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PREPARATION AND CHARACTERIZATION OF $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$
A precursor to prepare $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles

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A good precursor is foremost in the preparation of nanosized metal or mixed metal oxides. In the present study a novel precursor, cobalt zinc fumarato–hydrazinate $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ has been prepared which decompose at a much lower temperature to give nanosized mixed-metal oxides. X-ray investigations, confirms the formation of single spinel phase. The FTIR spectra show N–N stretching vibration at 965 cm^{-1} which confirms the bidentate bridging hydrazine. The thermal decomposition of the precursor has been studied by isothermal, thermogravimetric and differential scanning calorimetric analysis. The precursor shows two-step dehydrazination followed by decarboxylation to form $Co_{0.5}Zn_{0.5}Fe_2O_4$, the chemical analysis of the sample is corroborative of this.

Keywords: *autocatalytic decomposition, FTIR spectra, hydrazine carboxylate precursor, thermal analysis*

Introduction

Transition metal oxides are a well established class of materials having diverse application due to their useful properties like magnetic, electrical, catalytic, etc. [1–10]. A lot of research has been dedicated to synthesize such metal oxides having uniform nanosized particles and improved properties [11–15]. The method which we have been using for the preparation of nanosized metal oxide deals with the decomposition of a precursor having hydrazine and carboxylate bonded to metal ions.

The chemistry of hydrazine is interesting with respect to its ability to form complexes with transition metals. The thermal reactivity of metal–hydrazine complexes is also noteworthy, as the stability of complexes changes dramatically depending upon the cation and anion [16]. Hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes [17, 18]. These metal–hydrazine complexes, such as metal succinato hydrazinates are good precursors to obtain nanosized mixed metal oxides [17, 19, 20]. Many authors have investigated various organic-inorganic materials and also characterized them using various techniques such DSC, DTA, TG, SEM, TEM, XRD, AAS and FTIR spectroscopy [21–56]. Here we are reporting the synthesis, characterization and thermal decomposition of one such precursor namely, cobalt zinc ferrous fumarato–hydrazinate and its autocatalytic thermal decomposition to $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles.

Experimental

Preparation of cobalt zinc ferrous fumarato–hydrazinate

The method employed for the synthesis of cobalt zinc fumarato hydrazinate is similar to the one described elsewhere [57]. A requisite quantity of sodium fumarate in aqueous medium was stirred with hydrazine hydrate, $N_2H_4{\cdot}H_2O$ (99–100%) in an inert atmosphere for 2 h. To this, a metal ion solution containing cobalt, zinc and iron in stoichiometric amount was added dropwise with constant stirring. The precipitate thus obtained was filtered, washed with ethanol, dried with diethyl ether and stored in vacuum desiccators.

Methods

The hydrazine content in the sample was determined by titration using KIO_3 as the titrant [58] The percentage of cobalt, zinc and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [58]. The metal content in the sintered oxide sample were also determined by EDS.

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Table 1 Chemical and thermal analysis of cobalt-zinc ferrous fumarato hydrazinate

Precursor	Cobalt		Zinc		Iron		Hydrazine		Total mass loss		TG data		DSC peak/
	%										Temp. range/	Mass loss/	°C
	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	°C	%	
$Co_{0.5}Zn_{0.5}Fe_2$ $(C_4H_2O_4)_3$ $\cdot 6N_2H_4$	12.24	12.39	13.10	13.75	46.54	46.96	26.86	27.12	65.98	66.40	rT–120 120–160 160–410 410–900	4.1 26.43 34.17 2.35	88.7 (exo) 145.9 (exo) 196 (exo) 315 (exo) 356.6 (exo)

Infrared analysis of the precursor and its thermal products, i.e. $CoZnFe_2O_4$ was carried out on a Shimadzu FTIR (IR Prestige-21) instrument.

Simultaneous, differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were carried out on Netzsch, STA 409 PC (Luxx) analyzer, from RT to 900°C in dry air. The heating rate was maintained at 10°C min^{-1}. The isothermal and total mass loss studies of the sample were carried out at different predetermined temperatures. The isothermal products were also chemically analysed for its hydrazine content and characterized by infrared spectral analysis.

Autocatalytic decomposition of the precursor

The dried precursor was spread on a Petri dish and a burning splinter was brought near to it, a small portion of its caught fire which spread immediately to the entire bulk. Thus the precursor decomposed autocatalytically in an ordinary atmosphere.

Results and discussion

Chemical formula determination of cobalt zinc ferrous fumarato hydrazinate

The infrared spectra of the complex (Fig. 1) show three absorption bands in the region 3190–3310 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequencies at 970–960 cm^{-1} unambiguously prove the bidentate bridging nature of the hydrazine ligand. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1650 and 1370 cm^{-1}, respectively with the $\Delta\nu$ (ν_{asy}–ν_{sym}) separation of 280 cm^{-1}, which indicate the monodentate linkage of both carboxylate groups in the dianion. The IR data thus confirms the formation of cobalt zinc ferrous fumarato–hydrazinate complex.

