Preparation And Characterization Of Cobaltite Nanoparticles From Hydrazine Mixed Metal Carboxylate Precursors

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Abstract: Cobaltite Nanoparticles were synthesized from mixed metal carboxylate precursors by exposing at suitable temperature. The synthesized Cobaltite Nanoparticles were characterized by various physico-chemical techniques such as Infrared spectroscopy (IR), thermal analysis techniques like Differential Thermal Analysis (DTA) and Thermo Gravimetry (TG). X-ray powder diffraction technique (XRD) was used for the determination of crystallite size. The surface morphology and particle size were identified by Scanning Electron Microscope (SEM) and High Resolution Transmission Electron Microscope (HRTEM).This reasonably -priced method is employed for the preparation of mixed metal nanoparticles.

Keywords: Cobaltite Nanoparticles, Mixed metal carboxylates,thermal analysis,XRD and SEM.

I. INTRODUCTION

Hydrazine, also called as dinitrogen tetrahydride, is the simplest diamine and is unique in its class because of the presence of N-N bond. It is a colourless oily liquid and its melting and boiling points are 1.8^oC and 113^oC, respectively. It has specific conductivity of 1×10^{-6} ohm^{-1} at 0^oC. It dissolves in polar solvents such as water, alcohol, ammonia and amines. Hydrogen bonding is responsible for the high boiling point and viscosity of the liquid. Hydrazine is also of academic interest, the great growth of interest and versatility of hydrazine molecule are due to the presence of two free electron pairs and four replaceable hydrogen atoms and in addition to this it has one weak N-N bond. However, in most of the reactions, the anhydrous hydrazine is not used because the reaction with anhydrous hydrazine is violent and large amount of heat is evolved. So, usually hydrazine hydrate $[N_2H_4.H_2O]$ is used rather than anhydrous hydrazine. The hydrazine hydrate is also a colourless liquid which boils at 118.7^oC. Bibliographic works on hydrazine have been done by Audrieth and Ogg [1], Clark [2], Bottomley [3] and Schmidt [4]. The field of hydrazine chemistry and applications are ever widening. The prominent uses of hydrazine derivatives includes Rocket fuels, Antituberculin drugs,Plant growth regulators,Dye and explosive intermediates,Alagecides and fungicides etc.,

II. EXPERIMENTAL SECTION

2.1. Preparation of the precursor

Phenylacetic acid (1.3614 g, 0.01 mol) was added to 100 ml distilled water containing 99-100% pure hydrazine hydrate (1 ml, 0.02 mol). The mixture was stirred well and heated over water bath to get clear solution. It was filtered and added slowly to an aqueous solution of the corresponding nitrate hexahydrate with constant stirring. The clear solution obtained was kept aside for 45 minutes. This precipitated the precursor was filtered washed with distilled water, alcohol and ether and air dried.

2.1.1 Preparation of Cobaltite nanoparticles by Thermal decomposition

The precursor thus prepared was taken in a clean silica crucible and heated gently at the starting and strongly when the decomposition started. The precursor was heated to red hot. As a result, the precursor was completely decomposed to the corresponding metal oxide.

Compound	Color	Hydrazine %		Metal %	
		Found	Calculated	Found	Calculated
$ZnCo_2L_2$ $(N_2H_4)_2$	Pink	12.02	12.30	Zn(26.47) Co(47.19)	Zn(26.45) Co(47.66)
$MnCo_2L$ $(N_2H_4)_2$	Pink	17.03	17.15	Mn(23.89) Co(49.99)	Mn(23.19) Co(49.77)

2.2. Analytical methods

2.2.1 Estimation of hydrazine

The hydrazine content of the metal carboxylates were determined volumetrically using a standard KIO_3(0.025 M) solution under Andrew's conditions [1].

$$IO^-_3 + N_2H_4 + 2H^+Cl^- \longrightarrow IC1 + N_2 + 3H_2O$$

1 ml of 0.025 M KIO_3 = 0.0008013 g of hydrazine.

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 KIO_3 solution. The end point is the disappearance of violet colour in the organic layer.

