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NON ISOTHERMAL DECOMPOSITION AND THERMODYNAMICS OF MAGNETITE NANOPARTICLES

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ABSTRACT

Magnetite nanoparticles were synthesized by using chemical co-precipitation method. Structural properties were studied by X-ray diffraction. Non isothermal kinetics of solid state decomposition of magnetite nanoparticles was studied under air atmosphere using thermo gravimetric analysis (TGA) in the temperature range (25^0C-1000^0C). In the present study the data was analyzed using various solid state reaction models. Integral method using Coats–Redfern and Horowitz-Metzger equations were applied in dynamic data analysis. The activation energy (E*), frequency factor (A), change in Entropy (ΔS), change in Enthalpy (ΔH) and change in Gibbs free energy (ΔF) for magnetite nanoparticles were evaluated. It was found that magnetite nanoparticles show one step decomposition behavior. Results indicate that the thermal activation energy of magnetite nanoparticles vary between the ranges of values 15-23 $KJmol^{-1}$.

KEYWORDS: Magnetite nanoparticles, Non-isothermal decomposition, Coats–Redfern and Horowitz-Metzger method.

INTRODUCTION

Magnetic particles, having different sizes from nanometer to micrometer range are very attractive materials not only in the field of magnetic recording but also within the area of biological and medical applications[1]. The iron oxide nanoparticles are one of the promising particles with different derivatives like magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). They are widely used for various applications like magnetic media and for the storage[2], ferro fluids[3], magnetic resonance imaging (MRI) enhancement[4], catalysis, drug delivery[5], magnetic sensors[6]. However, magnetite nanoparticles (Fe_3O_4) are the most commonly employed for above applications due to their response to magnetic field through the superparamagnetic behavior at room temperature amongst various forms of iron–oxides[7].

The information about the thermal degradation kinetics and degradation mechanisms can improve the thermal behavior of any material. Thermal decomposition behavior of materials is useful in predicting stability of those materials. Simultaneous Thermogravimetric-differential thermogravimetry (TG- DTG-DTA) is an excellent tool for studying the kinetics of thermal degradation[8]. It gives composition of original substance of sample the composition & thermal stability of intermediate compounds and composition of residues and provides information on frequency factor or activation energy. Knowledge of kinetics parameters are one of the key parameter which gives useful information about the decomposition mechanism for high-temperature applications[9]. Thermal behavior studies at various temperatures provide the important information about its practical utility. Thermal analysis can tell us about composition, transition temperature, degree of purity decomposition kinetic thermal stability, oxidative stability, and thermal expansion, loss of modulus and energy dissipation[10,11]. To the best our knowledge, there is no report on non-isothermal decomposition kinetics and thermodynamics analysis for the magnetite nanoparticles. Here, we have synthesized magnetite nanoparticles via chemical co-precipitation method. The kinetics and thermodynamics of magnetite nanoparticles were evaluated from TGA-DTG-DTA using Coats-Redfern (CR) and Horowitz-Metzger (HM) methods. Motivation of this study is to investigate the thermal degradation behavior of magnetite nanoparticles for practical utility.

EXPERIMENTAL

Material used

Anhydrous ferric chloride, ferrous chloride, 30 % ammonia solution, hydrochloride acid and de-ionized water were used for synthesis.

Preparation of magnetite nanoparticles

The mechanism of the formation of Fe_3O_4 nanoparticles with ferrous and ferric salts at the ratio of 1:2, via 'co-precipitation' method is represented by the following equation. The stoichiometric amounts of ferrous and ferric ions react to produce-

$$Fe_3O_4:\ Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

$FeCl_2.4H_2O$ and $FeCl_3$ at 1:2 molar ratio were dissolved into a round bottom flask which contains 200 ml of deoxygenated distilled water at room temperature. The aqueous solution was heated at 80 °C so as to obtain a clear yellow solution under vigorous agitation. Then, 30% aqueous ammonia solution was added drop wise until the pH of the solution reached the value of 10. The reaction was maintained for an additional 45 min under vigorous stirring. The mixture was put to settle the precipitate. After filtration, the black precipitate of magnetite nanoparticles was obtained.

