

SYNTHESIS AND CHARACTERISATION COBALT FERRITE NANO COMPOSITE

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Abstract:

Polymer hybrids have become a major area of research and development owing to the remarkable properties and multifunctional behaviour deriving from their nanocomposite/nanohybrid structure. In this class, magnetic polymer nanocomposite are of special interest because of the combination of excellent magnetic properties, high specific area, surface active sites, high chemical stability and good biocompatibility. Crystalline, magnetic, cobalt ferrite nanoparticles were synthesized from an aqueous solution containing ammonium hydroxide as a capping agent by a thermal treatment followed by calcination at various temperatures. The structural characteristics of the calcined samples were determined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM). Magnetization measurements were obtained at room temperature by using a vibrating sample magnetometer (VSM), which showed that the calcined samples exhibited typical magnetic behaviors.

Key Words: Polymer Nano Composite, Alginate Cobalt Ferrite, Nano Composite, BET, TEM SEM, Core – Shell

Introduction:

Transition Metal Oxides

Transition metal oxides are technologically important materials that have found to be relevant in chemical applications.

Classifying metal oxides as catalysts are quite tedious since it involves a variety of crystal systems of different compositions with a wide range of physico-chemical properties. Oxide catalysts fall into two general categories. They are either poor electrical conductors or good conductors. Insulator oxides are those in which the cationic material has a single oxidation

state, so they have stoichiometric M:O ratios. The simple oxides, MgO, Al₂O₃ and SiO₂ and the more complex zeolites, which are aluminosilicates, fall into this category. These materials are not effective as oxidation catalysts and find most use as solid acids or bases^{1,2}. Semiconductor and conducting oxides are most commonly used in oxidations. They are materials in which the metal ion species is relatively easily cycled between two different valence states. There can be two different oxidation states under reaction conditions as in Fe₂O₃, V₂O₅, TiO₂, CuO or NiO, or the interconversion between the positive ion and neutral metal as with the more easily reduced oxides such as ZnO and CdO. Semiconductor oxides can be either n-type (e.g., Fe₂O₃, V₂O₅, TiO₂, CuO etc) or p-type (e.g., NiO, CoO, Cu₂O etc).

In general, oxides are prepared in single component or in multiple components; they may be crystalline or amorphous and they may be supported or unsupported. While simple oxides show activity for some oxidations they are more commonly used as solid acids or bases.

Mixed Metal Oxides

Oxides of two or more different kinds of cations are known as mixed metal oxides. They can be further classified based on whether they are crystalline or amorphous. If the oxides are crystalline the crystal structure can determine the oxide composition. For instance, perovskites have the general formula ABO₃, scheelites are ABO₄, spinels are AB₂O₄ and palmeirites are A₃B₂O₈. The common feature of mixed oxide catalysts, irrespective of the mode of mutual arrangement of their components, is the presence of M_Iⁿ⁺-O_x and M_{II}ⁿ⁺-O_x polyhedra, where M_I and M_{II} are different cations in their structure. These polyhedra can be connected in various ways, e.g., corner, or edge sharing, forming chains M_I-O-M_{II}-O, M_IO-M_I-O or M_{II}-O-M_{II}. Various arrangements of atoms of a given element, differing by the coordination, nature and the next neighboring cation and type of bonding may be then exposed on the catalyst surface. For mixed oxide catalysts it is not always evident which of the constituent elements plays a role of active centers. Although the industrial catalysts are usually multiphase systems, the presence of one phase, for example spinels, appears usually to be indispensable to render the systems active in a given reaction. One of the most important results of the studies on monophasic systems is the demonstration of different catalytic properties of different crystallographic faces in an oxide, which provided an experimental proof for structure sensitivity phenomenon in the oxide systems.

EXPERIMENTAL

Solvents and Chemicals:

Double Distilled Water: Electrochemically and spectrally pure water was used for all the procedures involving water. This water was obtained by first distilling the deionised feeder water with 0.2M KMnO₄ solution followed by double distillation of the distilled outputs. This water was stored in clean glass containers and all the operations were conducted using this water.

Analytical Grade (BDH/ E. MERCK) chemicals Ferric Citrate, Citric Acid, Zinc Nitrate, Nickel Nitrate, Manganese Nitrate (Fluka) were used as supplied, without any further purification for the synthesis.