2.2.2. Estimation of metal ions

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.

Estimation of Manganese

The only method which is at all widely used for the gravimetric determination of manganese is the precipitation as ammonium manganese phosphate, $MnNH_4PO_4H_2O$, in slightly ammoniacal solution containing excess of ammonium chloride and a considerable excess of diammonium hydrogenphosphate, $(NH_4)_2HPO_4$. The precipitate obtained as
$MnNH_4PO_4H_2O$ is dried and then manganese was estimated.

Estimation of Zinc

Zinc was precipitated as $Zn(C_{10}H_8ON)_2$ by the addition of 8-hydroxyquinaldine (2-methyloxine) in acetic solution. $Zn(C_{10}H_8ON_2)$ was dried and estimated.

III. ANALYTICAL DATA

Analytical data of the prepared precursors are given in table 1. They are best fit with the proposed omposition. Based on the observed and calculated percentage of hydrazine and metal ions, the chemical formula $MCo_2L_2(N_2H_4)_2$ (where M = Zn, Mn and L = Phenylacetate) has been tentatively fixed for the prepared precursors.

3.2. Infrared Spectra

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

IR Spectral data (cm⁻¹)

The IR spectra of the prepared precursors are given in Fig 1 and 2.
In the spectrum, the N-H stretching frequency for both the precursors is observed at 3294 cm⁻¹ as multiplet. The N-N

Compound	$\nu_{(N-H)}$ cm⁻¹	$\nu_{asy-(OCO-)}$ cm⁻¹	$\nu_{sym(OCO)}$ cm⁻¹	$\Delta\nu$ $(\nu_{asym}-\nu_{sym})$ cm⁻¹	$\nu_{(N-N)}$
$ZnCo_2L_2$ $(N_2H_4)_2$	3294	1612	1396	216	964
$MnCo_2L$ $(N_2H_4)_2$	3294	1604	1388	212	960

stretching frequency of N_2H_4 is seen at 960 & 964 cm⁻¹ respectively which confirms the bidentate bridging nature of hydrazine ligand. The asymmetric and symmetric stretching frequencies of the carboxylate ion are seen at 1612, 1604 and 1396, 1388 cm⁻¹ respectively with $\Delta\nu$ of 216 and 212 cm⁻¹ indicating the monodentate linkage of carboxylate group to the central metal ion.
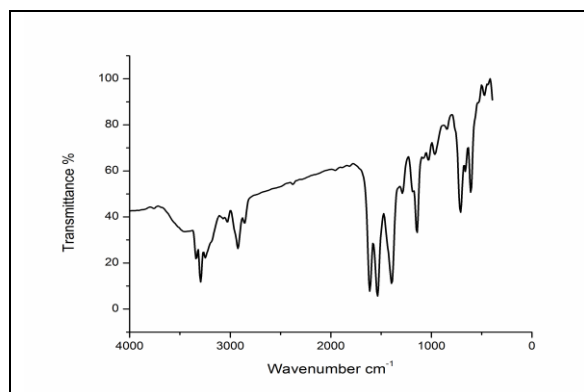
Fig 1. IR Spectrum of $ZnCo_2L_2(N_2H_4)_2$

Fig 2. IR Spectrum of $MnCo_2L(N_2H_4)_2$
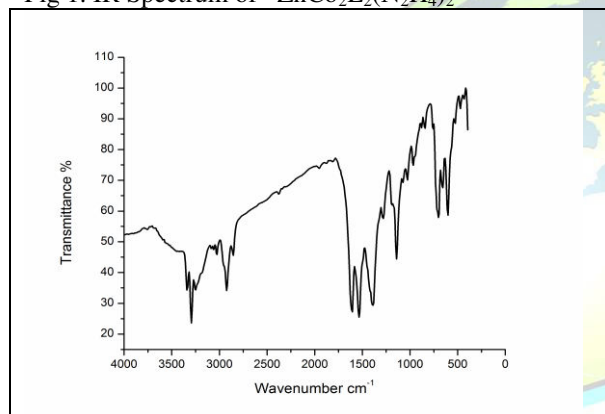