Characterizations

X-ray diffraction patterns of the samples were recorded using the powder X-Ray Diffrectometer (Bruker D8 ADVANCE) with Cu Kα irradiation (λ= 1.5406 Å). The operating voltage and current were kept at 40 kV and 30 mA respectively. Average crystallite size (D) of Fe_3O_4 particles was calculated using Scherrer's formula:

$D = \frac{0.93\lambda}{\beta cos\theta}$, where λ is is the X-ray wavelength, β is the full width at half maximum in radian and θ is the angle of diffraction.

The decomposition was followed in air using dynamic thermo gravimetric techniques in the temperature range (25^0C-1050^0C) using EXSTAR TG/DTA 6300 with the flow rate 250 of mL / min at the heating rate 10^0 C/min.

RESULTS & DISCUSSION

XRD analysis

Fig.1. (a) shows XRD pattern of Fe_3O_4 sample alongwith its respective Williamson-Hall (W-H) plot in fig.1. (b) to show strain in the sample. The data obtained from X-ray diffractometer was processed with the help of origin software. The sharp characteristic peaks show the existence of the nano phase. The diffraction peaks at 2θ =30.30^0, 35.66^0, 43.35^0, 57.3^0, 63.0^0 correspond to hkl value (220), (311), (400), (511) and (440) planes of cubic spinel structure of Fe_3O_4, having space group Fd3m (227) respectively, which shows that sample is formed in pure phase. The peak at 2θ =35.66^0 shows the maximum intensity and indexed as (311). All of the diffraction peaks can be identified from the Joint Committee on Power Diffraction Standards (JCPDS) card no 19-629. The similar pattern of magnetite nanoparticles are reported by different authors[12-14].The lattice parameter of Fe_3O_4 extracted from XRD data is a =8.359 A^0 which is in agreement with the literature value 8.396 (A^0) [JCPDS card no. 77-1545] which indicates that the product consists of cubic spinel structure and crystalline single-phase of Fe_3O_4.The average crystallite size, lattice parameter, density and specific area for magnetite nanoparticles are summarized in the table 1.

TABLE 1: Average crystallite size (D), lattice parameter (a), X Ray density (ρ_x), specific area (S) and strain of Magnetite nanoparticles

Crystallite size (D)	Lattice parameter (a)	X Ray density (g/cc)	Specific area (m^2/cc)	Strain
17 nm	8.3596 (A^0)	5.27 (g/cc)	66.91 (m^2/g)	0.00135

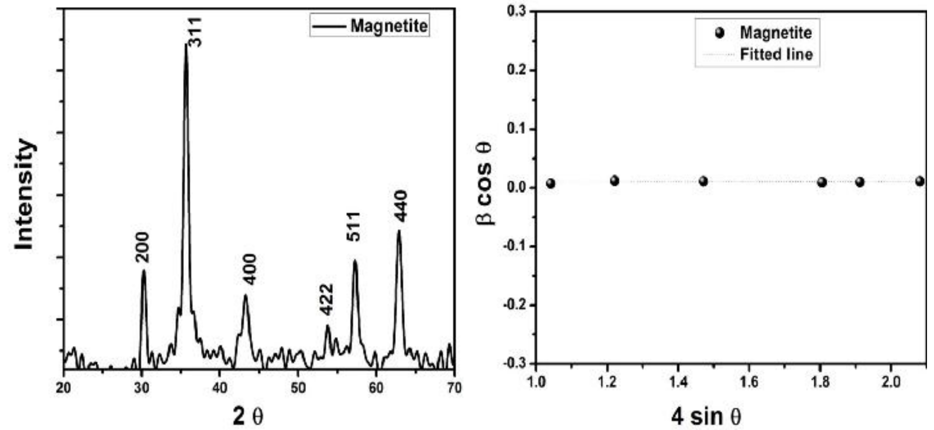

FIGURE 1: (Right) XRD pattern (left side) Williamson-Hall plot for magnetite nanoparticles

Thermal study

The study of non-isothermal kinetics and thermodynamics of solid state decomposition play an important role in the evaluation of quality control and thermal properties of wide range of materials. These parameters related to the mechanism of thermal decomposition of magnetite nanoparticles which were investigated through evaluating their thermal data from simultaneous TG-DTG-DTA.

