

CHAPTER 4**4.1 Introduction**

Nucleation is an elementary and crucial step toward forming sub-molecular-sized nuclei by the evolvement of high-temperature solid-state reactions or supersaturation [146]. These nucleation occur through the process of crystallization, growth, phase alteration, and heating, abbreviated as heterogeneous nucleation[136]. The knowledge of kinetic and thermodynamic barriers is of utmost importance to exploring the nucleation pathways, which simplifies the whole nucleation scenario understandable and lucid. Subsequently, the current research is centered on understanding nucleation rates by examining kinetic and thermodynamic barriers during solid-state reactions at high temperatures. A good hold on the calculation of kinetic and thermodynamic barriers is required to compute the nucleation rate at high temperatures. The nucleation rate is the product of kinetic barrier ($J_0 = A \exp(-E_a/RT)$) and thermodynamic barrier ($\exp(-\Delta G^*/RT)$), where E_a is the activation energy of nucleation, ΔG^* is the thermodynamic barrier, and T is the varying temperature [136]. Especially during the computation of nucleation rate, the accurate value of J_0 is barely known, and many scientific communities accorded J_0 as a constant term. For example, J_0 is calculated at room temperature as $D/5d$, D and d is the diffusion coefficient and diameter of monomers respectively [136].

On the other hand, in other approaches, J_0 at room temperature is calculated by acquiring the atomic force microscope technique [138]. For example, the value of J_0 in the case of silica nucleation on the substrates of NH_3/COO^- and carboxyl mixed hybrid were $10^{14.8}$ and $10^{13.5}$ nuclei $\text{m}^{-2} \text{min}^{-1}$, respectively [148]. However, for other nucleation systems, such approaches for calculating J_0 are still missing and no accurate method is governed for calculating J_0 at high temperatures. The kinetic computations for nucleation and growth were often ignored due to the complex calculation of reaction rate and complexity in

microscopic estimations [236]. Therefore, the kinetic barrier J_0 is computed precisely by computation of the apparent activation energy of nucleation (E_a) and pre-exponential kinetic factor (A) at high temperatures. These A and E_a are computed precisely at high temperatures by utilizing the utmost accurate iso-conversional methods by utilizing TGA data. Till now, InSe, crystallization was monitored at higher temperatures (40 °C - 550 °C) by using iso-conversional methods via TGA technology [152]. The calcite nucleation was investigated at 315 °C, and the corresponding activation energy of nucleation was computed. Metal nanocrystal nucleation and growth were examined by incrementing the temperature from 20 °C to 100 °C. Despite the observation of nucleation of metal crystals in a narrow temperature range from 20 °C to 100 °C and InSe crystallization-based nucleation in a high-temperature range, there is no computation of Kinetic barrier J_0 , Pre-exponential kinetic factor (A), nucleation rate, thermodynamic parameters (ΔG , ΔH , and ΔS) and interfacial energy of such crystals in high-temperature range. Thus, the computation of accurate activation energy (kinetic determination) of inorganic nanomaterials is required to estimate nucleation rate precisely at high temperatures.

Over the centuries, the kinetic determination of inorganic materials has been vastly investigated to render solid and gaseous product formation. In the current scenario, various models were proposed for the determination of apparent activation energy precisely. In the first step, inorganic material's mass loss concerning temperature is extracted through a TGA machine, and the kinetic barrier of nucleation, i.e., activation energy, is obtained through the utmost accurate Vyazovkin advance iso-conversional approach. Various scientific communities proposed mathematical models, such as KAS, Tang, and Starink methods for calculating apparent activation energy. But these methods are based on approximations. Despite that, In the Vyazovkin approach, activation energy values averaged from 0 to α .

Thus, the Vyazovkin AIC technique removes approximations and does not have an average activation energy value. Consequently, as the integrated approach in the Vyazovkin AIC technique contains no systematic error[143] over the range of $\Delta\alpha$ as compared to the KAS, Tang, Starink, and Vyazovkin approaches, the Vyazovkin AIC technique is used to compute the apparent activation energy of nucleation, i.e., kinetic barrier for inorganic materials over the specified conversion and corresponding thermodynamic parameters at high temperature.

Currently, several inorganic materials like alkaline earth metals have attracted substantial scientific attention owing to their exceptional high interfacial energy, accelerated chemical reactivity, commercial availability, and biocompatibility [237]. Due to these properties, they have been popularly used in the area of biosensing [183], optoelectronics [92], catalysis [75], energy storage [186], and displays [89]. Especially, calcium and magnesium-based nanomaterials have captivated much attention due to their anomalous properties such as low densities and high specific strength, aging resistance, recyclability, suitable mechanical property and better thermal and electrical conductivity [184]. Subsequently, new synthetic routes yielding materials with new properties are widely reported. In most of these reports, the primary focus is pinned on obtaining highly uniform size nanomaterials with a high degree of reproducibility. For instance, reports on thermal stability, nucleation rate, and interfacial energy related to magnesium nanomaterials have not been investigated to date. Therefore, an attempt has been made to evaluate the nucleation rate and interfacial energy of metallic magnesium nanocluster at high temperature.