Preparation of Ferro spinels:

The most common methods used to prepare complex oxides are co-precipitation^{1,2}, sol-gel method^{3,4}, complexation method², combustion method^{5,6} and ceramic method⁷.

Preparation of Copper and Cobalt Substituted Nickel-Zinc Ferrites:

The major classification of synthesis of these nanomaterials is of two types, 1. Top down approach and 2. Bottom up approach

Top-down approach:

The nanosized materials are prepared at the expense of the bulk material in this technique. Examples are ball- milling and laser ablation techniques. These methods enable one to synthesize the particles of polydispersity. Poly dispersity means the particles of different size range. This is the disadvantage of this method.

Bottom-up approach:

The nanosized materials are prepared from dissolved species to nano particles through the chemical reactions such as precipitation or reduction. Examples are chemical reduction, thermal decomposition methods, and controlled precipitation. Nevertheless, this method can be used to synthesize the particles of almost in the similar size range (monodispersity). The synthesis of Au nanoparticles using the sodium borohydride as reducing agent and citric acid as the capping agents is an opt example for this method.

This method yields the Au particles of 2-4 nm. It is not easy to achieve because it needs the some strategy using the chemistry of the reaction. In other words, the colloidal chemistry takes the main role in the synthesis based chemical methods in solution. The nucleation and growth rate should be controlled. In general, the growth of the nuclei occurs at once the saturation occurs in the growth solution. The kinetics of the growth of the particle is fast to attain the stable particle size. The initially formed tiny particles are called as nuclei over which the other atoms or molecules stacks and thus the growth occurs. The driving force for this growth is to reduce the surface energy of the small growth species. This growth extends as long as the atoms are available in the solution. In this case, if all nuclei are formed at once, this is known as homogeneous nucleation. All the nuclei may be formed at different times. Then it is called as heterogeneous nucleation. Homogeneous nucleation results in the monodispersed particle whereas the heterogeneous nucleation gives rise to the formation of poly-dispersed particles. Thus, by controlling the growth, one can achieve the needs in synthesis of the nanonmaterial.

Cobalt Ferrite CoFe_2O_4 has been synthesized by a chemical co-precipitation method. The samples were characterized by XRD, FT-IR, measurements. The samples were characterized by using XRD, thermogravimetry TEM, and SEM techniques.

Methods of preparation

Ferrites can be prepared by almost all the existing techniques of solid state chemistry, leading to a wide variety of forms: thin and thick films, single crystals and polycrystalline aggregates. The ideal characteristics of ferrite powders are:

- Small particle size
- Narrow distribution in particle size
- Dispersed particles
- High purity
- Homogeneous composition

For the exact reproducibility of the ferrite particles utmost care must be taken during the preparation stages. Minor changes in the preparation method can drastically alter their properties. The oldest method of preparation of ferrites is the ceramic method. The precursor compounds are usually iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) and oxides or carbonates of the other cations in the desired ferrite and these are ground well by mechanical milling. The major drawback found for this method is the lack of homogeneity of the material prepared. Again, the high temperature (1200 K) required to complete solid state reactions leads to drastic decrease in surface area of the resulting material by sintering.

Ferrite powders with all the ideal characteristics mentioned above can be prepared by various new methods. Their common feature is that the mixing of components takes place at the atomic or molecular scale. Co-precipitation is a very suitable method for the creation of homogeneous catalyst components or for the moulding of precursors with a definite stoichiometry, which can easily be converted to the active catalyst⁸. This method is based on the stoichiometric mixing of aqueous solutions of chlorides, nitrates and sulphates of Fe^{3+} , and of divalent Ni, Co, Mg, Ba, Sr, etc., in the concentrations required for the ferrite composition and their simultaneous precipitation in the form of hydroxides by NaOH^{9-13} . This is followed by filtration, washing and calcination of the product to form the oxide. The morphology, the texture, the structure and the size of the particles can be accurately controlled by altering the pH of the solution, temperature and nature of the reagents¹⁴. By this method ferrite particles with a narrow size distribution in the range 50-500 nm may be obtained, with high purity.

