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Research Paper Chemistry

Characterization of Nanostructured Cobalt Oxide Particles Synthesized By Thermal Treatment

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ABSTRACT

Cobalt oxide nanoparticles have been synthesized using an inorganic precursor via thermal decomposition route. The prepared inorganic precursor $Co(Di\text{-}PhAc)_2(N_2H_4)_{1.5}H_2O$ was characterized by hydrazine and metal analyses, electronic spectra, infrared spectra and thermal analysis. Using appropriate annealing conditions, cobalt oxide nanoparticles of average size 13 nm were synthesized by thermal treatment of the precursor. The nanoparticles were characterized for their size and structure using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscope (HRTEM) and Selected Area Electron Diffraction (SAED) techniques. The details of synthesis and characterization of the nanoparticles are reported in this paper.

KEYWORDS: Cobalt oxide; Inorganic precursor; Thermal treatment; Nanoparticle

INTRODUCTION

There is currently wide theoretical and practical interest in nanoparticles owing to their interesting physical and chemical properties as compared with their counterpart bulk materials [1]. Metal oxide nanoparticles show interesting changes in their optical, magnetic, electrical, and catalytic properties accompanied by improved physical properties like mechanical hardness, thermal stability, or chemical passivity [2]. The properties of nanomaterials are influenced by the presence of a significant number of surface atoms and by the quantum confinement effect of the electronic states [3]. The potential applications for nanostructured oxide materials include paint pigments, cosmetics, pharmaceuticals, medical diagnostics, catalysts and supports, membranes and filters, batteries and fuel cells, electronics, magnetic and optical devices, flat panel displays, biomaterials, structured materials, and protective coatings [4].

Cobalt oxide has wide range of applications such as a catalyst for the abatement of carbon monoxide (CO)[5] and in CO sensors [6], as a magnetic material [7,8] and electro-chromic devices [9]. In addition, transition element oxides like cobalt oxide have found application in Li ion batteries [10].

Now a days, several methods have been attempted in the preparation of crystalline cobalt oxide nanoparticles such as the chemical spray pyrolysis [11], chemical vapour deposition [12], sol–gel method [13], solvothermal synthesis [14], using organic surfactants [15], surfactant free method [16] and precipitation–oxidation method [17].

Among the large number of techniques employed for the synthesis of oxides, thermal treatment is found to be unique and highly versatile. It is an easy and fast process which yields high-purity, homogenous, crystalline oxides in a short time and with less energy. In this paper, we report a novel method of synthesis of cobalt oxide nanoparticles using the inorganic precursor $Co(Di\text{-}PhAc)_2(N_2H_4)_{1.5}H_2O$ and detailed structural characterization of these particles.

EXPERIMENTAL

The precursor complex was prepared by mixing an aqueous solution of the cobaltnitrate hexahydrate (1.4550 g, 0.05 mol) to the ligand solution containing Phenylacetic acid (1.3614 g, 0.1 mol) and hydrazine hydrate (1 mL 0.2 mol). The ligand solution was prepared by mixing Phenylacetic acid and hydrazine hydrate, stirred well and heated over water bath to get a clear solution. It is filtered and added slowly to the metal nitrate solution with constant stirring. The clear solution thus obtained is kept aside for 45 minutes. This precipitates the complex, which is filtered, washed with distilled water, alcohol, diethyl ether and air dried. The precursor complex thus prepared was taken in a clean silica crucible and heated gently at the starting and strongly when the decomposition starts. As a result the precursor complex was completely decomposed to give metal oxide nanoparticle as the end product.

