study.

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

1. Introduction

Oxides of two or more different kinds of cations are known as mixed-metal oxides. Among the mixed-metal oxides, spinel-type oxides are remaining prominent. The spinel oxides have general formula AB_2O_4, where A and B are cations with oxidation state 2+ and 3+ respectively. Spinel ferrites are very important materials due to their interesting structural, electrical and magnetic properties [1-3]. These properties are varying with their nature of ions, charge distribution and site preference energy among tetrahedral and octahedral sites. These compounds are technologically important and have been utilized in many applications viz. magnetic recording media, microwave devices, catalysis, gas sensors and pigments [4-11] and many more. The numerous uses of ferrospinels as selective and active catalysts for many organic transformation reactions are well known. Catalytic decomposition of alcohols, phenols and toluene [12-14], oxidation of alcohols [15-16], Friedel-Craft's alkylations and acylations [17-22], hydrogenation- dehydrogenation reactions [23-25], oxidation of carbon monoxide, H_2, methane, methanol [26-30] and benzoylation of toluene [31] etc. have been investigated in detail.

Spinel ferrites have also proved the ability as gas sensors and have been investigated for detection of both oxidizing and reducing gases. Different ternary oxides viz. $NiFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $CdFe_2O_4$ and noble metal doped spinel ferrites have been extensively studied for various oxidizing gas sensors [32-37]. These

electric, magnetic, catalytic and gas sensing activities of the materials are mainly depending upon their variable oxidation state, high surface area and uniform morphology

2. Experimental:

In the present investigation, the citrate-gel auto combustion method has been employed to synthesize Cr substituted cobalt ferrite nanoparticles [38]. It is a simple process, which offers a significant saving of time and energy consumption over traditional methods and requires less sintering temperature. The method was employed to reach improved powder characteristics, uniform grains and narrow particle size, thereby influencing structural, electrical and magnetic properties of ferrospinels. To investigate the formation of spinel structure, thermal analysis of dry citrate complexes of CoFeCr was carried out in the temperature range of room temperature - 1000°C in static air at the heating rate of 10°C/min. Various thermodynamic and kinetic parameters were also calculated from its study. To find out the kinetic parameters in spinel formation, Coat - Redfern [39] and Piloyan - Novicova [40] methods were applied. Room temperature XRD pattern was taken to confirms the phase formation.

3. Result and Discussion:

The TG-DTA curve for one of the dried citrate precursor form of CoCrFe oxide is shown in Fig 1. From TG-DTA curve, it is observed that, there is a gradual weight loss in the spinel formation up to 400°C [41]. Increase in temperature above 240°C, the loss of mass is slow, gradual which might be due to decomposition of mixed-metal citrate complexes by fragmentation of organic content. The purpose of this study is to obtain the detailed information concerning thermal stability of various substances in order to understand the decomposition reaction processes and access the corresponding thermal effect. Their thermodynamic and kinetic parameters were investigated in detail [42-44]. Thermogravimetry has been proved the importance of determination of nature of water and thermal decomposition of the precursor. A sharp exothermic peak in DTA curve in the temperature of 275-375°C indicates simultaneous decomposition of anhydrous precursor and formation of spinel ferrite [45]. Almost complete decomposition of organic substances were takes place at about 500˚C and is followed by single phase spinel formation.

Thermal decomposition appears to occur in two stages and their various thermokinetic parameters are shown in Table 1. In first stage, activation energy (Ea) is in the range of 11.04 to 11.49 kJ mol^{-1} for the precursors under study, while for second stage the activation energies are between 95.04 to 97.26 kJ mol^{-1} as listed in Table 2. Two stage decomposition of the sample were also reflected from the plots of ln [α /T^2] vs 1000/T (Fig. 2) and ln [$g(\alpha/T^2$] vs 1000/T (Fig. 3). The obtained values of frequency factor (log z) and entropy (ΔS) are in good agreement by both the methods. The negative values obtained for entropy of activation indicate that the reactions are slower than normal [46]. Above thermal data reflects that, 500˚C could be desired sintering temperature for single phase formation. Hence the sintered sample was scanned by XRD. The obtained X-ray diffraction pattern has no any additional peak rather than cubic spinel structure of $CoFeCrO_4$ reveals purity of spinel phase compound ((Fig. 4).