The precursor method allows the preparation of ferrites with a precise stoichiometry. It involves the synthesis of a compound (precursor) in which the reactants are present in the required stoichiometry. Upon heating in air (1200-1500 K), the precursor decomposes to yield the ferrite¹⁵⁻¹⁷. Particles with high magnetization, high purity and size in the range 20-60 nm can be obtained by this method. Sol gel techniques are receiving much attention because they can be applied to a wide variety of materials; they offer the possibility of controlling not only the size and distribution of particles, but also their shape. A broad range of ferrites with any desired shape can be prepared by this technique¹⁸⁻¹⁹. The process involves the preparation of a sol, which is a dispersion of a solid and a dispersed phase in a liquid (dispersion medium). The sol is prepared by mixing concentrated solutions containing the cations of interest, with an organic solvent as dispersion medium. The sol is then destabilized by adding water, leading to the formation of a gel. This is transformed to the solid phase by high

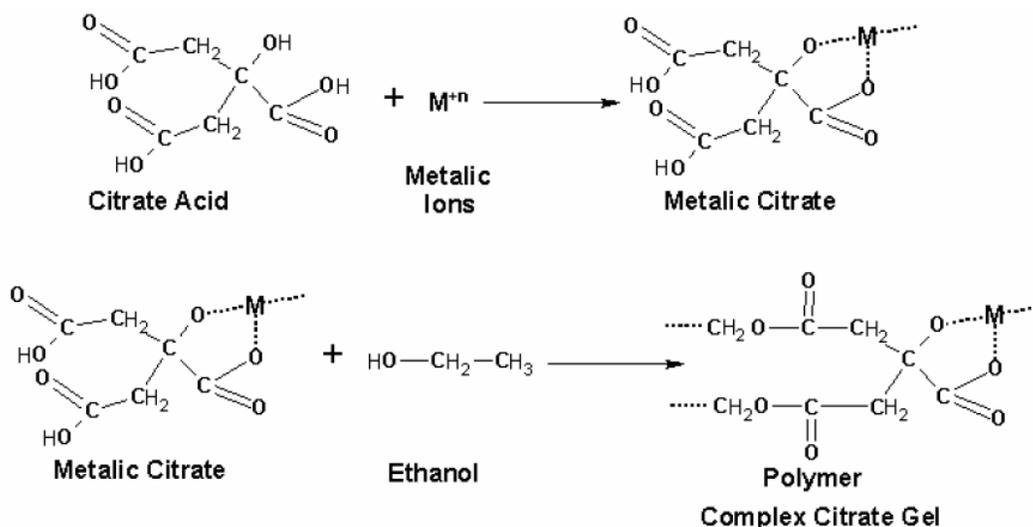
pressure heating whereby the liquid contained in the gel is transformed into supercritical vapours.

Spray-drying technique of preparation of ferrites involves precipitation from a concentrated solution of cations by solvent evaporation. To ensure that the particle size remains small, the concentrated solution is atomized at high pressure into fine droplets of 100-500 nm diameter; the solvent is rapidly evaporated by an upward stream of hot gas. Several alternative methods are currently under development, as an efficient way to control the texture, composition, homogeneity and structural properties of the ferrite particles¹⁸⁻²². In freeze drying method, the aqueous, concentrated solution is atomized into fine droplets, and are rapidly frozen by blowing into low temperature bath such as iceacetone, or liquid nitrogen. The droplets are then dried in vacuum and the anhydrous salts are calcined to produce fine powders. Ni-Zn ferrites have been obtained from freeze-drying with high density and Small and uniform grain size²³. Combustion synthesis is a novel method for the preparation of fine particles of ferrites making use of the exothermic redox reaction between metal nitrate and tetraformaltriazine or oxalic acid dihydrazine²⁴. In this process stoichiometric ratio of nitrates is dissolved in the minimum amount of water in a pyrex dish; the fuel is added and is heated at 350°C in a muffle furnace. A heating rate of 75°C/min is used to obtain good combustion. This method can be used for the synthesis offerrospinel.

In addition to the above-discussed methods, some other methods like molten salt synthesis²⁵ and shock wave synthesis²⁶⁻²⁸ are also applied in the ferrite synthesis.