Fig 3. TG-DTA curve of $ZnCo_2L_2(N_2H_4)_2$
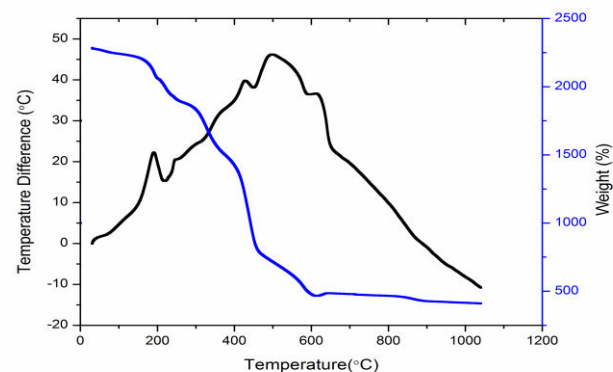

Fig 4. TG-DTA curve of $MnCo_2L(N_2H_4)_2$

3.3. Thermal Analysis (TG and DTA)

TG-DTA curves of the precursors are given in Fig. 3 and 4. The Precursors $ZnCo_2L_2(N_2H_4)_2$ shows two step mass loss. Initially it loses two hydrazine molecules exothermally in the temperature range from 30 - 176°C. The mass loss from 184 - 484°C can be attributed to the decarboxylation of the dehydrazinated precursor yielding $ZnCo_2O_4$ as the final product.

The precursor $MnCo_2L(N_2H_4)_2$ undergoes three step mass loss. The first step is attributed to the elimination of a hydrazine molecule exothermically in the temperature range of 30 - 195 °C. TG curve from 195 - 245°C shows the loss of another molecule of hydrazine. Finally, the dehydrazinated intermediate undergoes decarboxylation in the temperature range from 245 - 651°C to yield $MnCo_2O_4$ as the final residue.

Phase Analysis of MCo_2O_4 (where M= Zn or Mn)

The X-ray diffraction spectrum (Fig.5) of $ZnCo_2O_4$ has three characteristic peaks at 36.28^0, 44.2^0 and 65.14^0 which can respectively be indexed to the (3 1 1), (4 0 0) and (4 4 0) planes of a cubic pattern of $ZnCo_2O_4$ (JCPDS card no. 23-1390). The strong diffraction peaks in the XRD spectrum of $MnCo_2O_4$ (Fig. 6) at 2θ values of 35.61^0, 63.01^0 and 57.74^0 corresponding to the (3 1 1), (4 4 0) and (5 1 1) planes can be indexed to a cubic pattern of $MnCo_2O_4$ (JCPDS card no. 84-0482). The average crystallite size was calculated using Debye-Scherrer formula, $D = K\lambda/\beta\cos\theta$, where θ is Bragg diffraction angle, K is Blank's constant, λ is the source wavelength (1.54), and β is the

width of the XRD peak at half maximum height, zinc cobaltite and manganese cobaltite nanoparticles are found to be around 13 and 11 nm respectively. No characteristic peaks for other impurities were detected.
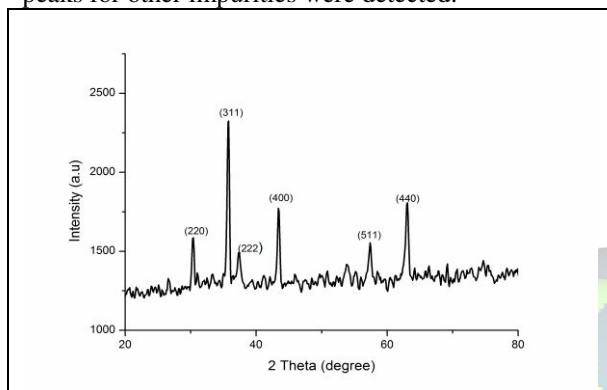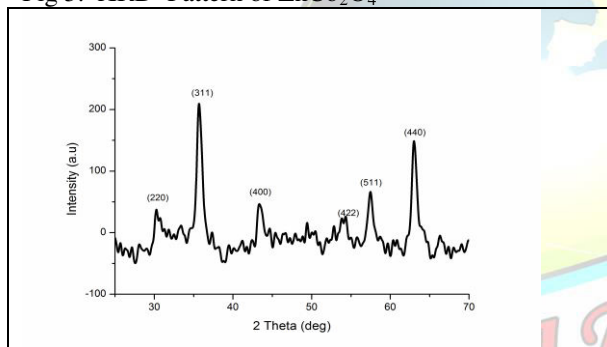

