Synthesis and Characterization of Nano Cobaltites from Hetero Bi-Metal Carboxylate Precursors

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Abstract—This report describes the novel synthesis of nanocobaltites from hetero-bimetal phenylacetate hydrazinates precursors by thermal decomposition method. The synthesized nanocobaltite was characterized using various analytical techniques. The crystallite size of the prepared nanocompound was determined from X-ray diffraction analysis (XRD). Scanning electron microscopy and transmission electron microscopy was used to study the surface morphology and particle size of nanocobaltites respectively. This simple and inexpensive synthetic procedure can be employed to prepare other transition metal oxide nanoparticles.

Index Terms—HRTEM, Nanoparticle, Cobaltite nanoparticles synthesis, Thermal decomposition method, Hetero-bimetal phenylacetate precursor.

I. INTRODUCTION

Hydrazine, a chemical compound with formula, N₂H₄, used as a rocket fuel is a colourless liquid (m.p. 2.0°C; b.p. 113.5°C) with weak basic properties similar to ammonia. Due to the alpha effect, the nucleophilicity is much stronger than that of ammonia, which makes it more reactive. It is soluble in alcohol and water. Bibliographic works on hydrazine have been done by Audrieth and Ogg [1], Clark , Bottomley and Schmidt [2]. The field of hydrazine chemistry and applications are ever widening. One of the major applications of hydrazine and its derivatives includes its use as fuel for guided missiles and rockets. A vivid interest in hydrazine as a powerful propellant has stimulated many investigations both of its thermal decomposition and of its oxidation.

The Precursor for nanocobaltite i.e., the binuclear transition metal complexes bridged by polyatomic ligands have gained much attention in the recent years towards synthesis and characterization [3-5].

Transition metal complexes have always been subject of thorough investigation due of their applications in mixed metal interactions, magnetic exchange, catalysis and binuclear metal reactivity [3]. The presence of two metals in the same molecule largely affects both the physical properties and the reactivity of the complexes [7-10]. 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, florescence etc) vary to a great extent [11].

II. EXPERIMENT SECTION

Chemical used in the present investigation includes absolute alcohol, Acetic acid, Carbon tetrachloride, Cobalt nitrate hexahydrate, Diethyl ether, Hydrazine hydrate, Hydrochloric acid, Diphenylacetic acid, Nickel nitrate hexahydrate, Potassium iodate, Manganese acetate tetrahydrate, Mercury (II) chloride, Ammonium thiocyanate, Dimethyl glyoxime. All the chemical used in this experiment were used without any modification.

A. Estimation of Hydrazine

The hydrazine content of the metal carboxylates were determined volumetrically using a standard KIO₃(0.025 M) solution under Andrew’s conditions [1].

\[ \text{IO}_3^- + \text{N}_2\text{H}_4 + 2\text{H}^+ + \text{Cl}^- \rightarrow \text{ICl} + \text{N}_2 + 3\text{H}_2\text{O} \]

In an iodimetry flask, 100 mg of the sample dissolved in 10 ml of concentrated hydrochloric acid, 20 ml of distilled water and 5 ml of carbon tetrachloride was added. It was titrated against standard potassium iodate (0.025 M) solution from the burette. The solution was shaken well after the addition of each ml of KIO₃ solution. The end point is the disappearance of violet colour in the organic layer.

B. Estimation of Cobalt

The metal oxide was dissolved in 1 mole of mercury (II) chloride and 5 moles of ammonium thiocyanate in water. The blue salt of cobalt tetrathiocyanatomercurate(II)
Co[Hg(SCN)₄] formed was filtered, dried in sintered crucible and then the cobalt content was estimated.

C. Estimation of Manganese

The widely used method for the gravimetric determination of manganese is the precipitation of ammonium manganese phosphate, MnNH₄PO₄·H₂O, in slightly ammoniacal solution containing excess of ammonium chloride and a considerable excess of diammonium hydrogenphosphate, (NH₄)₂HPO₄. Manganese was estimated from the dried precipitate obtained as MnNH₄PO₄·H₂O.

D. Estimation of Nickel

The nickel ion was precipitated as nickel dimethylglyoxime complex and the concentration of nickel present in the solution was estimated gravimetrically[2].