4. Conclusion:

Thermogravimetric tool (TG-DTA) is successfully applied to decide the sintering temperature to get single phase cubic spinel $CoFeCrO_4$ compound and it's confirmed by XRD study. Various theromkinetic parameters and thermal decomposition mechanism is studied by both the methods and they are in good agreement with each other. Broad X-ray peak pattern of the compound reveals the nanosized range of the material.

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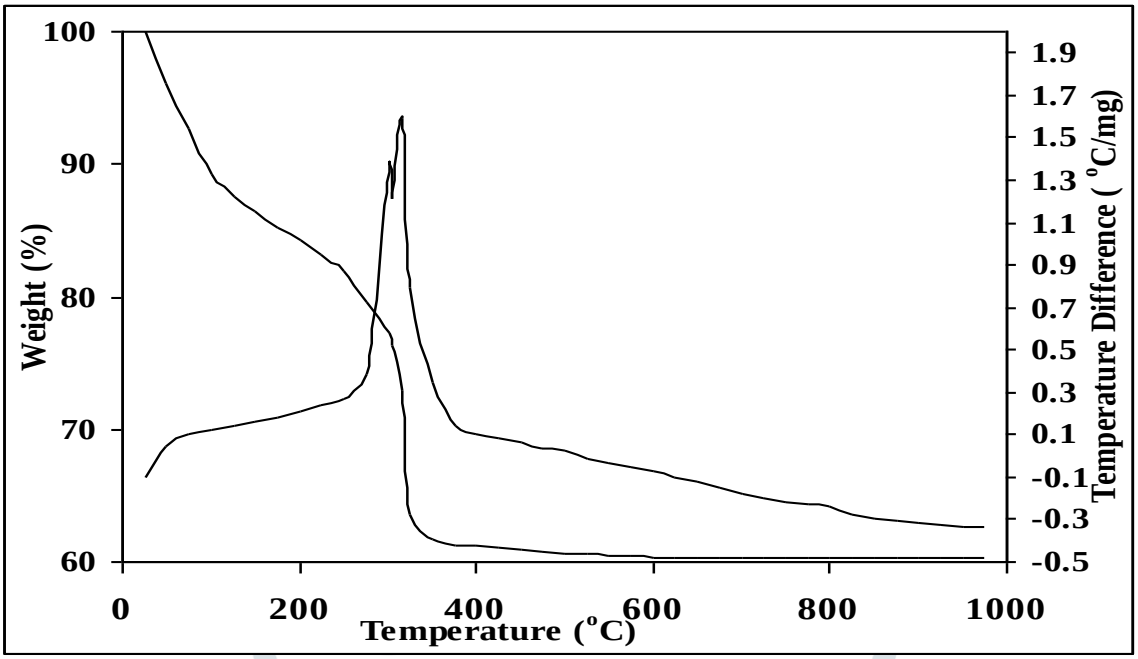

Fig. 1 TGA and DTA curve for citrate precursor of CoFeCr (before sintering)

