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Research Article

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Synthesis, characterization, infrared studies, and thermal analysis of bimetal carboxylates and its decomposition product Co_2NiO_4

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ABSTRACT

A good precursor is foremost in the preparation of nanosized metal or mixed metal oxides. Metal carboxylate-hydrazinates are very good precursors for the synthesis of metal as well as mixed metal oxides as these, most of the times decomposes to nanosized oxides with high surface area at comparatively lower temperatures. In the present study one such novel precursor has been prepared and characterized by IR and TG-DTA. The thermal decomposition of the precursor has also been studied by isothermal, differential thermal analysis (DTA) and thermogravimetric analysis (TG). The precursor shows dehydrazination followed by decarboxylation to form $NiCo_2O_4$. The infrared spectra show N–N stretching frequency at 980 cm^{-1}which confirms the bidentate bridging hydrazine.

Keywords: IR, hydrazine precursor, $NiCo_2O_4$nanoparticle, TG, DTA.

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 not only because it has a potent N–N bond, two free electron pairs and four substitutable hydrogen atoms but also because it forms various complexes with transition metals. Thermal reactivity of metal hydrazine complexes is of a great interest since the stability of complexes changes dramatically, depending upon the anions as well as the cation [16]. Secondly, hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes [17–19]. These complexes are important as precursors to obtain simple as well as mixed ultrafine metal oxides, which can have interesting electrical, magnetic and catalytic properties. Nanomaterials have attracted increasing interest of researchers all over the world. Therefore, many authors have synthesized and characterized various nanomaterials [20–36]. We are reporting here the preparation and characterization of cobalt nickel diphenylacetate hydrazinate hydrate and its thermal decomposition to $NiCo_2O_4$ nanoparticles

EXPERIMENTAL SECTION

A requisite quantity of diphenylacetic acid in aqueous medium was stirred with hydrazine hydrate, $N_2H_4 \cdot H_2O$ (99–100%). To this, a metal ion solution containing cobalt and nickel in stoichiometric amount was added drop wise with constant stirring. The precipitate thus obtained was filtered, washed with water, 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 [37]. The percentage of cobalt and nickel in the precursor was estimated by the standard methods given in the Vogel's textbook [37].

Infrared analysis of the complex was done on Shimadzu FTIR, model 8101 A. Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the complex was done from RT to 900°C in air. The heating rate was maintained at 10°C min^{-1}.

RESULTS AND DISCUSSION

Chemical formula fixation of cobalt nickel diphenylacetate hydrazinate hydrate

A chemical formula of $Co_2NiN_2H_4L_2.H_2O$ (L = Diphenyl acetate) for cobalt nickel diphenylacetate hydrazinate hydrate precursor has been fixed based on percentages of Hydrazine 6.49, Nickel 4.00 and Cobalt 9.00 which match closely with the calculated value of 7.40, 4.53 and 9.12 Hydrazine, Nickel and Cobalt respectively. The infrared spectra of the precursor (Fig. 1) showed bands in the region at 3430-3300cm^{-1} which is due to O-H stretching of the water molecules, 3295 - 3210cm^{-1} due to the N–H stretching frequencies. The N–N stretching frequency was observed at 980cm–1 which confirmed the bidentate bridging nature of hydrazine ligand [38]. The asymmetric and symmetric stretching frequencies of the carboxylate ion in the precursor are seen at 1617 and 1493 cm-1, respectively with (assym–sym) separation of 124 cm^{-1} indicating the bidentate bridging coordination of carboxylate ions [38]. Thus, the diphenyl acetate anions in the complex coordinate to the metal groups. These results suggest the formation of cobalt nickel diphenylacetate hydrazinate hydrate complex.

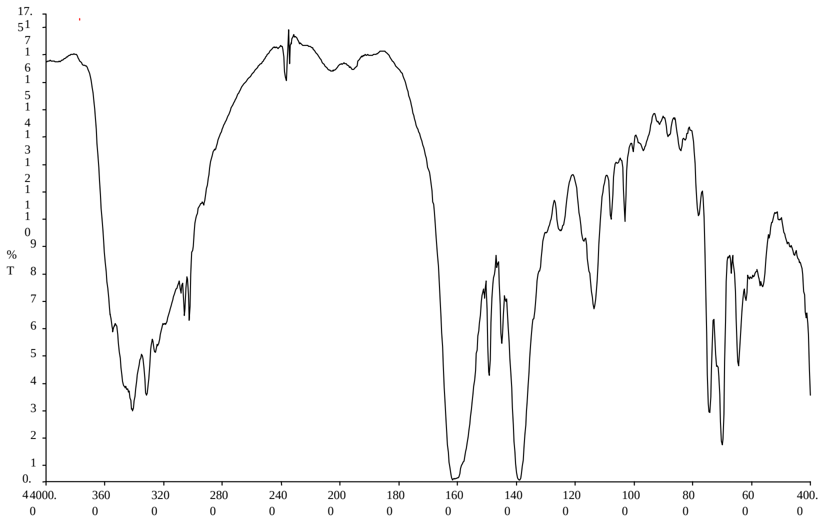

Fig.1 IR spectrum of $Co_2Ni\ N_2H_4L_2\ H_2O$ (L= diphenylacetate)

Thermal analysis of the complex

Since the TG curves of the complexes show continuous degradation, we were not able to isolate the intermediates. Hence, the compositions of the intermediates were proposed on the basis of TG-mass loss. However, the final products, the respective nickel cobaltites have been assigned on the basis of TG-mass loss. The compounds decompose exothermically to yield the nickel cobaltites as the final product. The observed weight losses match very well with the expected values.

CONCLUSION

The synthesis of transition metal oxides via the metal diphenylhydrazinate hydrate precursor is a convenient synthetic route to prepare nanosized mixed metal oxides. The chemical analysis, total mass loss, and infrared spectral analysis of the complex confirms the formation of the complex $Co_2NiN_2H_4L_2.H_2O$ (L = Diphenyl acetate). TG-DTA studies of the complex show dehydrazination followed by decarboxylation to form single phase Co_2NiO_4 nanoparticles. This is confirmed by XRD studies.

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