E. Preparation of Cobaltite nanoparticles

The metal cobaltites was obtained as residues by heating respective hydrazine mixed metal carboxylate precursors at 400°C in pre-heated silica crucible for about 15 minutes. While heating, the hydrazine mixed metal carboxylates was added in small portions to the crucible in order to avoid explosions. Cobalt oxide nanoparticles were obtained as the final residue by decomposing the respective solid precursors in a pre-heated silica crucible.

III. RESULTS AND DISCUSSION

A. Analytical Data

Analytical data of the prepared precursors are given in table 1. They are best fit with the proposed composition.

Table 1. Analytical data of the prepared precursors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydrazine %</th>
<th>Metal %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calculated</td>
</tr>
<tr>
<td>NiCo₂L₂N₂H₄·H₂O</td>
<td>6.49</td>
<td>7.40</td>
</tr>
<tr>
<td>MnCo₂L(N₂H₄)₂</td>
<td>7.82</td>
<td>8.83</td>
</tr>
</tbody>
</table>

Based on the observed and calculated percentage of hydrazine and metal ions, the chemical formula NiCo₂L₂N₂H₄·H₂O and MnCo₂L(N₂H₄)₂ was tentatively fixed for the prepared precursors.

The infrared spectral data of the prepared precursors are given in table 2.

Table 2. IR spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>νOH of water cm⁻¹</th>
<th>ν(N-H) (sym) cm⁻¹</th>
<th>ν asym (OCO) cm⁻¹</th>
<th>ν sym (OCO) cm⁻¹</th>
<th>Δν</th>
<th>ν(N-N) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo₂L₂N₂H₄·H₂O</td>
<td>3412</td>
<td>1617</td>
<td>1493</td>
<td>124</td>
<td>980</td>
<td></td>
</tr>
<tr>
<td>MnCo₂L(N₂H₄)₂</td>
<td>-</td>
<td>1604</td>
<td>1388</td>
<td>212</td>
<td>956</td>
<td></td>
</tr>
</tbody>
</table>

The IR spectra of the prepared precursors are given in figure 1 and 2.

![Fig 1. IR Spectrum of NiCo₂L₂N₂H₄·H₂O](image1.png)

The broad band at 3412 cm⁻¹ is due to O-H stretching of the water molecules. In the spectra the N-H stretching frequency for both the precursors is observed at 3290 and 3204 cm⁻¹ as multiplet. The N-N stretching frequency of N₂H₄ is seen at 956-980 cm⁻¹ which confirms the bidentate bridging nature of hydrazine ligand. The asymmetric and symmetric stretching frequencies of the carboxylate ion are seen at 1617, 1604 and 1493, 1388 cm⁻¹ respectively with Δν of 124 and 212 cm⁻¹ indicating the bidentate and monodentate linkage of carboxylate group to the central metal atom / ion.

![Fig 2. IR Spectrum of MnCo₂L(N₂H₄)₂](image2.png)
B. Thermal Analysis

TG-DTA curves of the precursors are represented in figures 3 and 4. The precursors show two and three step mass loss. Initially it loses hydrazine molecule exothermally. Then it undergoes the decarboxylation of the dehydrazinated precursor yielding metal cobaltites as the end product.

![Fig 3 TG-DTA curve of NiCo\(_2\)L\(_2\)N\(_2\)H\(_4\)H\(_2\)O](image)

![Fig 4 TG-DTA curve of MnCo\(_2\)L(N\(_2\)H\(_4\))\(_2\)](image)

C. Phase Analysis of MCo\(_2\)O\(_4\) (where M= Ni or Mn)

The X-ray diffraction spectrum of NiCo\(_2\)O\(_4\) has been displayed in figure 5. The ‘a’ value of cobaltites with cubic symmetry calculated from the pattern match well with the reported values. The strong diffraction peaks in the XRD spectrum of MnCo\(_2\)O\(_4\) (Fig. 6) at 2\(\theta\) values of 35.610, 63.010 and 57.740 corresponding to the (3 1 1), (4 4 0) and (5 1 1) planes can be indexed to a cubic pattern of MnCo\(_2\)O\(_4\) (JCPDS card no. 84-0482). The average crystallite size was calculated using Debye-Scherrer formula, \(D = \frac{K\lambda}{\beta\cos\theta}\), where \(\theta\) is Bragg diffraction angle, \(K\) is Blank’s constant, \(\lambda\) is the source wavelength (1.54), and \(\beta\) is the width of the XRD peak at half maximum height. Average crystallite size of nickel cobaltite and manganese cobaltite nanoparticles was found to be around 8 and 11 nm respectively. No characteristic peaks for other impurities were detected. This confirms that the products obtained are phase pure.