For this purpose, MgNCs were synthesized using a commercially available BSA and ascorbic acid. Recently, Bovine serum albumin has been extensively utilized for synthesizing nanomaterial due to its peculiar ability to control nucleation and growth of

nanosystem [183,202,238]. Hence, we acquired BSA as a model protein due to the presence of a disulfide bond and free cysteine, which provide steric protection to the nanoclusters.

Currently, many researchers have adopted several approaches to acquire thermodynamic and kinetic parameters to investigate the nucleation rate and interfacial energy of the alkali earth metal-based nanomaterial. In line with this, *in situ* determination of interfacial energies between heterogeneously nucleated calcite and quartz [8], non-isothermal degradation kinetics estimation of nanosized calcite [237], Homogeneous nucleation of magnesium hydroxide [21], Twin nucleation and growth study in the single crystal magnesium under dynamic loading [239] and estimation of nucleation and growth mechanism of nanosized magnesium hydride from the help of hydrogen sorption kinetics [240] have paved a solid foundation for investigating the nucleation rate and interfacial energies of the magnesium nanoclusters, which was used as a precursor for high-temperature studies.

Further, to the best of our knowledge, the kinetic energy barrier J_0 for the nucleation of magnesium cluster (MgNCs) of size 1-2 nm at high temperature was computed by the utmost accurate Vyazovkin AIC approach for the first time. The solid-state reaction mechanism of MgNCs at high temperature was investigated utilizing $Z(\alpha)$ master plots. Thus, by visualizing the kinetic reaction mechanism steps of MgNCs through $Z(\alpha)$ master plots, random nucleation within the MgNCs matrix was confirmed. Consequently, a new mathematical model was proposed at a high temperature and respective conversions to compute the nucleation rate and corresponding interfacial energy of MgNCs for the first time with the aid of TGA data. On the contrary, the existence of thermodynamic barriers (thermodynamic parameters) within the MgNCs matrix was also computed using the precise value of kinetic energy barrier, i.e., activation energy.

4.2. Theoretical background for determination of kinetic parameters

4.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis on MgNCs powder was carried out between 300K to 962K at three different heating rates of 10, 15, and 20 °C/min to evaluate the thermal stability and kinetics parameters under a nitrogen atmosphere (20 ml/min). The transformational activation energy at each conversional point is mathematically computed using different model-free iso-conversion methods. Next, the master plot ($Z(\alpha)$) was obtained by examining the solid-state transformation reaction mechanism by plotting $Z(\alpha)$ versus conversion (α). Where $Z(\alpha)$ is the product of differential function [$f(\alpha)$] and integral function [$g(\alpha)$]. The reaction mechanism is identified by following the experimental curve plotted on the master curve. Figure. 4.3 shows clearly that the experimental data follows third-order random nucleation.

4.2.2 Kinetic study

The rate of reaction of thermal degradation and conversion (α) with the time (t) of MgNCs can be described by Eq. (1) and (2).[138]

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (1)$$

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

Where, $K(T) = A \exp\left(\frac{-E_a}{RT}\right)$

$K(T)$ = Rate constant of reaction

Where $K(T)$ is the temperature (T) depending constant and t is reaction time, $f(\alpha)$ is a function suggesting the change in reaction rate constant with the extent of conversion (α),

W_o and W_f are the initial and final weight of the sample, whereas W_t is the weight of sample at a particular time (t).

Arrhenius equation describes the correlation between the rate constant of the reaction and temperature. Thus the decomposition rate of the solid can be described as follows in Eq. (3). [241]

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha) \quad (3)$$

The pre-exponential factor is denoted as A , E_a is the Arrhenius activation energy, and R is the universal gas constant (8.314 J/mol.K).

Further, the decomposition rate of the reaction described by Eq. (3) is transformed into a non-isothermal rate expression, Eq. (4), to relate the rate of reaction as a function of temperature at a constant heating rate (β).

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\frac{-E_a}{RT}} f(\alpha) \quad (4)$$

Where β is the constant heating rate.

Eq. (4) integration by separating variables gives Eq. (5) as mentioned below.

$$\int_0^x \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (5)$$

If T_0 corresponds to the initial temperature where the decomposition rate cannot be evaluated, the lower boundary of the integral disappears.

By substituting the $X = \left(-\frac{E_a}{RT}\right)$ in Eq (5), then rearranged Eq. (6) described as follows.

$$g(\alpha) = \left(\frac{AE_a}{\beta R}\right) \left\{-\frac{\exp^x}{x} + \int_0^\infty \left(\frac{\exp^x}{x}\right) dx\right\} = \left(\frac{AE_a}{\beta R}\right)^{p(x)} \quad (6)$$

Where $g(\alpha)$ is the integral function of conversion (α) and $p(x)$ is the temperature integral, Eq. (6) does not have an exact analytical solution. Most iso-conversional kinetic models have been derived using Eq. (4).

From the year 1960s, significant contributions were made for development of various mathematical models to determine the kinetics of the solid system. Two mathematical techniques were basically adopted for computation of kinetic triplet (activation energy (E), frequency factor (A) and order of reaction (n)). These two mathematical techniques were basically model fitting as and model free technique.

