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Nickel Ferrite Nanomaterials: Synthesis, Characterization and Properties

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In the present study, AB_2O_4 type nickel ferrite (NiFe₂O₄) nanoparticles (NPs) were prepared by a coprecipitation method. The crystal structure, phase purity, morphology, optical and kinetic properties of the NiFe₂O NPs were investigated by X-ray diffraction (XRD), Rietveld refinement, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and UV-Visible spectroscopy. The XRD diffraction pattern revealed the degree of crystallinity and confirming the cubic spinel system with the space group of Fd3m:2, a typical crystal structure of nickel ferrite spinel. The SEM studies exhibited that the synthesized NiFe₂O NPs had an average particle size of ~55 nm. Two stage decomposition pattern was observed for both as-synthesized and calcined NiFe₂O NPs. The TGA was further used to analyze the Coats-Redfern and Friedman methods in order to estimate the decomposition activation energy (E_a) which revealed that it obeyed the F1 solid-state nucleation-growth mechanism. Finally, a schematic mechanism for preparation of the AB₂O₄ type nickel ferrite NPs was proposed.

Keywords: Nickel Ferrite Nanoparticles, Crystal Structure, Nucleation Kinetics.

1. INTRODUCTION

Industrial demands for a wide range of chemical applications have generated a growing need for pure nanomaterials, synthesized with desirable particle sizes and shapes for variety of applications.¹⁻⁴ The nanomaterials inherently possess large surface areas as well as improved mechanical and catalytic properties.⁵⁻⁹ The unique quantum size effects exhibited by nanoparticles have been reported to enhance their electronic, magnetic, chemical, optical and surface properties, making them suited for use in catalysts, ferrofluids, data storage, biomarkers, bio-sensors, color imaging, pigments, and so on.¹⁰⁻¹² Amongst the various nanomaterials, mixed metal oxides (MMOs) with different structural geometries have attracted increasing technological and industrial interest, mainly due to their synergetic properties and improved overall application performance with regards to magnetic, electrical, optical, and catalytic properties.^{13–15} The MMO fabrication method can critically influence the morphology of the resulting material and consequently its technological applications. Various routes to synthesize nano-structured MMOs exist, including co-precipitation, sol–gel, solvothermal, micro-emulsion, combustion, vapor condensation, spray pyrol-ysis, and templated/surface-derivatized techniques.^{16–21} MMOs of the AB₂O₄ type occupy a special place in the globalized competitive lifestyle. They show great potential for use in catalysis, electronic ceramics, and various optical devices. NiFe₂O₄ is one well-known example of the AB₂O₄ type of material.^{22–24} In the pure phase, Fe³⁺ ions are equally distributed between tetrahedral A- and octahedral B-sites, and the Ni²⁺ ions are located in the octahedral B-sites.²⁵

Nanoparticulate MMOs usually exhibit high BET surface areas and consequently higher reaction rates than their bulk phase counterparts, making them great potential candidates for chemical conversion and heterogeneous catalytic reactions, particularly refining.^{26,27} Different parameters such as atmosphere, heating procedure, particle size, and presence of impurities can influence the

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thermal kinetics of solid-state materials.²⁸ Thermal techniques have been used to investigate the thermal decomposition kinetics of solid materials.²⁹ Solid-state reactions are more complicated than reactions in homogenous media, because of various possible rate limiting steps, including nucleation, nuclei growth, and diffusion. For thermal degradation processes and mechanisms, thermogravimetric analysis (TGA) has been used to investigate kinetic parameters such as the activation energy (E_{α}) .^{30,31} Kinetic data obtained from TGA analysis are very useful for understanding thermal degradation processes and mechanisms. Surprisingly, there is not a great deal of information in literature about the reaction kinetics of MMOs.

Herein, a facile synthesis method to prepare nickel ferrite NPs has been reported. The synthesized NPs were characterized using different techniques in terms of their morphological, structural and optical properties. The thermodynamic properties were examined by thermogravimetric analysis (TGA) and the activation energy of each step, along with its decomposition process, was determined by two methods, i.e., Coats-Redfern method³² and the Friedman differential.³³ Finally, a schematic mechanism is proposed for the formation of NPs.