Fig 5. XRD Pattern of $ZnCo_2O_4$

Fig 6. XRD Pattern of $MnCo_2O_4$

3.4. SEM analysis

The SEM images of $ZnCo_2O_4$ and $MnCo_2O_4$ nanoparticles are shown in Fig. 7 and 8. The SEM pictures clearly show prism shaped particles $MnCo_2O_4$ structures with spherically agglomerated particles. EDX spectra of $ZnCo_2O_4$ and $MnCo_2O_4$ nanoparticles are presented in Fig. 9 and 10, which furnish the chemical compositional analysis of the nanoscale $ZnCo_2O_4$ and $MnCo_2O_4$. No other impurity elements are visible.
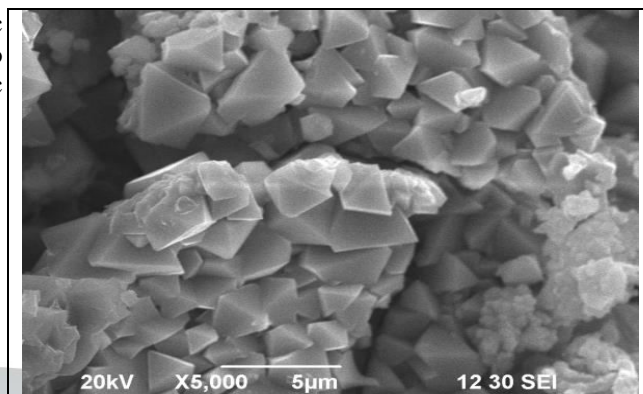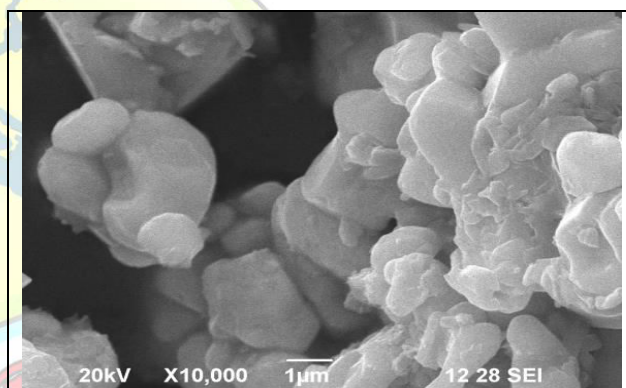