Model fitting mathematical technique was used basically to compute the Arrhenius kinetic triplet (E , n and A) by adopting already predicted models $f(\alpha)$ like geometrical contraction models nucleation models, nucleation and growth models, reaction order-based models and diffusion models. Coats Redfern method is widely used non-isothermal model fitting technique to predict activation energy variation with heating rate[242]. The temperature integral in the Eq. (5), is approximated as $g(\alpha)$ is adopted through predefined models. Such technique is successful in prediction of activation energy at respective heating rate.

Thus model-fitting methods can predict the reaction kinetics with respect to heating rate. However, for the non-isothermal decomposition process, these predictions of kinetics by model fitting approach is supposed to have less accurate due to variation of $K(T)$ with T during non-isothermal operation [243,244]. This reproduction of kinetic parameters that strongly depend on the $g(\alpha)$ models for non-isothermal run can create many doubts in the calculated values of activation energy, which raises doubts about the physical meaning of these values. The applicability of model fitting method for computation of kinetics basically relies on the isothermal experiments, where $k(T)$ is a constant with temperature. Here, both $k(T)$ and $f(\alpha)$ in Eq. (5) govern the reaction rate of isothermal experiment.

However, during the isothermal run, $f(\alpha)$ variation with α being less prominent than the $k(T)$ variation with T .

On the other hand, model free techniques (i.e., iso-conversional approach) relies on the calculation of kinetic parameters with respect to conversion and is basically free from any pre-defined reaction models [244]. At different heating rate, T_α is chosen at particular point of conversion, and without use of any pre-defined integral based models i.e., $g(\alpha)$, the activation energy is calculated accurately for non-isothermal run.[137]

Various iso-conversional approaches were adopted for computation of kinetic parameters. Starink presented a detailed review of different techniques to get E_α , and basically two groups were divided (Type 1) and p(I)-iso-conversional methods, (Type 2), where I is $(-E_\alpha/RT)$.[141] The method in Type 1 is free of any approximation but Type 1 method is dependent on the variation reaction rate with individual stages of reaction at different heating rates. This Type 1 method is abbreviated as Friedman et al. [142]. The main disadvantage of such method is fluctuation of activation energy with conversion. The other one is Type 2 method, which strongly depends on the approximation of the temperature integral in Eq. (5). These different iso-conversional methods includes Kissinger [142], FWO[245] and Starink techniques [141].

Apart from above mentioned types, there are other iso-conversional methods that are free from any type of approximation and are more accurate. For instance, Vyazovkin proposed a model, that depend on function minimization for computation of activation energy with respect to conversion and abbreviated as model free method [143,144]. But, as already explained, in Vyazovkin approach the activation energy got averaged with respect to conversion. Thus, we adopted Vyazovkin advanced iso-conversional (V. AIC) method, which is free of any type of approximation and temperature integral is solved by trapezoidal

rule. Due to integration of temperature integral by trapezoidal rule in small interval ($\Delta\alpha$), the accuracy in the computation of activation energy get enhances. In our investigation, $\Delta\alpha$ is taken to be 0.005. Thus, we used V.AIC iso-conversional model free method in our study.

In this study, we used Flynn-wall-Ozawa (FWO), Kissinger (KAS), Starink, Tang, Vyazovkin, and Vyazovkin AIC methods to evaluate kinetic parameters at each conversion point, and $Z(\alpha)$ master plot were employed to gain insight the reaction mechanism followed by the thermal degradation process.

The Kissinger-Akahira-Sunose (KAS)[246] method is a differential iso-conversional method, generally used to predict the kinetic parameters such as Arrhenius activation energy (E_a), frequency factor (A), and order of reaction (n) at each conversion. An Assumption $p(x) = X^{-2} e^{-X}$ was utilized to determine the following equation.

$$\ln \frac{\beta}{T^2} = \ln \frac{AE\alpha}{Rg(\alpha)} - \frac{E\alpha}{RT} \quad (7)$$

Where β is the constant heating rate.

The slope of the plot between $\ln \frac{\beta}{T^2}$ vs. $\frac{1}{T}$ gives the activation energy at each conversion value (α).

The Flynn-Wall-Ozawa method [247] is an integral iso-conversional method that uses Doyle's empirical approximation instead of the temperature integral.

$$\log \beta = \log \frac{AE\alpha}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E\alpha}{RT} \quad (8)$$

The exponential value $p(x) = -2.315+0.457x$ were evaluated using Eq. (8), and the slope of the linear plot between $\log \beta$ vs. $\frac{1}{T}$ yielded E_a/R

By combining KAS and FWO methods, Starinks [141] proposed the following method:

$$\ln\left(\frac{\beta}{T_\alpha^S}\right) = C - \frac{BE_\alpha}{RT_\alpha} \quad (9)$$

Using integral temperature approximation, Starink calculated the value of S and B as 1.92 and 1.0008, respectively, and put them in the above Eq. (9) to achieve reformed Eq. (10).[248]

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = \text{const} - 1.0008\left(\frac{E_\alpha}{RT}\right) \quad (10)$$

At each conversional point, the plot between $\ln\left(\frac{\beta}{T^{1.92}}\right)$ and $\frac{1}{T_\alpha}$ gives a straight line, with a slope $\left(-1.0008\frac{E_\alpha}{R}\right)$ that can be utilized to obtain activation energy.