Thermal characteristics of magnetite nanoparticles are provided in fig. 2. Fig. 2(a) shows TG curves of magnetite nanoparticles. Thermal decomposition of sample has been expressed in the terms of their TG weight loss (% w/w), heat of composition (J/mg) deduced DTA (figure 2 (b)) and rate of decomposition (mg/min) through DTG (fig. 2(c).

The TG thermogram of magnetite nanoparticles is shown in figure 2(a). Fe_3O_4 nanoparticles degradation starts at TG onset of 200^0C with the weight loss of 1.51 %. Beyond onset temperature, it displays a slow weight loss (0.66 %) till 400^0C. This slight decrement in the weight is due to the phase change of magnetite into maghemite in the temperature range 200^0C- 400^0C and afterwards above 420^0C there is no weight loss. The results are similar to earlier reported work[15]. Magnetite shows a exotherm centred at 584^0C in the temperature of 200 – 600^0 C with the corresponding DTA signals at 3.95 μV. During this temperature range, magnetite displays heat of decomposition -53.53 mJ/mg. DTG revealed the rate of decomposition 11 μg/min with the corresponding peak temperature of 261^0 C .

Non isothermal kinetics

Non-isothermal decomposition of magnetite nanoparticles has been evaluated for investigation of thermodynamic and kinetic data of the reaction. Energy of activation

(KJ/mol), frequency factor A (s^{-1}) were elect as a kinetic data and change in entropy ΔS ($JK^{-1}s^{-1}$) as thermodynamic data. The kinetic and thermodynamic parameters of the magnetite nanoparticles were investigated in terms of energy of activation, frequency factor, entropy change, entropy change and Gibb's free energy in thermal degradation from CR and HM methods.

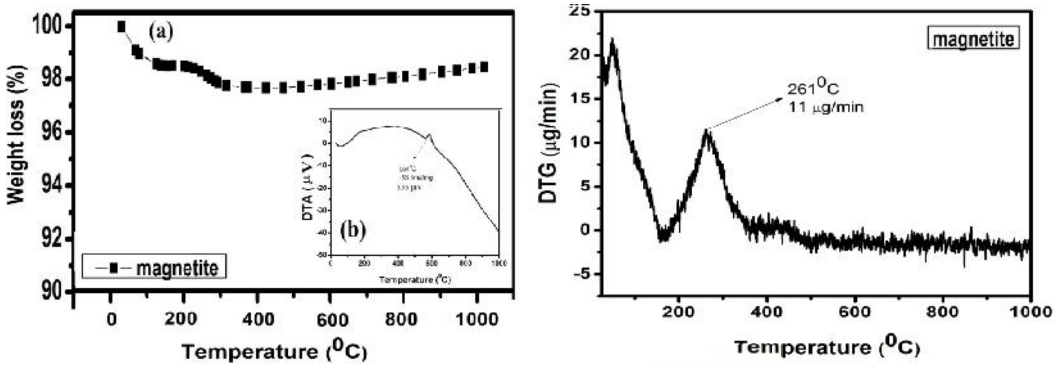

FIGURE 2: (a) TGA (b) DTA and (c) DTG for magnetite nanoparticles

According to Coats-Redfern (CR) integral formula [16], the relation between heating rate (β) and activation energy (E^*) is

$$\log_{10}[g(\alpha)] = \log_{10}\frac{AR}{\beta E^*}\left[1 - \frac{2RT}{E^*}\right] - \frac{E^*}{2.303RT}$$

Where $g(\alpha)=\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right]$, α is the decomposed fraction of material, A is pre-exponential factor and R ($J\ mol^{-1}\ K^{-1}$) is the gas constant .Accordingly, the graph is plotted between $\log_{10}g(\alpha)$ against 1/T and best fitted straight line determines the operating mechanism. E^* and A values are calculated from slope and intercept respectively. The entropy of activation ΔS^* in ($J\ K^{-1}\ mol^{-1}$) is calculated by using the equation: $\Delta S^*=R\ \ln(Ah/k_B\ T_S)$, where k_B is the Boltzmann constant, h is the Plank's constant, Ts is the maximum peak temperature [17].