CHARACTERIZATION

Hydrazine content of the precursor complex was analysed by titration using KIO_3 as titrant[18]. The metal content was estimated by the standard methods given in the Vogel's textbook[18]. The infrared spectrum of the complex was recorded on a Perkin-Elmer model 597 spectrophotometer using KBr pellets. The solid state electronic absorption spectra of the complex in Nujol mull was recorded on a Shimadzu UV-Vis 240 A spectrophotometer. The simultaneous TG-DTA of the complex in nitrogen atmosphere was carried out using a STA 1500 system. X-ray Diffractometer (XRD-Philips-PW3020) was employed for phase analysis and crystalline size measurement and Scanning Electron Microscope (SEM) for structural morphology analysis. The shape and size of nanoparticles were also characterized by Jeol Jem 2100 Advanced Analytical High Resolution Transmission Electron Microscopy (HR-TEM).

RESULTS AND DISCUSSION

SPECTRAL ANALYSIS

Electronic spectral data of the precursor complex reveals that the band obtained at 28,330 cm^{-1} is assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. This band and pink colour of the compounds are indicative of the octahedrally co-ordinated Co (II) ion [19].

The infra-red spectrum of the precursor complex shows a broad band in the region of 3321 cm^{-1} due to O- H stretching of H_2O molecule [20]. The separation of asymmetric and symmetric (υ_{asymm} - υ_{sym}) carboxylate stretching of 227 cm^{-1} indicates the unidentate coordination [21] of carboxylate ions. The N-N stretching frequency of hydrazine moieties are observed at 961 cm^{-1} indicating their bidentate bridging nature [22].

THERMOGRAVIMETRY ANALYSIS

The TG-DTA curves (Fig.1) of the precursor complex indicate that the weight loss begins at 150˚C and 26% of the mass loss with DTA exothermic peak at 179˚C. This decomposition indicates the presence of H_2O as water of crystallization, but not the coordinated one. One of the carboxylate ligand is reduced to formate ligand. On further heating, hydrazine is completely lost shown by an exothermic peak at 251˚C. An exothermic peak at 329˚C, indicates the decomposition of the dehydrazinated complex to cobalt formate which slowly decomposes to metal oxide as the final product.

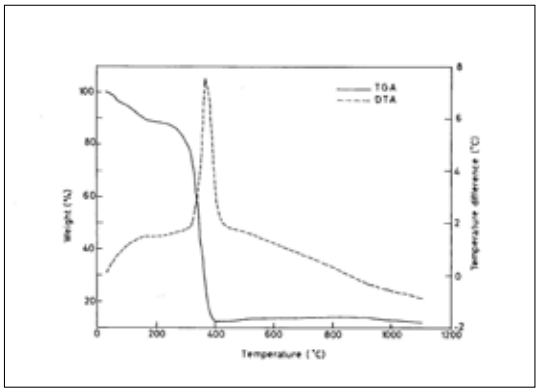


Fig.1 TG-DTA of the precursor

XRD PATTERNS

The crystal structure of the product was examined by X-Ray Diffractometry (XRD). Fig.2 shows the typical XRD patterns of CoO nanoparticles prepared by thermal decomposition method. All the diffraction peaks of as synthesized cobalt oxide nanoparticles have been indexed to cubic(fcc) phase with lattice parameter $\alpha = 4.244$ which is consistent with the reported value (JCPDS No.75-0533). The three diffraction peaks at 2θ are 36.85, 42.6 and 61.69° have been assigned to (111), (200) and (220) lattice planes, which are in good agreement with those of corresponding standard pure cobalt oxide [23]. The XRD patterns of as-synthesized CoO nanoparticles reveal that the average size of the nanoparticles using Scherrer's equation is 13 nm.

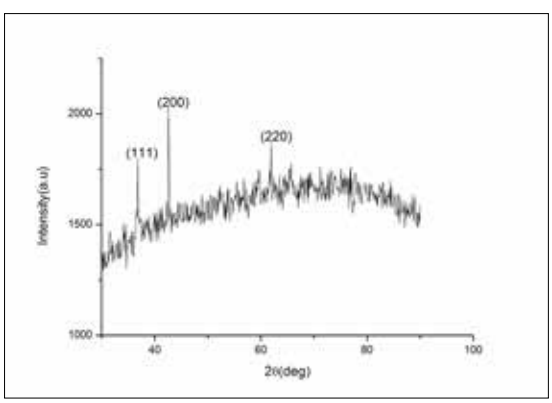
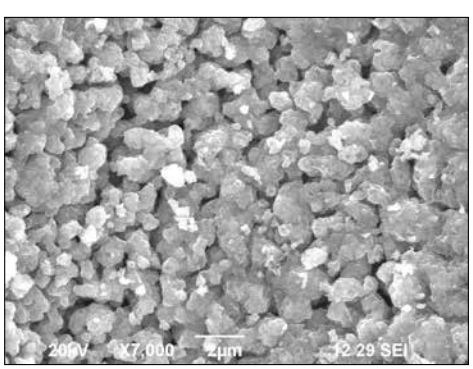