In the Tang method [140] the apparent value of activation energy is calculated using the following Eq. [245].

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = C_1 - 1.001450 \frac{E_\alpha}{RT} \quad (11)$$

At the conversional point 0.1 to 0.9, a plot between $\ln\left(\frac{\beta}{T^{1.894661}}\right)$ vs. $\frac{1}{T_\alpha}$ gives a straight line with a slope $1.001450 \frac{E_\alpha}{R}$.

Vyazovkin [144] is a non-linear iso-conversional method, generally used to increase the accuracy of the activation energy of the system. This method depends on Eq. (12) for the evaluation of the activation energy (E_a) at a particular value of conversion (α), which minimizes the following function.

$$\Phi = \sum_i^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} = \min \quad (12)$$

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT \quad (13)$$

The numerical value of activation energy at a particular conversion was obtained by substituting the experimental T and β into Eq. (13) and varying E_a to obtain the minimum value of the function. The accurate value of $I(E_a, T_\alpha)$ were evaluated with the help of the Senum-Yang approximation [249] [250]. The same minimization procedure was repeated for each conversion (0.1 to 0.9), and the accurate activation energy at each extent of conversion was evaluated.

$$I(E_a, T_\alpha) = \frac{\exp(-x)}{x} \cdot \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (14)$$

Vyazovkin AIC [143](advanced iso-conversional) model is a modified version of the Vyazovkin model, which avoids the unwanted flattening of the E_a Vs. Conversion (α) curve.

In this modified integral iso-conversional model, E_a is assumed for a small change in conversion ($\Delta\alpha$), and the temperature integral is evaluated by varying $T_{\alpha-\Delta\alpha}$ and T_α using the trapezoidal rule.

$$J(E_a, T(t)) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E_a}{RT(t)}\right) dt \quad (15)$$

$$\varphi(E_a) = \sum_i^n \sum_{j \neq i}^n \frac{I(E_a, T_i(t_\alpha))}{I(E_a, T_j(t_\alpha))} = \text{minimum} \quad (16)$$

In Eq. (16), $T_i(t)$ ($i= 1, \dots, n$) is the actual variation of temperature, and the E_a into Eq. (16) varies until the minimum value of the function is reached.

4.2.3 Calculation of pre-exponential kinetic factor

Iso-conversional methods accurately computed the apparent value of activation energy, but these models are incompetent to predict the value of the solid-state reaction system's pre-exponential factor and reaction model. To obtain both the apparent activation energy and pre-exponential factor, the following modified Kissinger's Eq. (17) was used [142].

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{RT_m} + \ln\left(\frac{AR}{E}\right) \quad (17)$$

Where T_m represents the peak temperature of the DTG curve at all the heating rates.

As we know, the KAS method is based on different heating rates and gives a single apparent value of activation energy for the overall reaction conversion. Therefore, this method is not suitable for computing activation energy. Therefore, activation energy computed by the Vyazovkin AIC method is substituted in Eq. (18) to obtain a pre-exponential factor.

$$A_\alpha = \frac{\beta E_\alpha \exp\left(\frac{E_\alpha}{RT_m}\right)}{RT_m^2} \quad (18)$$

A_α and E_α represent the value of the pre-exponential factor and apparent activation energy, respectively, at all the conversions point (0.1 to 0.9).

4.2.4 Computation of Thermodynamic Barriers of MgNCs for Initiation of Random Nucleation

The computation of thermodynamic parameters allows us to interpret the system's feasibility [134]. The apparent activation energy of MgNCs was obtained using six model-free iso-conversional methods; among them, activation energy calculated from most accurate Vyazovkin AIC method is utilized to obtain frequency factor at different conversions by KAS method derived equation.

So, the following equation has been utilized for calculating pre-exponential factor and thermodynamic parameters such as ΔH , ΔG , and ΔS [135].

$$A = \beta E_\alpha \exp\left(\frac{E_\alpha}{RT_m}\right) \quad (19)$$

$$\Delta H = E_\alpha - RT_\alpha \quad (20)$$

$$\Delta G = E_\alpha + RT_m \ln\left(\frac{K_b T_m}{hA}\right) \quad (21)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T_m} \right) \quad (22)$$

Where K_b refers to the Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$), h is Plank's constant ($6.626 \times 10^{-34} \text{ JS}$). T_m refers to peak temperature in the DTG curve. ΔH suggested the difference of energy between reactants and MgNCs activated complex. The change in entropy of the system (ΔS) measures the system's randomness, while average change in Gibbs energy (ΔG) represents the available free energy to the system.