Horowitz and Metzger [18] have demonstrated the method of calculation of energy of activation of the substances using the following equation:

$$ln(ln\left(\frac{W_0}{W_t}\right)) = \frac{E^*\theta}{RT^2}$$

Where, θ is the difference between the peak temperature and the temperature at particular weight loss (θ = T – Ts); A plot of $ln(ln\left(\frac{W_0}{W_t}\right))$ vs. θ gives an excellent approximation to a straight line (Fig.3).

In the determination of activation energies and frequency factor for the individual steps it was observed that CR method equation gives somewhat higher values than HM equation for magnetite nanoparticles. Change in Gibb's free energy (ΔG) in thermal degradation has shown short discrepancies through both CR and HM methods whereas the change in entropy (ΔS) and enthalpy (ΔH) of thermal degradation has shown slightly large discrepancy (Table 2). Negative values of entropy remark the more ordered structure of magnetite than the reactants.

TABLE 2: Thermal behavior and kinetic parameters determined using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for magnetite

Sample	Decomposition Range	T_S (K)		Parameters					
				E ($KJmol^{-1}$)	A (s−1)	ΔS ($Jmol^{-1}K^{-1}$)	ΔH ($KJmol^{-1}$)	ΔG ($KJmol^{-1}$)	R^2
Fe_3O_4			CR	22.76	5.3298	-235.88	18.32	144.2	0.996
	473K-673K	534	HM	15.38	0.9776	-249.80	10.94	144	0.990

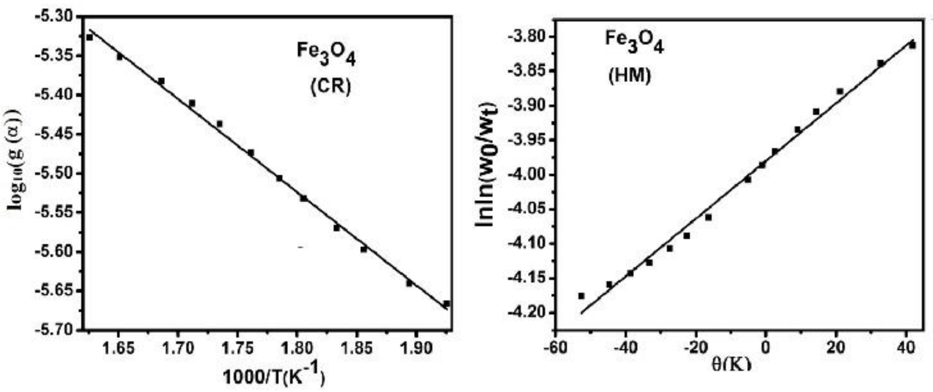

FIGURE 3: Coat's Redfern and Horowitz and Metzger methods for magnetite

CONCLUSION

17nm magnetite nanoparticles are successfully synthesized via chemical coprecipitaion method. Non isothermal kinetics of solid state decomposition for these nanoparticles has been investigated through simultaneous TG-DTG-DTA under air atmosphere. Synthesized magnetite nanoparticles have shown one step decomposition process. Based on variation of $\log_{10} g(\alpha)$ and 1/T, the kinetics and thermodynamic parameters were evaluated in terms of energy of activation, frequency factor, entropy change, enthalpy change and Gibb's free energy in thermal degradation using Coats Redfern and Horowitz Metzger methods. Magnetite nanoparticles have shown weight residue (%) ranging 98.46-100 indicating their resistance against thermal decomposition in the temperature 25^0C-1000^0C. A large discrepancies were ascertained within the all the parameters of thermal decomposition of the magnetite nanoparticles evaluated through Coats Redfern and Horowitz Metzger methods.

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