Synthesis of cobalt nickel ferrite nanoparticles via autocatalytic decomposition of the precursor

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Abstract The chemistry, structure, and properties of spinel ferrites are largely governed by the method of preparation. The metal carboxylato-hydrazinate precursors are known to yield nanosized oxides at a comparatively lower temperature. In this study, we are reporting the synthesis of one such precursor, cobalt nickel ferrous fumarato-hydrazinate which decomposes autocatalytically to give cobalt nickel ferrite nanoparticles. The XRD study of this decomposed product confirms the formation of single-phase spinel, i.e., $Co_{0.5}Ni_{0.5}Fe_2O_4$. The thermal decomposition of the precursor has been studied by isothermal, thermogravimetric (TG), and differential scanning calorimetric (DSC) analysis. The precursor has also been characterized by FTIR, EDX, and chemical analysis, and its chemical composition has been determined as $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3 \cdot 6N_2H_4$.

Keywords Nanoparticles · Ferrite · Autocatalytic decomposition · Fumarato-hydrazinate precursor

Introduction

There has been a surge of research reports focusing on nanosized magnetic materials, having significant potential for many applications [1–6]. Research in this area for better and improved materials still continues. In recent times, many innovative synthetic strategies [7–12] have been devised which have led to engineering new and efficient materials exhibiting fascinating properties.

Over the years, our research group has been involved in synthesizing nanomaterials from novel precursors which are hydrazine derivatives of metal carboxylates [13–22]. The chemistry of hydrazine is of particular interest since it forms a number of complexes with transition metals, and being a fuel, it not only supports combustion but also lowers the decomposition temperature of the metal complexes [18, 19]. Thermal analysis, X-ray, and spectral studies are very important techniques for material characterization. Therefore, many authors have used these techniques for various materials characterization [23–55]. Here, we are reporting the synthesis, X-ray and spectral characterization, and thermal decomposition of a new precursor, cobalt nickel ferrous fumarato-hydrazinate, which decomposes autocatalytically to give nanosized $Co_{0.5}Ni_{0.5}Fe_2O_4$.

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Experimental

Preparation of cobalt nickel ferrous fumarato-hydrazinate

The cobalt nickel ferrous fumarato-hydrazinate precursor was synthesized by employing the method first devised by our group [20]. 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 mixed metal ion solution containing cobalt, zinc, and iron in stoichiometric amount was added dropwise with constant stirring. The precipitate thus obtained was filtered off, washed with ethanol, dried with diethyl ether, and stored in vacuum desiccators.

Methods of characterization

The precursor was chemically analyzed by titration to determine its hydrazine content using KIO_3 as the titrant [56]. The percentage of cobalt, nickel, and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [56]. The metal content in the sintered oxide sample was also determined by EDX. Infrared analysis of the precursor and its thermal products, i.e., $Co_{05}Ni_{05}Fe_2O_4$ was carried out on a Shimadzu FTIR IR Prestige-21 spectrophotometer.

The thermal decomposition pattern of the precursor was studied by simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis on a NET-ZSCH, 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 also carried out at different predetermined temperatures.

Autocatalytic decomposition of the precursor

The dried precursor was spread on a Petri dish and ignited with a burning splinter. A small portion of it caught fire which spread immediately to the entire bulk. The precursor decomposes autocatalytically in this manner in an ordinary atmosphere to yield nanosized particles of the ferrite.
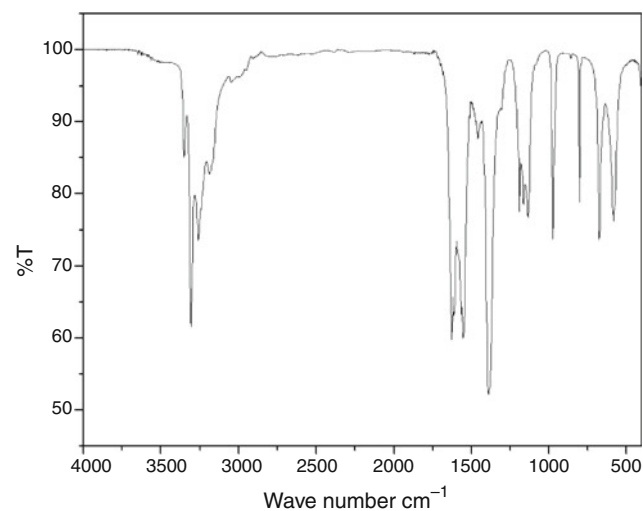
Results and discussion

Chemical formula determination of cobalt nickel ferrous fumarato-hydrazinate

The infrared spectra of the complex (Fig. 1) show three absorption bands in the region 3,150–3,300 cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequencies at 975 cm^{-1} prove the bidentate bridging nature of the hydrazine ligand unequivocally. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1,590 and 1,370 cm^{-1}, respectively, with the Δv ($v_{asy} - v_{sym}$) separation of 220 cm^{-1}, which indicate the monodentate linkage of both carboxylate groups in the dianion. The IR data confirm the formation of cobalt nickel ferrous fumarato-hydrazinate complex.