Fig.2 XRD patterns of the as-synthesized CoO nanoparticles

SEM

The surface morphology of the as prepared cobalt oxide nanoparticle was carried out by using Scanning Electron Microscope (SEM). Fig.3 shows the SEM image of the nanoparticle which clearly indicates that the nanoparticles are homogeneous and agglomerated. It can be seen from the image that the particle size is in the range of nanometre having spherical structure. The composition of obtained cobalt oxide nanoparticles was then analysed by means of Energy Dispersive X-Ray Analysis (EDX). As shown in Fig.4, the EDX result showed the presence of CoO by the appearance of Co and O peaks in this spectrum.



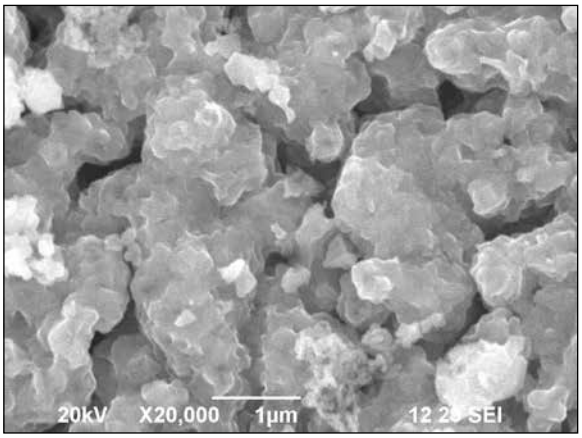


Fig.3 SEM images of the as-synthesized CoO nanoparticles (two different magnifications)

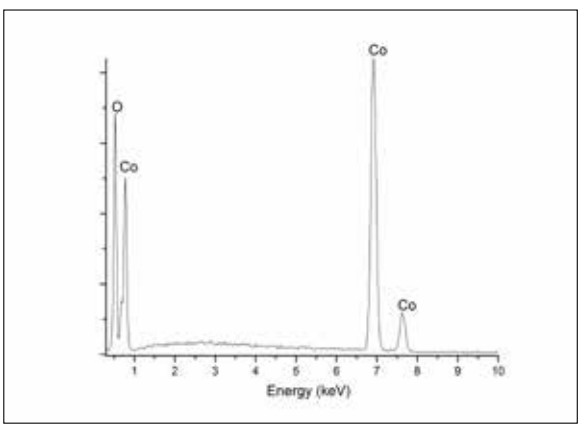
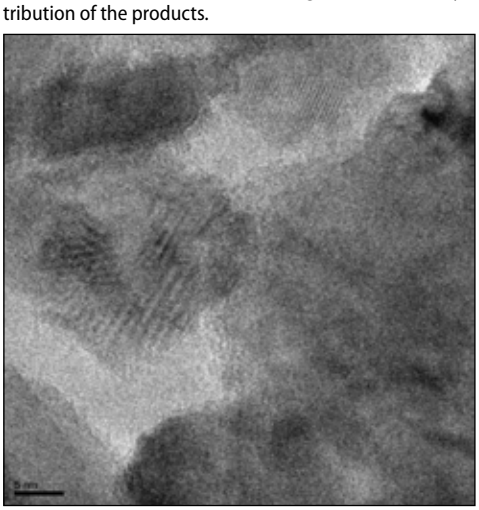


Fig.4 SEM EDX of the as-synthesized CoO nanoparticles

HRTEM & SAED

HRTEM images of the CoO nanoparticles with average diameter of 13 nm are shown in Fig 5 which reveals that the particles are monodispersed. The average particle size obtained from HRTEM are consistent with those estimated from the XRD peak broadening. The d-spacing of 0.236 nm corresponds to the interplanar separation of (111) lattice plane of cubic CoO phase [24].