![Fig 5 XRD Pattern of NiCo\(_2\)O\(_4\)](image)

![Fig 6 XRD Pattern of MnCo\(_2\)O\(_4\)](image)

D. SEM analysis

The SEM images of NiCo\(_2\)O\(_4\) and MnCo\(_2\)O\(_4\) nanoparticles has been displayed in Fig 7(a & b) and Fig 8(a & b). The SEM images clearly represent cube shaped NiCo\(_2\)O\(_4\) particles with agglomeration. EDX spectra of NiCo\(_2\)O\(_4\) and MnCo\(_2\)O\(_4\) nanoparticles have been presented in Fig. 9 and 10, which furnish the chemical compositional analysis of the nanoscale NiCo\(_2\)O\(_4\) and MnCo\(_2\)O\(_4\). Unlike XRD, no other impurity elements were visible.

![Fig 7a SEM Image of NiCo\(_2\)O\(_4\)](image)
E. HRTEM Analysis

The size and morphology of the as-produced sample in detail were investigated by HRTEM. High resolution transmission electron microscopy (HRTEM) images of NiCo$_2$O$_4$ (Fig 9) and MnCo$_2$O$_4$ (Fig 10) shows that the obtained nanoparticles were almost spherical, ultrafine and homogenously dispersed with agglomeration. From figures the crystallographic orientation of the nanoparticles was investigated and the prominence of the lattice fringes was found to agree well with the separation between the lattice planes. The particle size calculated by HRTEM micrography was in the range of 8–13 nm, which is in agreement with that calculated using the Debye-Scherrer formula.

The electron diffraction pattern from the HRTEM image (Fig 11 and Fig 12) shows multiple diffraction rings, indicating crystalline structure formation. A careful analysis of the SAED pattern reveals that besides the diffraction rings of NiCo$_2$O$_4$ and MnCo$_2$O$_4$ no additional rings were observed. The bright electron diffraction rings of as-synthesized nanoparticles showed that the particles are fine nanocrystalline and are around 13 nm size.
IV. CONCLUSION

Our work is mainly concerned with the synthesis of cobaltite nanoparticles by thermal treatment. The precursors were prepared from the aqueous solutions of the corresponding metal salts, hydrazine hydrate and diphenyl acetic acid.

The prepared precursors were characterized by analytical, IR and Thermal analyses. The cobaltite nanoparticles were characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) analysis and High Resolution Transmission Electron Microscope (HRTEM).

The observations made on the synthesis and characterization of cobaltite nanoparticles obtained from the thermal decomposition of the precursors MCo$_2$L$_2$(N$_2$H$_4$)$_2$ lead to the following conclusions.

- Infra red spectral study of the precursor revealed the bidentate co-ordination nature of N$_2$H$_4$ and monodentate co-ordination behaviour of carboxylate groups.
- Thermal analysis explained the decomposition of the precursor and confirming the formation of cobaltite as the final residue.
- Phase analysis (XRD) showed the purity of the particles. The more intense peaks reveal that no impurity peaks were present. All the diffraction peaks of the as-synthesized nanoparticles were consistent with that of the reported values (JCPDS). The broadening nature of the XRD peaks showed the crystallite sizes of the particles are in nanoscale. The average crystallite size of the nanoparticles were calculated using Debye-Scherer formula in the range of 8-13nm.
- Morphology analysis from SEM images of the nanoparticles showed that the nanoparticles illustrating spherical-shaped grains with large agglomeration. The purity of the nanoparticles was confirmed by EDX spectrum which furnished the chemical composition, that the presence of corresponding elements and no other contaminated elements are seen.
- High Resolution Transmission Electron Microscope (HRTEM) analyses showed that the nanoparticles are almost spherical. The average grain size observed from the micrograph was in agreement with the calculation using Scherer’s equation. The corresponding Selected Area Electron Diffraction (SAED) pattern consists of bright diffraction rings, proving the nanocrystalline nature of nanoparticles.

REFERENCES