Citrate Precursor Method:

The citrate precursor method is a promising technique for the synthesis of certain technical ceramics²⁹⁻³⁰. Since all the reactants are solutions, they can be uniformly mixed on an atomic or molecular level, and the amount of the reactants can be accurately controlled.



Characterisation of Nano Ferrites:

The calcined samples were characterized by adopting various physico-chemical methods such as X-ray diffraction analysis, Infrared spectroscopy, SEM and TG-DTA,

Theory and Experimental Procedure

X-Ray Diffraction Analysis

The diffraction patterns can be used to identify various phases in a catalyst. Diffraction can occur whenever Bragg's law $n\lambda = 2d \sin\theta$ is satisfied. The XRD method involves the interaction between the incident monochromatized X-rays (like Cu K α or Mo K α source) with the periodic structures of polycrystalline material. Bragg peaks are measured by observing the intensity of the scattered radiation as a function of scattering angle 2θ . The interplanar distances or d-spacings are calculated from the values of the peaks observed from the above Bragg equation, where, 'n' is order of reflection and the values are 1,2,3 etc.

The width of diffraction peaks carries information on the dimensions of the reflecting planes. Diffraction lines from the perfect crystals are very narrow. For crystals with size below 100 nm, line broadening occurs due to incomplete destructive interference in scattering directions where the X-rays are out of phase. The Debye-Scherrer formula³¹, $D_{hkl} = 0.91/\lambda \cos\theta$ (1) is used to estimate the crystallite size, where D_{hkl} , λ , θ and q are the volume averaged particle diameter, x-ray wavelength, full width at half maximum (FWHM) and diffraction angle, respectively. It is possible to find out the symmetry and cell constant of a given powder by x-ray diffraction technique.

Powder X-ray diffraction (XRD) patterns of the all catalysts reported in this study were recorded using a Rigaku Geigerflex instrument equipped with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) with Ni-filter.

Infrared Spectroscopy

Infrared techniques have got remarkable importance in the field of heterogeneous catalysis and in the field of surface chemistry and catalysis over metal oxides. A variety of IR techniques have been used in order to get information on the surface chemistry of different solids. The theory of diffuse reflectance spectra was developed by Kubelka and Munk³² and extended by Kortum et al³³. According to this theory, $f(R_a) = (1-R_a)^2/2R_a = K/S$ (2) where R_a is the diffuse reflectance from an 'infinitely' thick sample, K is the extinction coefficient and S is a scattering coefficient. It is known that structure plays an important role in the catalytic activity of many heterogeneous systems. The IR spectrum of the ferrite samples reported here were recorded through a DR mode (Shimadzu) in the range 400 cm^{-1} to 4000 cm^{-1} .

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is considered to be a powerful tool to get informations about morphology and particle size. SEM is carried out by passing a narrow electron beam over the surface and detecting the yield of either secondary or back scattered electrons as a function of the position of the primary beam. The size and morphology of the crystals of all the compositions were examined using a JEOL JSM-840A scanning electron microscope.

Thermal Analysis (TG and DTA)

Thermal analysis includes a group of methods by which the physical and chemical properties of a substance, a mixture and/or reaction mixtures are determined as a function of temperature (or time), while the sample is subjected to a controlled temperature program. In thermogravimetry, the mass of the sample is monitored as a function of temperature (or time), while the sample is subjected to a controlled temperature program. Differential Thermal Analysis (DTA) measures the difference in temperature between a sample and a thermally inert reference as the temperature is raised. A plot of this differential provides information on

exothermic and endothermic reactions taking place in the sample, which include phase transitions, dehydration, decomposition, redox, or solidstate reactions. Thermogravimetry and differential thermal analysis measurements were performed with a Mettler TA-1 apparatus equipped with a control and data acquisition system developed by the AnatechBv. About 100 mg samples of spent catalysts were measured in air at a heating ramp of 2 K min⁻¹ up to 1070 K.