As can be seen in the SAED pattern in Fig.6, pure cubic symmetry was clearly identified for the CoO nanoparticles. This is also consistent with the XRD data. The Selected Area Electron Diffraction (SAED) pattern has many widening diffraction rings consisting of many diffraction spots, which is indicative of the disordered grain and relatively wide size distribution of the products.



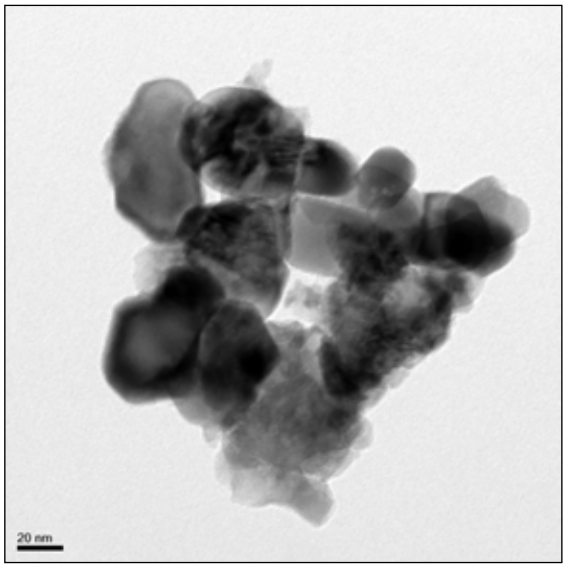


Fig.5 Tem images (two different magnifications)

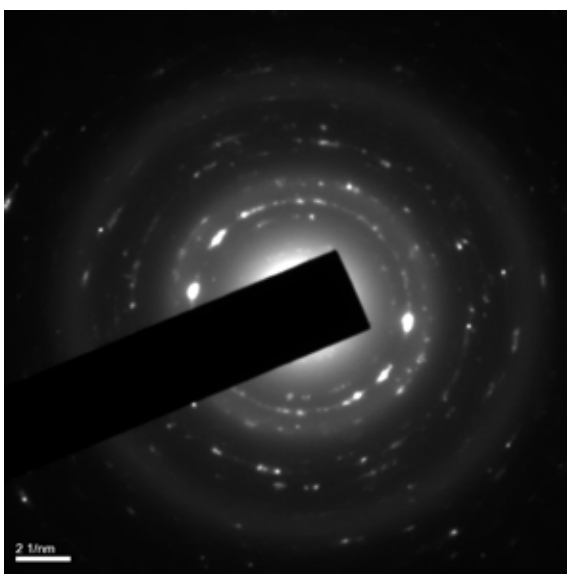


Fig.6 SAED patterns of the as-synthesized CoO nanoparticles

CONCLUSION

In summary, cobalt oxide nanoparticles were synthesised from the precursor complex $Co(Di\text{-}PhAc)_2(N_2H_4)_{1.5}H_2O$ via thermal decomposition. From IR Spectra, the separation of asymmetric and symmetric (υ_{asymm} - υ_{sym}) carboxylate stretching of 227 cm^{-1} indicates the unidentate coordination of carboxylate ions. The N-N stretching frequency of hydrazine moieties are observed at 961 cm^{-1} indicating their bidentate bridging nature. Thermal studies of the precursor complex show multi step degradation to form CoO nanoparticles, which is also confirmed by XRD studies. From the HRTEM observations, the cobalt oxide nanoparticles are found to be of the average size of 13 nm which is consistent with the XRD result.

Thus, this novel route gives an efficient method of preparation of CoO nanoparticles.

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