



SYNTHESIS AND CHARACTERIZATION OF NICKEL COBALT CINNAMATE HYDRAZINATE : A PRECURSOR FOR COBALTITE NANOPARTICLES

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ABSTRACT

In the present work, a novel precursor nickel cobalt cinnamate hydrazinate has been prepared, which decomposes at 400°C to give the corresponding nanosized mixed-metal oxide. The elemental analysis and spectral studies of the synthesized complex has been carried out. The thermal behaviour of the complex has been studied by thermogravimetry and differential thermal analysis. The infrared analysis of the residue shows two absorption bands in the region 662 cm⁻¹ and 560 cm⁻¹ corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltites. Formation of cobaltite has been confirmed by thermogravimetry (TG) weight loss and X-ray diffraction. Combustion of the precursor in air yields fine powder of cobaltites with large surface area which has been confirmed by XRD patterns.

Key words: Hydrazine, Cobaltites, IR Spectra, Thermogravimetry, Differential thermal analysis, XRD.

INTRODUCTION

Binuclear and polynuclear transition metal complexes bridged by polyatomic ligands have gained much attention in the recent years towards synthesis and characterization¹⁻¹⁰. Transition metal complexes have been subject of thorough investigation because of their application on the study of mixed metal interactions, magnetic exchange, catalysis and binuclear metal reactivity^{11,12}. The presence of two metals in the same molecule largely affects both the physical properties and the reactivity of the complexes^{13,14}. This is either due to the significant modification in the individual properties of the metals or in the development of novel characteristics, which do not occur in monometallic compounds. The physical properties of these binuclear metal complexes (redox properties, fluorescence etc) vary to a great extent^{14,15}.

Researchers have given a considerable attention in synthesizing cobaltite system by exploring the precursors used, preparation methods, processing control and firing temperatures. Among the binary cobaltites of transition metals with the general formula MCo₂O₄, where M is a divalent cation of a d element, Ni, Cu and Zn cobaltites are of definite interest due to their diverse applications as oxide electrode materials,

magnetic materials, thermistors and catalysts¹⁶⁻²⁵. Cobaltites have attracted much attention of the chemists due to their application as low cost fuel cell electrodes.

A wide option of preparative methods can be employed to obtain the desired novel products. Some of the methods applied are traditional ceramic preparation or better known as solid-state route and chemical techniques such as sol-gel, electrochemical, solvothermal, hydrothermal, combustion and co-precipitation. Thermal treatment of co-precipitated precursors is proven to be the most promising method in preparing cobaltite spinels²⁶⁻²⁹.

Nickel cobaltite, NiCo₂O₄ is one of the promising metal oxides in the family of cobaltite materials which has a spinel structure AB₂O₄. This mixed metal oxide spinel has shown exceptional ability to serve as an oxygen evolution electrode and has been studied quite extensively by electrochemical methods for this purpose^{30,31}. NiCo₂O₄ can be utilized as electrode material in sodium and sodium ion cells as well as electrocatalyst in advanced alkaline water electrolyzer due to its high electrical conductivity and desirable optical properties in the infrared regions³². However, there appear limited studies on NiCo₂O₄ for energy storage in supercapacitors. It is highlighted that incorporation of nickel into cobalt oxide would further enhance the electrical conductivity of the prepared samples^{33,34}.

The possibility of synthesis of NiCo₂O₄ as a high-dispersity material using the nickel cobalt cinnamate hydrazinate as precursor is studied in the present paper.

EXPERIMENTAL

Preparation of nickel cobalt cinnamate hydrazinate

Stoichiometric quantities (1:2 molar ratio) of metal nitrate hydrate Ni(NO₃)₂.nH₂O and Co(NO₃)₂.6H₂O were dissolved in 50 mL of water. The resultant solution was treated with 50 mL of aqueous solution containing the cinnamic acid and hydrazine hydrate. The complex was precipitated after 20-30 minutes, filtered off, washed with distilled water, alcohol, ether and air dried.

Preparation of cobaltites

The cobaltite, NiCo₂O₄ has been obtained as residue by heating the precursor at 400°C in a pre-heated silica crucible for about 15 minutes. While heating, the precursor should be added in small portions to the crucible in order to avoid explosions, since it decomposes violently.