The chemical formula, $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ has been assigned to the complex, cobalt zinc ferrous fumarato–hydrazinate based on the observed percentage of hydrazine (26.86), cobalt (12.24), zinc (13.10) and iron (46.54) which match closely with the calculated values of 27.12, 12.39, 13.75 and 46.96% for hydrazine, cobalt, zinc and iron, respectively (Table 1). Similarly, the observed mass loss of 65.98% in total mass loss studies (~800°C) matches with the calculated value 66.40% based on the above mentioned formula.

Thermal analysis of the precursor

The TG-DSC trace of thermal decomposition of $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3{\cdot}6N_2H_4$ is shown in Fig. 2. The TG curve, from room temperature to 900°C shows four mass loss steps with two major ones (Table 1). The mass losses of 4.1 and 26.43% from rT to 120°C and from 120 to 160°C were due to the loss of one N_2H_4 and five N_2H_4 molecules, respectively. DSC curve shows a weak exothermic peak at 88.7°C followed by a sharp exothermic peak which is due to dehydrazination. The major mass loss of 34.17% on the TG curve from 160 to 410°C is attributed to the decarboxylation of dehydrazinated fumarate precursor. DSC curve shows three more exothermic peaks in this region with the peak temperature at 195, 315 and 356.6°C, respectively due to the three-step oxidative decarboxylation. A marginal mass loss of 2.35% was observed from 410 to 900°C on the TG curve due to the oxidation of unburned carbon. Mass loss studies carried out at 400°C shows that total mass loss of 66.36% takes place at 400°C. It has been reported that the hydrazinated precursors loses the hydrazine molecules in presence of air between 150–300°C [19]. It reacts explosively with atmospheric oxygen liberating enormous amount of energy which is sufficient to oxidatively decompose the hydrazinated complex into its respective metal oxide. The single phase $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticle formation in the present study soon after the autocatalytic thermal decomposition has been confirmed by XRD.

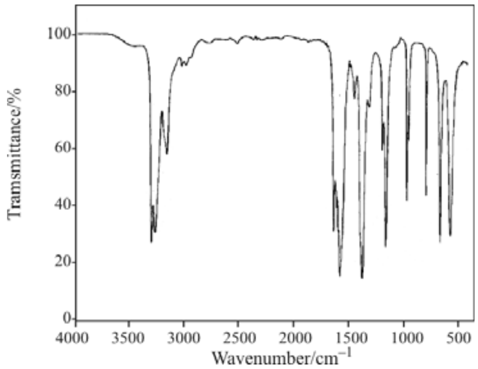

Fig. 1 Infrared spectra of $Co_{0.5}Zn_{0.5}(C_2H_2O_4)_3{\cdot}6N_2H_4$

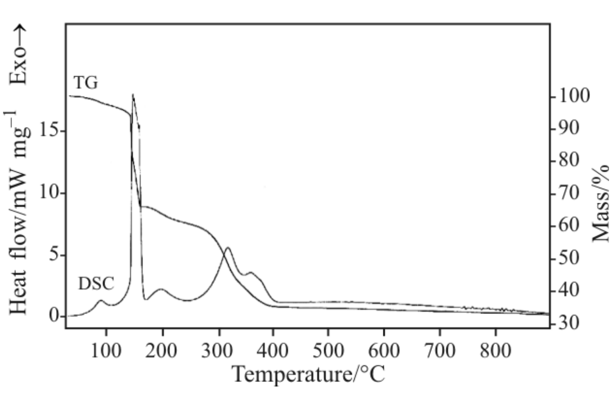

Fig. 2 TG-DSC curves of $Co_{0.5}Zn_{0.5}(C_2H_2O_4)_3{\cdot}6N_2H_4$

Conclusions

The synthesis of transition metal oxides via the metal–fumarate hydrazinate precursor is a convenient synthetic route to prepare nanosized mixed metal oxides. In this method hydrazine complex exhibits an autocatalytic behaviour after ignition in air. The precursor decomposes autocatalytically on ignition forming nanosize $Co_{0.5}Zn_{0.5}Fe_2O_4$.

The chemical analysis, total mass loss, and infrared spectral analysis of the complex confirms the formation of the complex $Co_{0.5}Zn_{0.5}Fe_2(C_4H_2O_4)_3\cdot 6N_2H_4$.

TG-DSC studies of the complex show two-step dehydrazination followed by three-step decarboxylation to form single phase $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles. This is confirmed by XRD studies.

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