2. THEORETICAL APPROACH TO KINETIC ANALYSIS

The rate of a decomposition process as measured using TGA can be described as the product of two separate functions of the temperature-dependent rate constant k(T) and the temperature-independent conversion $f(\alpha)$, as follows:

$$d\alpha/dt = \beta d\alpha/dT = k(T)f(\alpha) = A\exp(-E_{\alpha}/RT)f(\alpha)$$
(1)

where α is the fraction of material decomposed at time *t*, β is the linear heating rate, *A* is the frequency factor, E_{α} is the activation energy, and *R* is the gas constant (8.314 Jmol⁻¹ K⁻¹). Rearrangement of Eq. (1) gives:

$$(d\alpha/dT) = (A/\beta)f(\alpha)\exp(-E_{\alpha}/RT)$$
(2)

On integration and approximation of Eq. (2) we obtain:

$$\ln(g(\alpha)) = -E_{\alpha}/RT + \ln[AR/\beta E_{\alpha}]$$
(3)

where $g(\alpha)$ is an integral function of α , dependent on the mechanism of the reaction. The right-hand side of the equation is a temperature integral, which can be evaluated using several techniques. In the present article, the Coats-Redfern integral³² and Friedman differential³³ methods have been used to evaluate kinetic parameters. Results obtained may be compared with one another because they are superior to other methods and show the best data linearity.

The Coats-Redfern integral equation may be written as:

$$g(\alpha) = \int_0^\alpha d(\alpha)/f(\alpha) = (A/\beta) \int_{T_0}^T \exp(-E_\alpha/RT) dT$$
(4)

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where T_0 is onset temperature of decomposition reaction at which no conversion occurs; therefore, T_0 can bet set equal to zero for convenience. This equation, on integration for the first-order degradation process gives:

$$\ln -\frac{\ln(1-\alpha)}{T^2} = -E_{\alpha}/RT + \ln AR/\beta E_{\alpha}$$
(5)

The activation energy, E_{α} , can be calculated from the slope of a plot of the left-hand side against 1/T.

The Friedman differential method may be written as:

$$\ln(d\alpha/dT) = \ln(\beta d\alpha/dT) = \ln A + \ln f(\alpha) - E_{\alpha}/RT \qquad (6)$$

Where β , A, E_{α} , and T represent the same quantities as the ones used in Eq. (1).

For a fixed degree of conversion, the activation energy E_{α} can be calculated from the slope of a plot of the lefthand side against 1/T.

3. EXPERIMENTAL DETAILS

3.1. Synthesis of NiFe₂O₄ NPs

Mixed metal oxide nanoparticles (MMO-NPs) were synthesized by the co-precipitation method, using $Ni(NO_3)_2$. 6H₂O, Fe(NO₃)₃·9H₂O and NaOH solution. All the chemicals used for the synthesis were purchased from Sigma-Aldrich and used as-received. For this reaction, $Ni(NO_3)_2$. 6H₂O (50 mM) and Fe(NO₃)₃ · 9H₂O (50 mM) were mixed in double deionized, distilled water (from a Milli Q system, 18 mega ohm, <3 ppb TOC) under constant stirring for around 30 min, to obtain a transparent solution. The pH of the solution was measured during the dissolution process by pH meter; reaction proceeded until the pH reached a value of 2.67. To this mixture 0.1 M sodium hydroxide, NaOH, was added, drop by drop, until the pH reached 12.3. After complete dissolution, the resulting solution was refluxed at 120 °C for 3 h to remove water. The obtained product was washed sequentially with methanol, acetone, and water to remove ionic impurities, and then dried at room temperature. The dry nanoparticles were calcined in air at 300 °C for 3 h to obtain the final product NiFe₂O₄ NPs. The as-prepared and calcined NiFe₂O₄ NPs were examined using various physicochemical methods.