Catalytic Study:

The acetylation of amines, alcohols and phenols is an important reaction in organic synthesis. Pyridine and 4-dialkylaminopyridine are the most commonly used basic catalysts. Recent Literature describes numerous catalysts which are either acidic or basic. H-FER has been reported for the acetylation of alcohols and phenols under solvent free conditions. Substituted Nanoferrites have been used for the acetylation of amines under solvent free conditions. The product formed had been checked with TLC and the final product has been separated by washing the ferrite-product mixture with EtoAC+Petroleum ether (1:9) and recrystallised. The reactions were carried out at room temperature by reacting with acetyl chloride. The reaction involves the mixing up of 1mmol of amine , 1 mmol of acetyl chloride and 100 mg of ferrite)

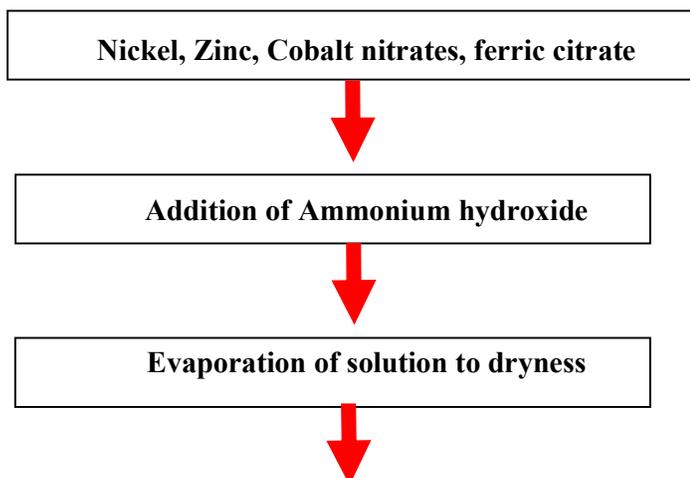
Separation, Washing and Reuse of Catalysts:

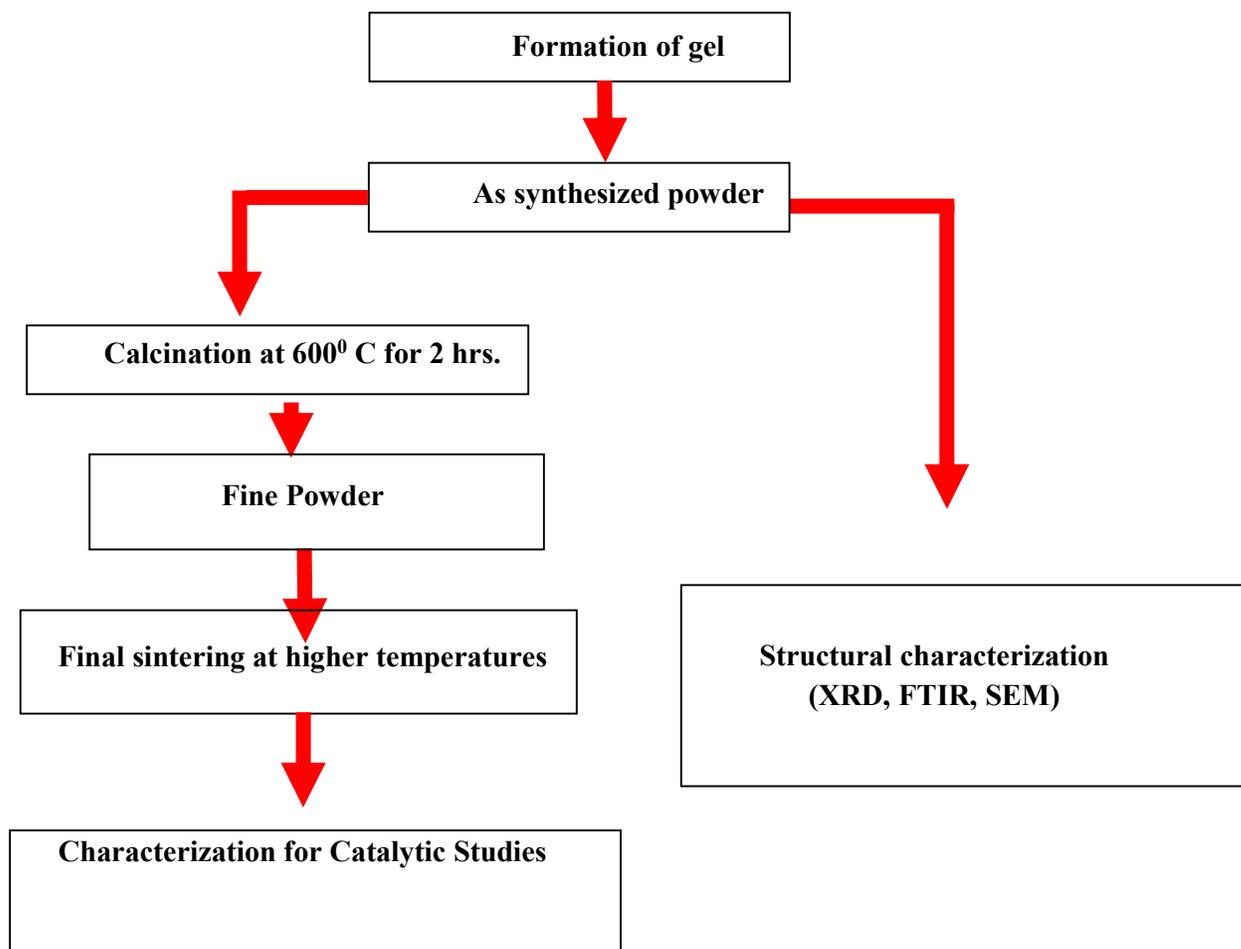
The catalysts were removed from the reaction using a strong magnet. They were washed with water, alcohol, acetone and dried at room temperature and further heated in the hot air oven at 200^oC for 4 hours. The catalysts were reused for 5 times.