The chemical formula $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$ has been assigned to the complex cobalt nickel ferrous fumarato-hydrazinate based on the observed percentage of hydrazine (26.84), cobalt (12.53), nickel (12.49), and iron (47.52) which match closely with the calculated values of 27.25, 12.56, 12.51, and 47.63% for hydrazine, cobalt, nickel, and iron, respectively (Table 1). Similarly, the observed mass loss of 65.92% in total mass loss studies ($\sim$800 °C) matches with the calculated value 66.71% based on the above-mentioned formula.
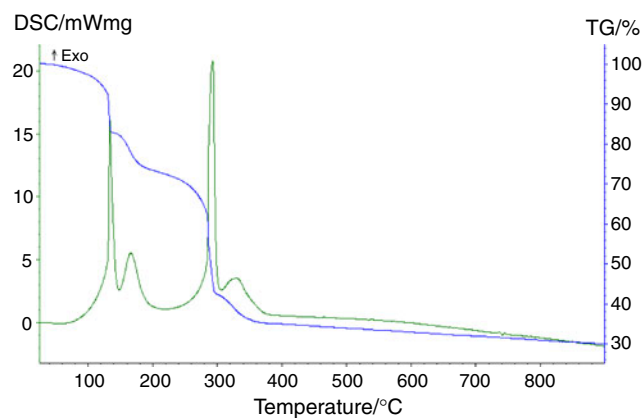

Fig. 1 Infrared spectra of $Co_{0.5}Ni_{0.5}(C_4H_2O_4)_3\cdot6N_2H_4$

Fig. 2 TG-DSC curves of $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$

Table 1 Chemical analysis and total mass loss data of cobalt nickel ferrous fumarato-hydrazinate precursor, $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$

Complex	Cobalt/%		Nickel/%		Iron/%		Hydrazine/%		Total mass loss/%	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$	12.53	12.56	12.49	12.51	47.52	47.63	26.84	27.25	65.92	66.71

Table 2 TG-DSC data of cobalt nickel ferrous fumarato-hydrazinate precursor, $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$

Complex	TG		DSC	Remarks
	Temp range/°C	Mass loss/%	Peak temp/°C	
$Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$	RT-135	18.12	133.5 (exo)	Loss of four N_2H_4 molecule
	135–170	9.08	165.6 (exo)	Loss of two N_2H_4 molecule
	170–300	31.22	291.7 (exo)	Two-step decarboxylation of dehydrazinated precursor
	300–375	7.05	328.6 (exo)	
	375–900	5.20	–	

Thermal analysis of the precursor

The TG-DSC curves of thermal decomposition of $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$ are shown in Fig. 2. The TG curve from room temperature to 900 °C shows four mass loss regions with two major ones (Table 2). The mass losses of 18.12 and 9.08% from room temperature (RT) to 135 °C and from 135 to 170 °C were due to the loss of four N_2H_4 and two N_2H_4 molecules, respectively. The DSC curve shows a corresponding sharp exotherm with a peak at 133.5 °C followed by another small exotherm with a peak at 165.6 °C due to dehydrazination as explained above. The major mass loss of 31.22% followed by minor mass loss of 7.05% from 170 to 300 °C and from 300 to 375 °C, respectively, on the TG curve was due to two-step decarboxylation of dehydrazinated fumarate precursor. DSC curve shows one sharp exothermic peak followed by an exothermic hump in this region with the peak temperature at 291.7 and 328.6 °C, respectively, due to this two-step oxidative decarboxylation. A marginal mass loss of 5.2% was observed from 375 to 900 °C on the TG curve due to the oxidation of unburned carbon.

The mass loss studies of the precursor carried out separately at 400 °C show total mass loss of 65.92%. It has been reported that the hydrazinated precursors lose the hydrazine molecules in presence of air between 100 and 300 °C [18]. 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 formation of monophasic $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles soon after the autocatalytic thermal decomposition of the precursor has been confirmed by XRD. The bands in the IR spectra of $Co_{0.5}Ni_{0.5}Fe_2O_4$ are in agreement with the reported ones [8].

Conclusions

The mixed metal fumarato-hydrazinate precursor offers a convenient synthetic route to prepare nanosized mixed metal oxides. The hydrazine precursor exhibits autocatalytic decomposition behavior after ignition in air, forming nanosize $Co_{0.5}Ni_{0.5}Fe_2O_4$ in this study too. The chemical analysis, total mass loss, and infrared spectral analysis of the complex confirms the formation of the complex with the formula $Co_{0.5}Ni_{0.5}Fe_2(C_4H_2O_4)_3\cdot6N_2H_4$. The TG-DSC studies of the complex show two-step dehydrazination followed by two-step decarboxylation to form single-phase $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles. The formation of $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles was confirmed by XRD and IR.

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