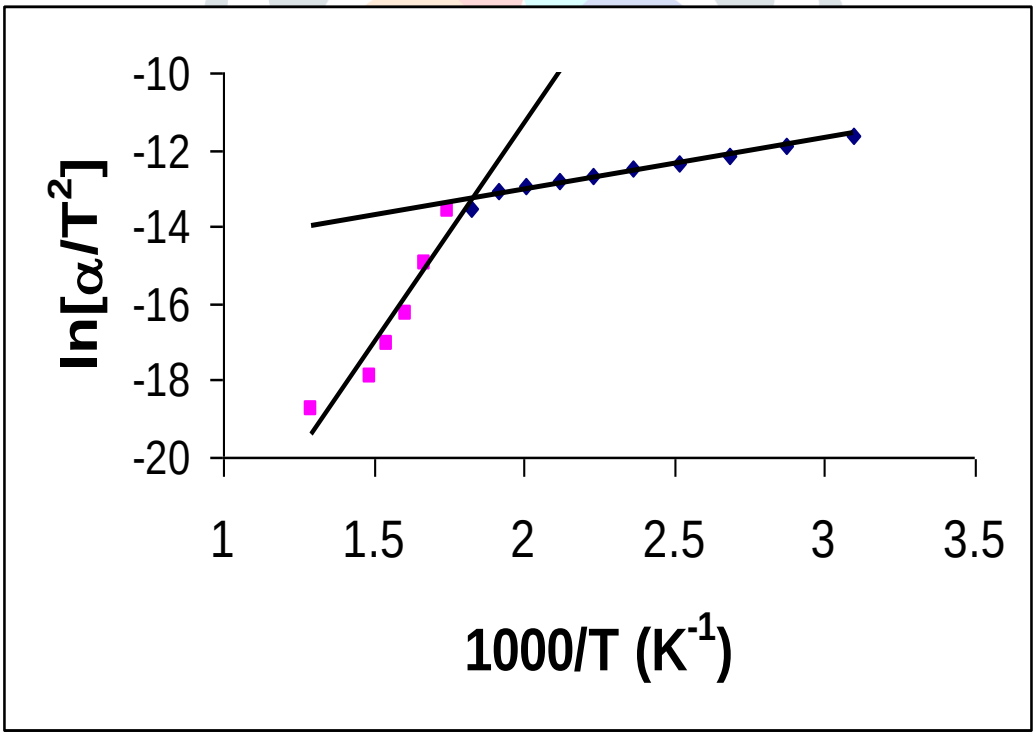

Fig. 2 Graph of ln [α /T^2] vs. 1000/T for citrate precursor of CoFeCr (before sintering)

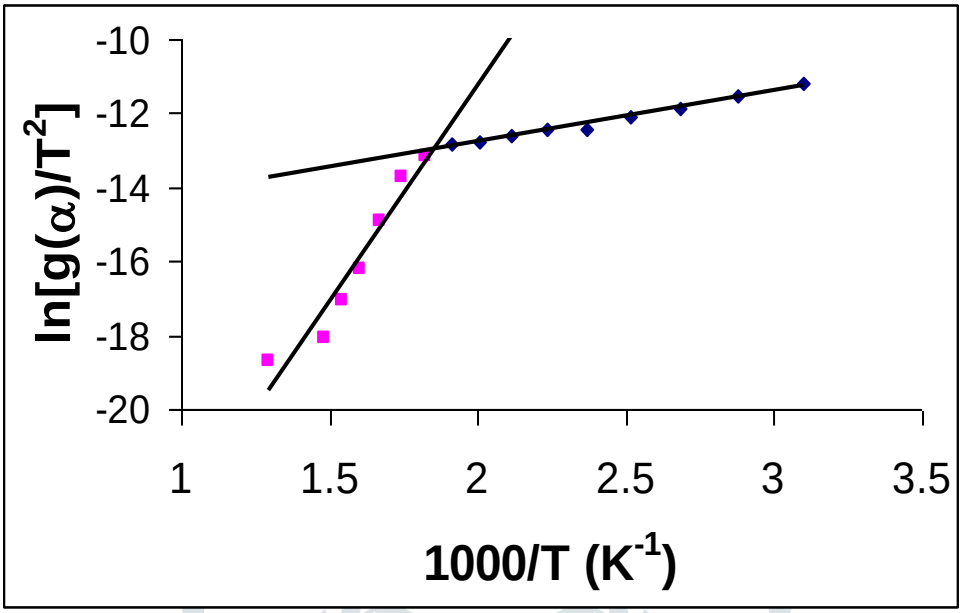

Fig. 3 Graph of ln [g (α)/T^2] vs. 1000/T citrate precursor of CoFeCr (before sintering)