SYNTHESIS AND CHARACTERISATION

Synthesis of Cobalt Ferrite:

The aim of this work is to present a novel and economical method of preparation of Cobalt Ferrite by the citrate precursor method in order to achieve sintering at lower temperatures.





Characterisation of the Cobalt Spinel Ferrite:

Chemical compositions structural and textural properties of CoFe_2O_4 spinel system ferrites are prepared in the present study are summarized in the following Table.

Catalyst Composition	Crystallite Size (nm)
CoFe_2O_4	22nm

Sintering Temperature	400°C	500°C	600°C
System	Crystallite Size (nm)		
CoFe_2O_4	19	25	32

4.3 X-Ray Diffraction Spectral Analysis:

4.3.1 X-Ray Diffraction Spectra of CoFe₂O₄

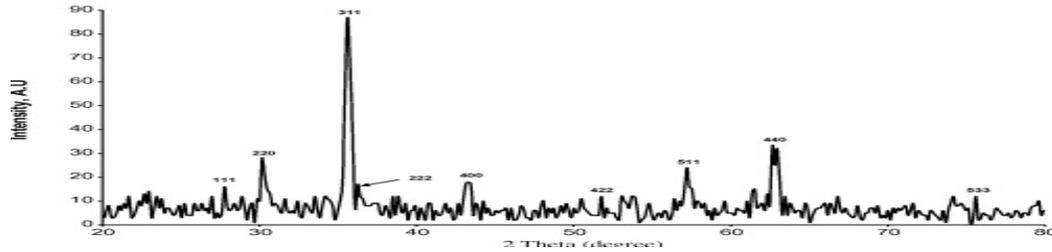


Figure 4.1 : XRD Spectrum of CoFe₂O₄

The XRD patterns of the sample are shown in Fig. 4.1 shows the obtained product after precipitation. The powders calcined at 600°C showed pure CoFe₂O₄ phase. All of the main peaks are indexed as the CoFe₂O₄ in the standard data (JCPD No. 3-864 and 22-1086). The peaks can be indexed to (111), (220), (311), (222), (400), (422), (511) (440) and (533) planes of a cubic unit cell. The broadness of the diffraction peaks indicates the small size of the ferrite crystals. The average crystallite sizes of CoFe₂O₄ samples were calculated from Scherrer's equation:

$$D_c = \frac{K\lambda}{\beta \cos \theta}$$

where b is the breadth of the observed diffraction line at its half-intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and k is the wavelength of X-ray source used in XRD and were found to be 23, 33, 37 nm for the samples of CoFe₂O₄ nanocrystals calcined at 400, 500, and 600°C, respectively.