3.2. Characterizations

The chemical composition of the synthesized NPs was determined using a Perkin-Elmer FT-IR spectrophotometer, scanning in the region from 4000–400 cm⁻¹. The UV-Vis spectrum of the NPs was recorded using a Shimadzu UV-1800 spectrophotometer in absorbance mode, scanning in the region from 200–800 nm. The NPs were well-dispersed in distilled water by exposing the water-NP mixture to sonication for 10 minutes. An X-ray diffraction (XRD) pattern of the nickel ferrite NPs was obtained at room temperature, using CuK_{α} radiation ($\lambda = 1.54178$ Å) generated at an accelerating voltage and intensity of 40 kV

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and 40 mA in contentious mode. The scan was performed in the range from 10° to 85° at a scan speed of 2°/min, with a 0.5° divergence slit a 0.3 mm open receiving slit. The Savitzky, Sonnevelt, and Rachinger profile smoothing methods were applied to the raw diffraction data, which were then background-subtracted. False peaks arising from the Ka₂ radiation were removed, and Rietveld Refinements were performed using X'Pert High Score Plus software (PANalytical, 2012). The average crystallite size was determined from diffraction peakbroadening anlaysis using the Scherrer formula, t =0.9 $\lambda/(B \cos \theta)$.^{34,35} The diffraction spectra were indexed and compared against the Joint Committee on Powder Diffraction Standards (JCPDS) database. Particle surface morphologies and sizes were examined using a JEOL JSM-6380 LA, Japan, scanning electron microscope operated at 20 kV in back-scattered electron and secondary electron detector modes.³⁶ For SEM observation, the NPs were uniformly sprayed onto carbon tape then coated with a thin conducting layer of platinum for 3 s. TEM studies conducted with a JEOL-1011 electron microscope, operated at 100 kV. The synthesized material was prepared for TEM by dispersing NPs in ethanol using an ultrasonic bath, then depositing them on a 300 mesh carbon-coated copper grid. TGA was conducted under a nitrogen atmosphere (100 ml min⁻¹) at a 20 °C/min heating rate from room temperature to 800 °C to determine the decomposition patterns and kinetics of the samples (Mettler Toledo TGA/DSC; Mettler Toledo AG, CH 8603, Schwerzenbach, Switzerland). For TGA, about 5 mg of sample was placed in a platinum (Pt) crucible, with α -Al₂O₃ analyzed as a reference material. Using a 0.01 degree of conversion (α) increment, the activation energy E_a was calculated by the Coats-Redfern and Friedman methods.

4. RESULTS AND DISCUSSION

4.1. X-ray Diffraction and Rietveld Refinement

XRD patterns of the pre-calcined and calcined nanomaterials are shown in Figure 1. The X-ray diffraction pattern for the pre-calcined NPs (Fig. 1(a)) displays two crystalline reflections at 2θ values of 37.49° and 43.74°. A diffraction peak at 37.49° can be attributed to Fe(OH)₃, which matches JCPDS card number (046-1436).³⁷ The calcined NPs (Fig. 1(b)) exhibited the cubic spinel crystalline structure of nickel-iron oxide (nickel ferrite). The peak positions and relative intensities indexed from diffraction patterns from the calcined NPs matched well with JCPDS card number (044-1485).³⁸ It is clear from Figure 1(b) that the NP material consists of a single phase without any detectable secondary phase. The change in diffraction peaks between as-synthesized and calcined NPs is due to the thermal treatment, which enhanced the NP crystallinity by imparting additional nucleation energy. Using the Scherrer equation, volume-average crystallite sizes for the as-synthesized and calcined NPs were



Fig. 1. Typical X-ray diffraction (XRD) patterns of NiFe₂O₄NPs: (a) assynthesized and (b) calcined.

calculated from the (311) and (400) reflections: values of 41.053 nm and 32.503 nm, respectively, were obtained for as-synthesized material, whereas values of 47.19 nm and 36.74 nm, respectively, were obtained for the calcined material. The results confirm that calcining increased the nano-crystallinity of the as-synthesized material. The XRD patterns indicate that NiFe₂O₄ was successfully synthesized as nanoparticles.