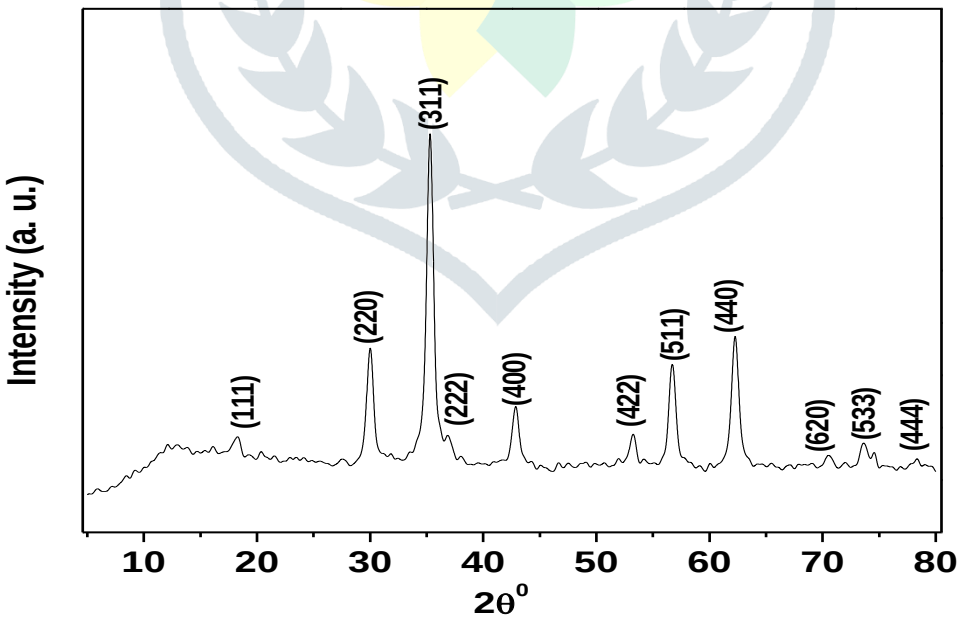

Fig. 4 XRD pattern of $CoFeCrO_4$

Table No. 1 Evaluation of kinetic parameters of citrate precursor of CoFeCr (before sintering)

W_0 = 6.4177 mg

Sr. No	Temp. (^{0}C)	Residual Weight (Wt) mg	$\alpha = \frac{W_t - W_f}{W_0 - W_f}$	ln [α /T^2]	g (α)	ln [g(α)/ T^2]	1000/T (K^{-1})
1	50	6.2038	0.9166	-11.6423	1.4266	-11.2028	3.0959
2	75	5.9898	0.8331	-11.8870	1.1830	-11.5363	2.8753
3	100	5.7759	0.7499	-12.1309	1.0001	-11.8431	2.6809
4	125	5.6475	0.6999	-12.3297	0.9044	-12.0733	2.5125
5	150	5.5621	0.6666	-12.5003	0.8452	-12.4297	2.2321
6	175	5.4979	0.6416	-12.6533	0.8024	-12.4297	2.2321
7	200	5.4337	0.6166	-12.8017	0.7618	-12.5902	2.1141
8	225	5.3694	0.5903	-12.9483	0.7200	-12.7497	2.0080
9	250	5.2840	0.5583	-13.1020	0.6710	-12.9181	1.9120
10	275	5.1342	0.5000	-13.3056	0.5858	-13.1478	1.8246
11	300	4.7064	0.3333	-13.8000	0.3670	-13.7041	1.7452
12	325	4.1502	0.1167	-14.9353	0.1209	-14.8909	1.6722
13	350	3.9342	0.0333	-16.2712	0.0336	-16.2023	1.6051
14	375	3.8935	0.0167	-17.0419	0.0168	-17.0341	1.5432
15	400	3.8721	0.0084	-17.8113	0.0084	-18.0800	1.4858
16	500	3.8615	0.0042	-18.7732	0.0044	-18.7260	1.2936

Table No 2 Thermokinetic parameters of the precursor samples of the $CoCrFeO_4$ (before sintering)

Compound	Method	Step	TGA Activation energy (E) kJ mol^{-1}	Frequency factor (log z)	Entropy (ΔS) kJ mol^{-1+}
$CoFeCrO_4$	Coat- Redfern	I	11.49	6.23	-139.12
		II	97.26	8.68	-87.97
	Piloyan- Novicova	I	11.04	6.29	-138.64
		II	95.04	8.70	-88.12