4.2.5 Computation of Nucleation Rate, Kinetic barrier, Thermodynamic barrier, and Interfacial energy

The nucleation rate of the upcoming solid phase (MgNCs) can be computed by Eq. (23):

$$J = A J_0 \exp\left(\frac{-\Delta G^*}{RT}\right) = A \exp\left(\frac{-E_a}{RT}\right) \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (23)$$

Where J ($\mu\text{m}^{-2} \text{ min}^{-1}$) represents nucleation rate in nuclei, R ($\text{J mol}^{-1}\text{K}^{-1}$) and T (K) represent universal gas constant and temperature in K, respectively. ΔG represents the thermodynamic energy barrier, which is directly correlated to interfacial energy. The J_0 in Eq. (23) represents the system's kinetic energy and can be expressed as $\exp\left(\frac{-E_a}{RT}\right)$. Furthermore, the Thermodynamic parameter (Q) is stipulated by $\Delta G^*/RT$ and can be ascribed by the following Eq. [136]. (Discussed in Appendix- Section B2)

$$Q = \frac{16\pi v_0^2 Y^3}{3(K_B T)^3} \quad (24)$$

Where v_0 represents the molecular volume of the nanomaterial given by $\frac{M}{\rho_{nm} N_A}$, where M and ρ_{nm} represent the nanomaterial's molar mass and density, and N_A is the Avogadro number. This particular Eq. (24) was utilized to obtain interfacial energy as a function of temperature and conversion.

4.2.6 Computation of atoms present in one cluster by using TEM data

TEM images suggested the formation of spherical MgNCs.

Hence, $V_{\text{cluster}} = V_{\text{atom}} \times N_{\text{atom}}$

Where, $N_{\text{atom}} = (rc/ra)^3$

rc (0.82/2=0.41 nm) is the radius of MgNCs and ra is the radius of Mg atom (141 pm).

V_{cluster} is the cluster volume, and V_{atom} and N_{atom} are the volume of atom and number of atoms in one cluster, respectively [183].

$$\left(\frac{4}{3}\right) \times \pi \times rc^3 = \left(\frac{4}{3}\right) \times \pi \times ra^3 \times N_A$$

4.3 Experimental sections

4.3.1 Chemical used

Pure high-grade magnesium chloride salt (99.9%) and L- ascorbic acid were purchased from Sigma Aldrich, and High-quality bovine albumin serum (98%) was purchased from SRL. All mentioned chemicals were purchased from local suppliers and used as received without any adulteration.

4.3.2 Synthesis of MgNCs

All the glassware was washed with aqua regia and rinsed thoroughly with deionized water. In an optimal synthesis, bovine serum albumin (450 mg/ml, 1ml) and magnesium salt solution (10 mM, 10 ml) were mixed in a 150 ml conical flask, followed by the addition of L-ascorbic acid (35 mg/ml, 3ml) and kept for 2 hr at 55°C under continuous stirring. (Appendix- Figure B1) The resultant light-yellow colored solution was further incubated for 15 hrs. at the same temperature to obtain newly synthesized metallic magnesium

nanocluster (MgNCs). During the entire reaction process, the reacting system was tightly sealed to prevent oxidation of newly synthesized clusters.

4.3.3 Characterization

Prepared metallic magnesium nanocluster (MgNCs) was characterized using spectroscopic and microscopic techniques. The UV-Vis absorbance spectra were recorded by using Elico SL210 spectrophotometer. The thermogravimetric analysis (TGA) at different heating rates (10, 15, and 20 °C/min) was carried out using a PerkinElmer STA 6000/TGA 4000(sample pans). Size of the prepared clusters was estimated with the help of High-resolution transmission electron microscopy (HR-TEM) of model FEI Tecnai G2 20 Twin with an accelerating electron beam voltage of 200 kV utilized, phase and crystallinity of the MgNCs were interrogated by using Bruker, Mode-D8 advance Eco XRD machine, XPS spectra were obtained with the assistance of FEI, Nova Nano SEM 450. Fourier transform infrared spectroscopy was carried out using Nicolet is5 (Thermo electron scientific instrument using KBr pellets in 4K to 400 cm^{-1}) range, CD spectra were acquired by using CD Polarimeter J-500 circular dichroism spectrophotometer.

4.4 Results and discussion

Vacuum oven dried MgNCs (60 °C for 24 hrs.) powder was used for XPS, FTIR, XRD, and TGA characterization, while size analysis was performed using an aqueous solution drop cast over a TEM grid.

4.4.1 UV-Vis absorbance

Figure. 4.1 a show the UV-Vis absorption spectrum of BSA and BSA templated magnesium nanocluster. The absorption spectra of BSA displayed a sharp prominent peak at 280 nm designated to aromatic residue (Tryptophan, Tyrosine, and Phenylaniline) and disulfide bond [201,251], whereas the absorption spectra of BSA templated nanoclusters displayed

a strong absorption in the UV region, which exponentially decay toward the visible region without the presence of any SPR band, this spectral phenomenon hint the formation of nanocluster with size range less than 2 nm [202]. No localized surface plasmon resonance peak in the 400-600 nm range of UV-Vis spectra indicated the absence of larger-sized MgNCs [165].