The crystallographic parameters for the calcined NPs were refined using Rietveld analysis, using X'Pert High Score Plus software,^{39,40} as shown in Figure 2. The crystal structure refinement was performed in the cubic spinel structure, space group Fd3m:2 in which Ni atoms lie at the 16d Wykoff position (0.5, 0.5, 0.5), Fe atoms lie at the 8a Wykoff position (0.125, 0.125, 0.125) and O atoms lie at the 32e Wykoff position (0.1175, 0.1175, 0.1175). During Rietveld analysis, profile parameters, peak shape parameters and fractional coordinates were refined. The Rietveld refinements results of calcined NiFe₂O₄ material measured at room temperature was observed which revealed the lattice constants of 8.3054 Å, cell volume of 572.903 Å³,



Fig. 2. Rietveld refinement fit for calcined NiFe $_2O_4$ NPs. Below is the difference between the data and the calculated values.



Fig. 3. Microscopy images of NiFe₂O₄: (a) TEM image of calcined NPs (b) SEM image of as-prepared NPs and (c) SEM image of calcined NPs.

space group of Fd-3m:2, R_{exp} of 32.349%, R_p of 18.663%, R_{wp} of 30.527% and goodness of fit (*R*) around 0.890%.

4.2. Electron Microscopic Studies

TEM studies were conducted to explore the shape and size of the as-prepared NPs. As seen in Figure 3(a), the ascalcined NPs are well crystallized, irregular cubes with number-average particle sizes ranging from 40-55 nm. These results closely correlate with the XRD observations. SEM micrographs taken of the material before and after calcination are shown in Figures 3(b) and (c). It is clear that in both cases NPs were successfully prepared. The microstructure of the as-prepared NPs (Fig. 3(b)) shows small dots of irregular cubic and spherical shape with a narrow particle size distribution, with numberaverage sizes ranging from 50-60 nm. In addition to the individual particles, some aggregated particles are also present. The agglomeration of NPs may be attributed to their small dimensions and high density. After the asprepared NPs were heated at 300 °C for 3 h, particles appear interconnected with each other, forming flowerlike micro-structures (Fig. 3(c)). From the SEM image, it is evident that the estimated diameter of each individual flower-shaped structure lies in the range of 4–5 μ m (a 'microflower'). The 'microflower' structure appears to be composed of an arrangement of small sheets with a diameter of \sim 60–70 nm, which were stacked one by one on the surface core of the 'microflower.'

4.3. Optical Properties

The surface chemistry and phase purity of the as-prepared NPs before and after calcination were explored by FTIR within the wavelength (λ) range of 400–4000 cm⁻¹, as shown in Figure 4. The broad, weak absorption peaks located at 3000–3500 cm⁻¹ and 1635 cm⁻¹ in both the as-prepared (Fig. 4(a)) and calcined (Fig. 4(b)) samples can be attributed to the stretching and bending vibrations of physically adsorbed surface moisture (O–H groups), respectively.^{41,42} The strong absorption band located at 1723–1760 cm⁻¹ can be attributed to the typical C=O stretching vibration of saturated ions or CO₂ molecules, whereas the peaks assigned to 1370–1386 cm⁻¹ and 885 cm⁻¹ can be attributed to NO₃⁻ in the as-prepared sample.⁴³ As seen in Figure 4(b), after calcination, the

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 NO_3^- peaks seem to be disappearing, indicating the phase purity of the nanoparticles. No other absorption bands, related to any other impurities, were detected in the FTIR spectra, suggesting the as-prepared nickel ferrite NPs is pure. Strong infrared peaks located at 538 and 562 cm⁻¹ correspond to the stretching vibrations arising from Fe–O and Ni–O, respectively.^{44,45}

In order to explore the band gap of as-synthesized and calcined NP samples, the optical absorption spectra were measured at room temperature in the UV-Vis range from 200–800 nm. The optical band gaps were calculated from the absorption spectra using the Tauc equation, shown below:⁴⁶

$$(\alpha h\nu) = A(h\nu - E_g)^n \tag{7}$$

where α is the absorbance coefficient, A is a constant, $h\nu$ is the photon energy, $E_{\rm g}$ is the energy band gap of the material, and n is equal to two for indirect transition. The experimentally calculated band gap energy according to the Tauc and Menths formula for as-synthesized and calcined NPs are 4.8 and 3.9 eV, respectively (Figs. 5(a) and (b)).⁴⁶ It was observed that the band gap energy decreased after calcination, likely due to the increase in aggregation of small particles, which also increases the grain size of the NPs, indicating the existence of a quantum confinement effect.^{47–49} The band gap and crystal structure data suggest



Fig. 4. FT-IR spectra of $NiFe_2O_4$: (a) as-synthesized NPs and (b) calcined NPs.