Quantitative methods

The hydrazine content in the sample was determined by titration using KIO₃ as the titrant³⁵. The percentage of nickel and cobalt in the precursor was estimated by the standard methods given in the Vogel's textbook³⁵.

RESULTS AND DISCUSSION

Chemical formula determination of nickel cobalt cinnamate hydrazinate

From the IR spectrum of the prepared complex, it is observed that the N-N stretching frequency is seen at 962 cm⁻¹, which unambiguously proves the bidentate bridging nature of the hydrazine ligand³⁶. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1604 and 1398 cm⁻¹,

respectively with the $\Delta\nu$ (ν_{asymm} - ν_{sym}) separation of 206 cm^{-1} , which indicate the monodentate linkage of both carboxylate groups in the dianion. The N-H stretching is observed at 3295 cm^{-1} . The IR data thus confirms the formation of nickel cobalt cinnamate hydrazinate complex. The chemical formula, $\text{NiCo}_2(\text{Cinn})_2(\text{N}_2\text{H}_4)_2$ has been assigned to the complex, nickel cobalt cinnamate hydrazinate based on the observed percentage of hydrazine (13.22), nickel (3.52) and cobalt (8.37), which are found to match closely with the calculated values 14.29, 4.66 and 9.37 for hydrazine, nickel and cobalt, respectively.

Thermal analysis of the precursor

From the thermal decomposition data of the prepared complex, the compound decomposes exothermically to yield the corresponding cobaltite, NiCo_2O_4 as the final product. The observed weight loss matches very well with the expected values. The major weight loss of 81.07% on the TG curve from $256\text{--}465^\circ\text{C}$ is attributed to the decarboxylation of dehydrazinated cinnamate precursor.

Cobaltites

The chemical analysis of the cobaltite prepared from the precursor shows that the nickel and cobalt in the residue are present in 1 : 2 ratio. Formation of cobaltite by the thermal decomposition of the mixed metal complex was confirmed by XRD patterns. The Infrared analysis of the residue shows two absorption bands in the region 662 cm^{-1} and 560 cm^{-1} corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltites³⁷. Further investigation has been carried out by obtaining X-ray powder diffraction pattern of the residue. The X-ray pattern of NiCo_2O_4 is shown in Fig. 1.

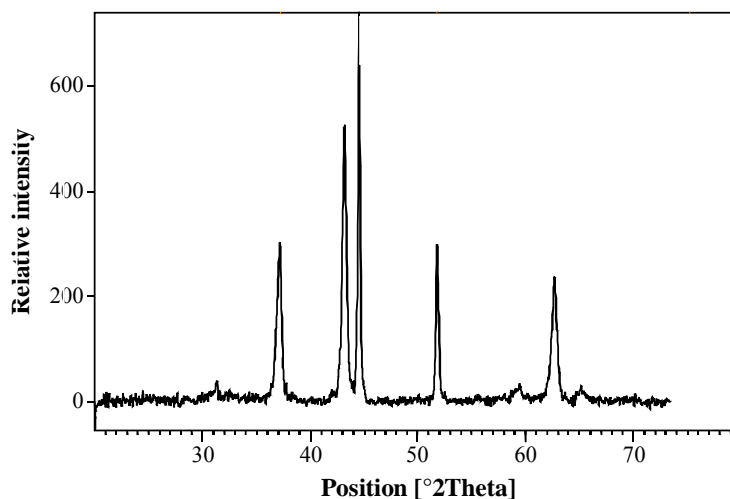


Fig. 1: X-ray pattern of NiCo_2O_4

CONCLUSION

The synthesis of transition metal oxides via the mixed metal cinnamate 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 nanosized NiCo_2O_4 .

The chemical analysis, total weight loss and infrared spectral analysis of the complex confirm the formation of the complex $\text{NiCo}_2(\text{Cinn})_2(\text{N}_2\text{H}_4)_2$. The TG-DTA analysis shows that the complexes have good thermal stability with initial decompose temperature at above 250°C .

The TG studies of the complex show the formation of single phase NiCo₂O₄ nanoparticles, which is also confirmed by XRD studies.

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