4.4.2 Size and phase analysis

The size distribution of developed BSA templated MgNCs was characterized by HRTEM, and the microscopic image was shown in Figure. 4.1 b. microscopic data analysis revealed that the average diameter of as-prepared clusters was 0.82 ± 0.24 nm, based on sampling more than 250 clusters. Additionally, the number of Mg atoms in a cluster is determined by utilizing TEM data and found 25 atoms in a cluster. Furthermore, phase purity and crystallinity of MgNCs were investigated by XRD analysis (Figure. 4.1 c). The XRD pattern of BSA templated MgNCs shows absence of any characteristic peak of magnesium, but displayed only one broad halo peak ,which clearly indicated the amorphous nature of MgNCs due to ultrasmall size ($< 1\text{nm}$).[52,220]

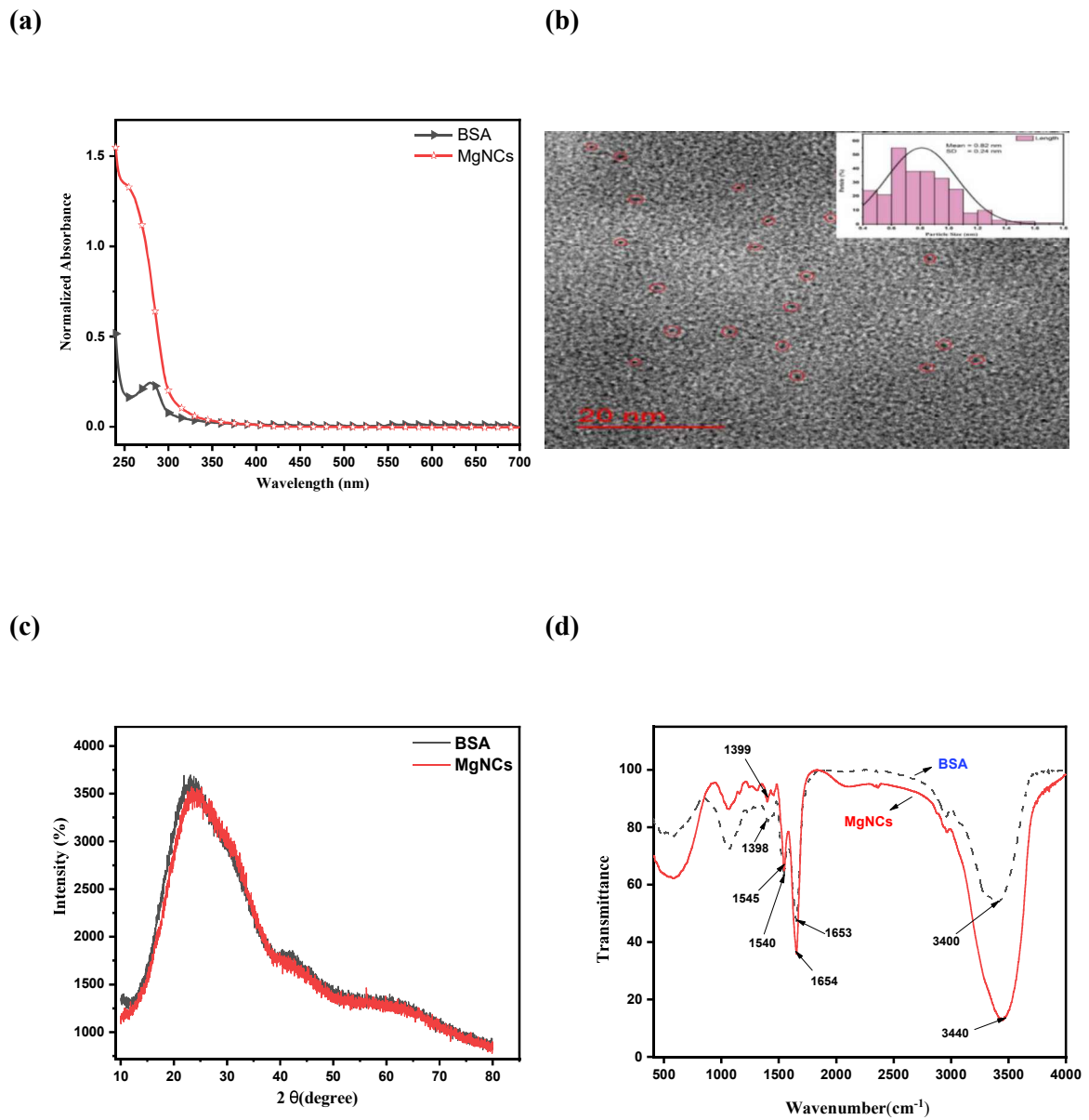


Figure. 4.1 (a) UV-Vis absorption spectra of BSA and MgNCs, (b) HR-TEM image of the MgNCs at 50 nm scale bar inset Histogram with the distribution of MgNCs, (c) XRD of BSA and BSA capped MgNCs, (d) FTIR spectra of BSA and MgNCs.