Fig. 5. Band gap spectra of NiFe₂O₄NPs: (a) as-synthesized and (b) calcined nanoparticles.

that the calcined material may be used as a photocatalyst in the visible region.

4.4. Thermogravimetric Behavior and Decomposition Kinetics

The thermal behavior of the as-prepared and calcined NPs has been examined by thermogravimetric analysis (TGA) at a heating rate of 20 °C/min under nitrogen flow to investigate their thermal stability, purity, and decomposition pattern. Typical TGA curves as % mass loss verses temperature are presented in Figure 6. The TGA curve of the as-prepared material (Fig. 6(a)) showed a two-step mass loss between 120-300 °C and 300-800 °C, respectively. The first step began at 120 °C and completed below 300 °C with a mass loss of about $\sim 12\%$, likely due to desorption of surface H₂O and organic impurities. The second, major mass loss began at 550 °C and completed at 700 °C with $\sim 18\%$ mass loss. The total mass loss of these processes determined from the TGA curve is around $\sim 30\%$. The decomposition of the calcined 'microflowers' (Fig. 6(b)) occurred in two steps. The first mass loss began at 150 °C, completing at 165 °C. At this point, about ~10% mass loss had occurred. The second mass loss was observed between



Fig. 6. Thermogravimetric analysis (TGA) of the decomposition of $NiFe_2O_4NPs$: (a) as-synthesized and (b) calcined.

265 °C and 300 °C, and increased to around 20%. The overall mass loss observed was approximately 25%. Thus, the 'microflower' aggregate material appears to be more stable, with less mass loss observed when compared to the as-prepared nano-structures. The results clearly justify concluding that both the as-prepared and calcined nano-structures are stable at a higher temperature.

In order to explore more thoroughly the decomposition mechanism/kinetics of the as-prepared and calcined MMO, the data were analyzed by the Coats-Redfern and Friedman methods. The activation energy of the decomposition steps at different conversions can be calculated from a plot of the left-hand side of Eqs. (5) and (6) against 1000/T and fitting a straight line, using the mass-loss curves recorded by TGA. The linear curve fitting for as-prepared and calcined material by the Coats-Redfern and Friedman methods are shown in Figures 7 and 8, respectively. The calculated activation energies by Coats-Redfern were found to be 39.83 (E_a Ist step; $r^2 = 0.997$) and 2.18 (E_a IInd step; $r^2 =$ 0.998) for as-grown NPs, while 24.65 (E_a Ist step; $r^2 =$ 0.999) and 5.38 (E_a IInd step; $r^2 = 0.999$) for calcined MFs. In a similar manner, the calculated activation energies by Friedman method were estimated as 23.94 (E_a Ist step; $r^2 = 0.998$) and 1.92 (E_a IInd step; $r^2 = 0.999$) for as-grown NPs, while 20.04 (E_a Ist step; $r^2 = 0.998$) and 8.77 (E_a IInd step; $r^2 = 0.999$) for calcined MFs. Figures 7 and 8 show that the fitting lines are very nearly straight lines, supporting the applicability of these methods to our prepared mixed oxide system in the conversion range studied, determined at 0.01 fraction mass intervals up to 0.30 and 0.25 for as-prepared and calcined MMO, respectively. The results suggest the values obtained by both methods are in good agreement. These facts strongly support that the solid state decomposition process follows random nucleation with one nucleus on the individual particle (an F1-type reaction mechanism), e.g., a firstorder F1 deceleratory reaction mechanism is operative.^{47–52}



Fig. 7. Coats-Redfern plots of $NiFe_2O_4$ NPs under nitrogen atmosphere: (a) as-synthesized I-step, (b) as-synthesized II-step, (c) calcined I-step, and (d) calcined II-step.