Fig 7. SEM Image of $ZnCo_2O_4$
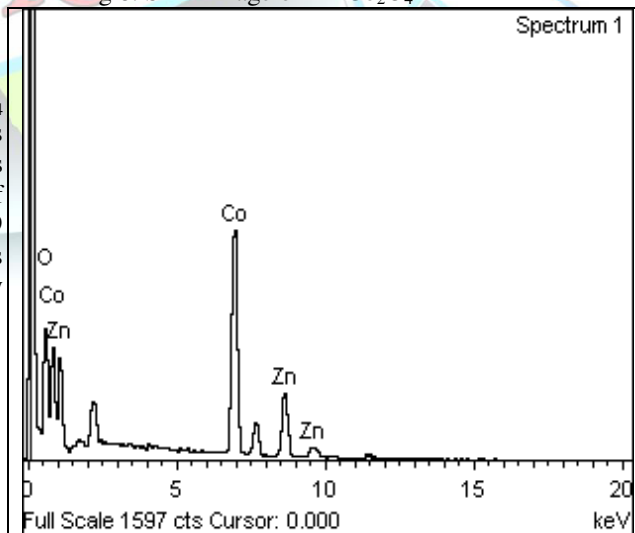

Fig 8. SEM Image of $MnCo_2O_4$
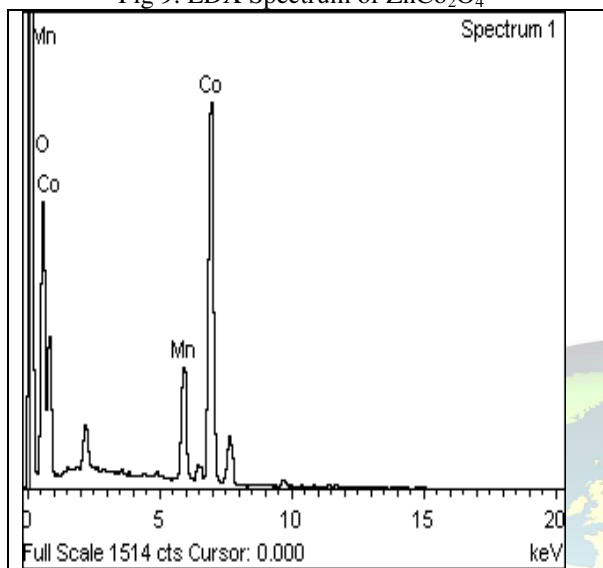
Fig 9. EDX Spectrum of $ZnCo_2O_4$

Fig 10. EDX Spectrum of $MnCo_2O_4$

CONCLUSION

This toil mainly concentrated on the synthesis of cobaltite nanoparticles by method. The thermally decomposed 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 The studies illustrated the nature of the as-synthesized nanoparticles.[5]

Infra red spectral study of the precursor revealed the bidentate co-ordination nature of N_2H_4 and monodentate co-ordination behavior of carboxylate groups.

The thermal decomposition pattern, confirm the formation of cobaltite as the final residue. XRD patterns were showed the purity of the particles. No impurity peaks were present. All the diffraction peaks of the as-synthesised nanoparticles were in consistent with that of the reported values (JCPDS). The broadening nature of the XRD peaks showed the crystallite size of the particles are in nanoscale. The average crystallite size of the nanoparticles were calculated using Debye-Scherer formula, it is found to be 11nm and 13nm respectively.

The SEM images of the nanoparticles showed the morphology of the nanoparticles illustrating spherical-shaped grains with large agglomeration. EDX spectrum of the nanoparticles furnished the chemical composition, which indicated the presence of corresponding elements and no other contaminated elements are seen. This confirmed the purity of the nanoparticles.

REFERENCE

1) L.F. Audrieth and B.A. Ogg, The Chemistry of Hydrazine', John Wiley, New York (1951) 1244.
2) C.C. Clark, "Hydrazine", Mathieson Chem. Corp Baltimore, Md., 1953.
3) F. Bottomley, Quart. Rev., Chem. Soc., 24 (1970) 617.
4) E.W. Schmidt, "Hydrazine and its Derivatives – Preparation, Properties and Applications", Wiley Interscience, New York, 1984.
5) Agatheeshwaren.A, Synthesis and Characterization of Nano Cobaltites from Hetero Bi-Metal Carboxylate Precursors,IRD India, ISSN 2347-7601, ISSN (Online): 2347-761X, Volume -3, Issue -1, 2015
6) Curtius, T. Prakt. Chem., 39 (1889)107
7) C.A.L. DeBruyun, Rec. Trav. Chim., 14 (1895) 85.
8) F. Raschig, Ber., 40 (1907) 4587.
9) F. Raschig, Z. Angew. Chem., 20 (1907) 2065
10) R.N.F. Thorneley, Nature, 272 (1978) 557.
11) R. Powell, 'Hydrazine Manufacturing Process', Noyes Devpt. Corp. Park Ridge, New Jersey (1968).
12) J.R. Dilworth, Coord. Chem. Rev., 21 (1976) 29.
13) S. Vairam, T. Premkumar, S. Govindarajan, J. Thremal Anal and Calorimetry, (2009)
14) K.C. Patil, C. Nesamani and V.R. Paivernekar, Synth. React. Inorg. Met.- Org. Chem., 12 (1982) 383.