4.4.3 Surface and infrared spectroscopy

The chemical composition and oxidation state of MgNCs were further investigated by XPS analysis; the high-resolution XPS spectra are shown in Figure. 4.2. The obtained spectra of C 1s at 284.4 eV are used as reference spectra to adjust further and deconvolute the peak of interest. The C 1s spectra of MgNCs deconvoluted into five peaks with binding energies at 284.4 eV (sp^2 hybridized carbon)[252], 284.8 eV (sp^3 hybridized carbon)[253], 285.7 eV (C-N)[254], 287.5 eV(C=O)[255] and 287.7 eV (C=O)[256]. XPS spectra of MgNCs were obtained and displayed in Figure. 4.2 (a, b). The deconvoluted peak of Mg 2s and Mg 1s displayed a sharp prominent peak at 88.5 eV [164,257–259] and 1303.5 eV respectively [260–262], attributed to metallic magnesium. The obtained XPS analysis result confirmed the successful grafting of MgNCs onto the BSA surface. FTIR spectra of BSA and BSA templated MgNCs are displayed in Figure. 4.1, d. The characteristic band of protein amide I (1600-1700), amide II (1480-1575), and amide III (1229-1301) is corresponded to C=O stretching, N-H bending and the combination of C-N and C-C stretching, and C=O bending [183]. The significant decrease in spectral intensities of amide I and II bands of BSA templated MgNCs compared to free BSA revealed the interaction of Mg^{+2} with C=O, COO, and N-H functional groups of the protein. The binding interaction between BSA functional moieties (CN and N-H) and Mg^{+2} was further revealed by shifting the amide A band concerning free BSA ($1653\text{cm}^{-1}\rightarrow 1654\text{ cm}^{-1}$). However, the decrease in the spectral intensity of the amide I band concerning free BSA revealed the reduction of an alpha helix in the secondary structure of the protein [222]. A significant shift in spectra of MgNCs ($3400\text{ cm}^{-1}\rightarrow 3440\text{ cm}^{-1}$) corresponds to the amide C=O band, resulting in the successful scaffolding of BSA onto MgNCs surface.

The changes in conformation of BSA by reduction of an alpha helix was further confirmed by Circular dichroism study (Figure. 4.2 d). [263] The CD spectra of pure BSA and BSA templated MgNCs were carried out at 25 °C in the wavelength range between 190 nm to 290 nm. The spectra of BSA contain two bands at 208 nm and 222 nm, these bands are characteristic of π - π^* and n- π^* transition in the α helix of BSA.

The α helix content of BSA and MgNCs was found to be 55.7% and 22% respectively, which demonstrate drastic change in the BSA secondary structure after MgNCs formation.[201] (Discussed in Appendix- Section B1)