The activation energy values of the as-prepared and calcined MMO, as calculated by both methods, decreased in the following order: first stage mass loss > second stage mass loss.

4.5. Growth Mechanism for the Flower-Shaped Mixed Metal Oxide Aggregates (MMO-MFs)

On the basis of the synthesis process and obtained results, we propose a possible chemical reaction and growth



Fig. 8. Friedman plots of $NiFe_2O_4$ NPs under nitrogen atmosphere. (a) as-synthesized I-step, (b) as-synthesized II-step, (c) calcined I-step (d) calcined II-step.



Fig. 9. Proposed mechanism for the growth of the 'microflower' structures.

mechanism for the 'microflowers' structures (MFs), based on the synthetic process and the obtained results. Figure 9 shows a schematic for the systematic growth of NiFe₂O₄ nanostructure arrays, or MFs though the solution process. During synthesis, a dark-red $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution was mixed with green aqueous Ni(NO₃)₂ · 6H₂O, with constant stirring at a low temperature. NaOH was added drop-wise to this aqueous solution to co-precipitate the product when the pH reaches 12.30. Next, the solution was transferred to a refluxing pot and refluxed at 120 °C for 3 h to produce the NPs.

NaOH plays a crucial role in the nucleation and formation of the resulting NiFe₂O₄ NPs. In solution, hydroxyl ions from NaOH react with iron and nickel nitrate to form their respective hydroxides (Eqs. (8) and (9)). As the hydrated particles of Fe(OH)₃ and Ni(OH)₂ are calcined at 300 °C for 3 h, the hydration water evolves from the prepared material and pure NiFe₂O₄ forms (Eq. (10)). The subsequent NiFe₂O₄ 'microflower' structures form through a two-step nucleation and growth mechanism. Initially, in the nucleation phase, the small NPs (Fig. 9(a)) grow in the refluxing pot and as reaction temperature and time increases, these small product NPs form small NP cores in solution (Fig. 9(b)). We believe that after acquiring optimum thermal energy from the refluxing pot, the newly formed NPs, continually supplied by the reactants in solution, may start to aggregate onto the previously formed small nanocluster cores (Fig. 9(c)). Calcining provides additional energy to the system, to promote aggregation and arrangement of sheets of the NP cores (Fig. 9(d)).

The size of these cores increases with rising calcine temperature. On the surface of the core cells 'stems' or 'rachis' form, which furnishes the growth pathway for the base plates/sheets of the MMOs (Fig. 9(e)). When the aggregates become saturated at their ideal refluxing and calcining temperature, the structures fully mature into flower-like morphology ('microflowers'; Fig. 9(f)).

 $Fe(NO_3)_3 \cdot 9H_2O + 3NaOH \rightarrow Fe(OH)_3 + 2NaNO_3 + 9H_2O$ (8)

$$Ni(NO_3)_2 \cdot 6H_2O + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3 + 6H_2O$$
(9)

$$2Fe(OH)_3 + Ni(OH)_2 \rightarrow NiFe_2O_4 + 4H_2O\uparrow$$
(10)

5. CONCLUSION

In summary, nickel ferrite NPs were synthesized by a single step co-precipitation method and characterized in detail in terms of their morphological, structural, compositional, optical and thermal properties. The detailed studies confirmed that the synthesized material possess well crystallinity with pure phase and grown in high density. The thermogravimetric analysis confirmed that the thermal stabilities of the calcined nanomaterials was better than the as-synthesized ones. The probable thermal degradation of the NPs, deduced from the Coats-Redfern and Friedman methods, appears to be a two-step nucleation and growth, F1, mechanism. The activation energy calculated by the Coats-Redfern and Friedman methods are in good agreement with a calculated correlation coefficient

which is greater than 0.99. The obtained results confirmed that ferrite nanoparticles can be simply synthesized by co-precipitation method.

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