Infrared Spectral Data Analysis:

Infrared Spectral Data Analysis of CoFe₂O₄

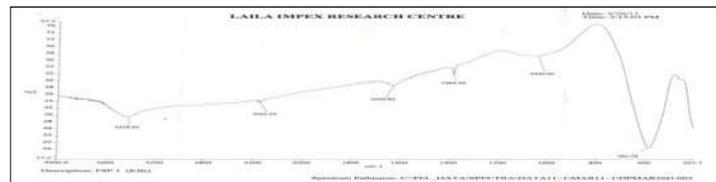


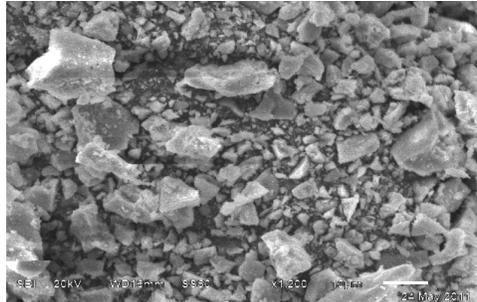
Figure 4.3 : Infrared Spectrum of CoFe₂O₄

IR studies were carried out to understand the band positions attributed to the lattice sites. Figure 4.3 shows the metal ions distributed in two different environments in spinel at 567cm⁻¹ (n1) and at 400 cm⁻¹ (n2) (solid arrows), attributed to metal-oxygen bands and the phase formation can be very well assigned from the appearance of two broad DR-IR bands

Scanning Electron Microscope Analysis:

Scanning Electron Microscope Analysis CoFe₂O₄

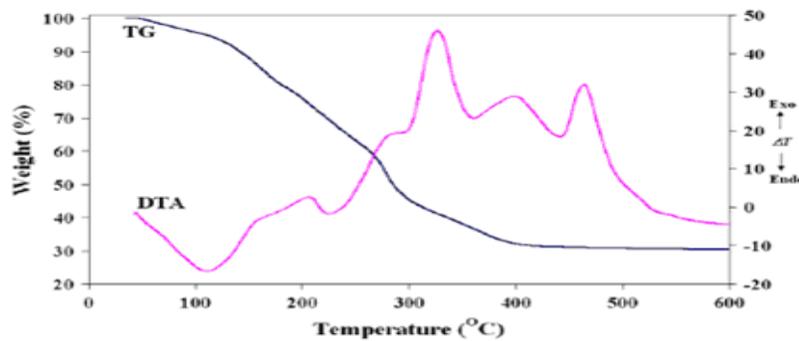
Scanning electron micrograms of calcined samples showed particles of size in the range 40-50 nm, which confirm the crystalline nature of the material. Thus the crystalline nature of the material, as revealed from the XRD data, is supported by SEM images.

Fig 4.4 SEM image of CoFe₂O₄

Thermo Gravimetric Analysis

Thermo Gravimetric Analysis CoFe₂O₄

DTA curve for the dried samples of CoFe₂O₄ series are presented in Figure 4.5. It shows the DTA curve of the as-synthesized powder.

Figure 4.5 TG-DTA of CoFe₂O₄

The very broad endothermic DTA peak with peak temperature at 118⁰ C characterizes the dehydration process. The four successive exothermic DTA peaks with peak temperatures at 210, 325, 400 and 467⁰C characterize the nitrate organic decomposition. No obvious weight loss can be detected behind 410⁰ C. The small exothermic DTA peak at 541⁰ C which is not accompanied by any weight loss can be attributed to the ferrite formation. Thus, according to these obtained data, the minimum calcination temperature for the precursor can be taken as 600⁰.

CONCLUSION:

This analysis involving the above spectral data shows that spinel structures have been obtained by this chemical route at lower temperatures. This method is time saving when compared to the time consuming and tiresome processes involved in the manufacturing of nano ferrites.

The powder synthesized by the citrate precursor method demonstrated considerable sinterability. The fine particle morphology of the powder synthesized by this method is responsible for its higher sintering activity. The highly active powders can be sintered at relatively low temperatures to obtain highly dense and homogeneous polycrystalline ferrites for high frequency applications.

Cobalt ferrite systems were studied for alkylation of aniline using methanol as the alkylating agent. It was observed that these systems can effectively alkylate aniline to give N-methyl aniline selectively. More than 99% NMA selectivity was observed under the optimized

reaction conditions. Even at low concentration of methanol in the feed, these systems exhibited high activity.

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