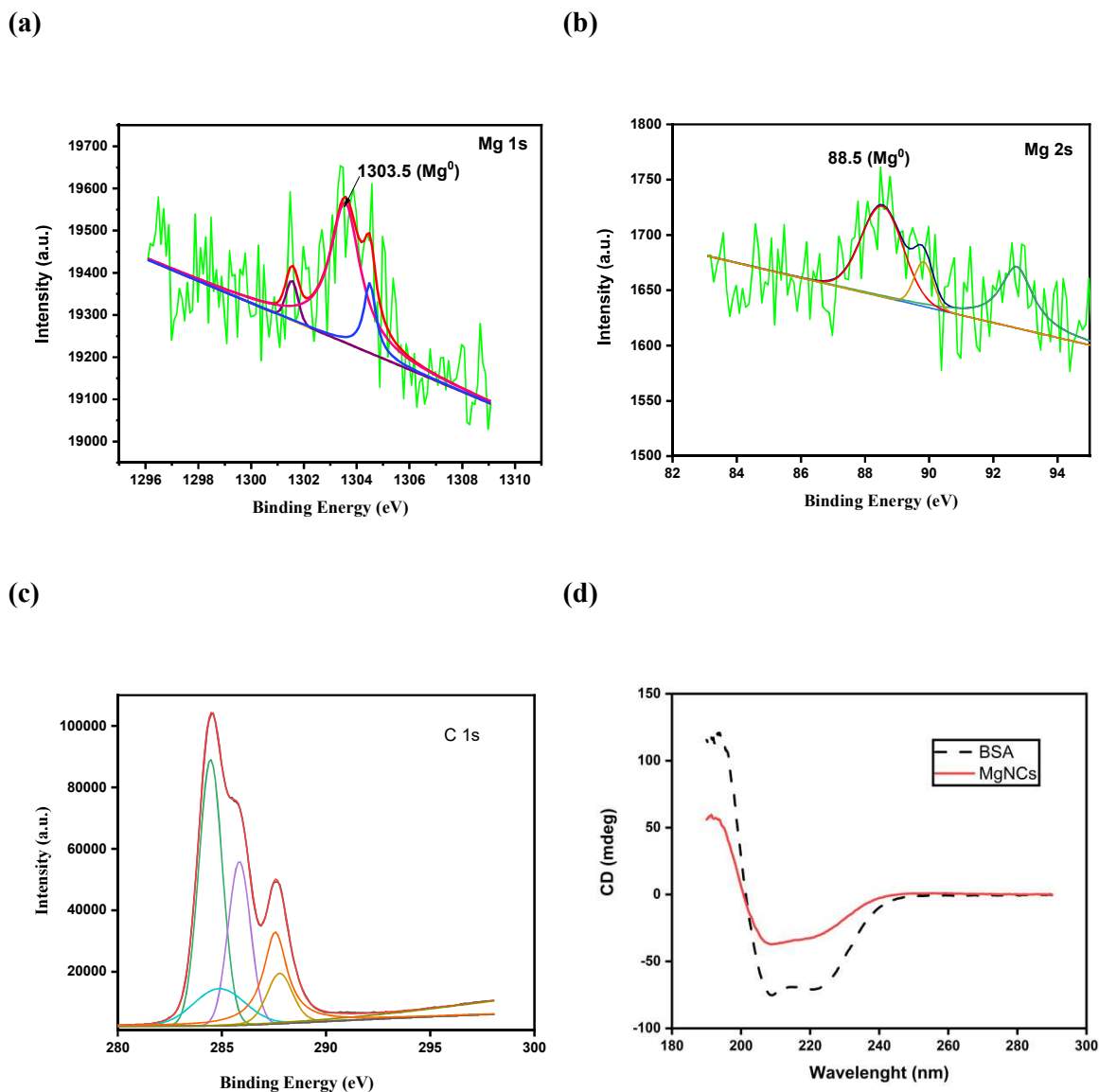


Figure 4.2 XPS spectra of MgNCs (a) Mg 1s (b) Mg 2s (c) C1s (d) CD spectra of BSA and MgNCs

4.4.4 Prediction of reaction kinetics and corresponding pathways

This work utilized a Z-master plot based on the p(u) method to identify the mechanism behind the thermal degradation pattern and existing kinetics models based on integral and differential methods, as mentioned (Appendix-Table B1).

The Z -master plot provided insight into the thermal degradation's mechanistic behavior as a function of conversion (α). Calculated experimental data at each conversional point were compared with the theoretical model-derived data to obtain the reaction kinetics. The TGA data for the 10, 15, and 20 °C/min heating rates were fitted and plotted in a kinetic $Z(\alpha)$ master plot, which is a product of integral and differential function. The master plot is achieved by plotting $\frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)}$ as a function of conversions, i.e., by taking $\alpha=0.5$ as a referral point.

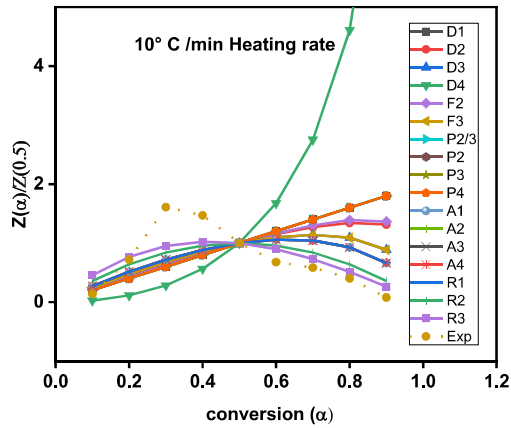
The master plots for different solid-state reaction models are abbreviated by Khawam [264].

For $\alpha = 0.5$, Eq. 25 can be written as:

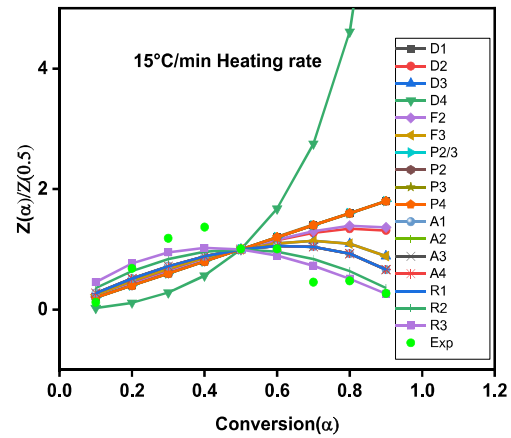
$$z(\alpha) = \frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)} = \left(\frac{T_\alpha}{T_{0.5}} \right)^2 \times \frac{(d\alpha/dt)\alpha}{(d\alpha/dt)_{0.5}} \quad (25)$$

Afterward, plotted $Z(\alpha)$ master plot $\frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)}$ as a function of conversion (α) for the different dynamic oxidation models such as geometrical contraction model, nucleation models, diffusion models, and reaction order models and compared that with the experimentally obtained TGA data [134]. It can be clearly observed from Figure. 4.3 that in the conversional range from 0.1 to 0.9, the experimental $Z(\alpha)$ curve is closely following the theoretical curve of the R3 mechanism, which is linked to the 3rd order random nucleation process.

(a)



(b)



(c)

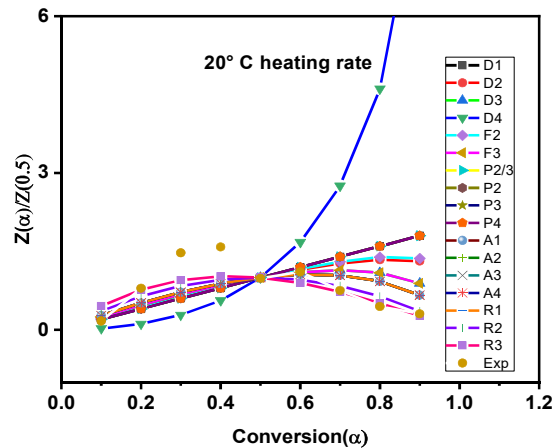


Figure 4.3 (a) $z(\alpha)$ master plot for estimation of thermal decomposition reaction mechanism of MgNCs at 10°C/min (b) $z(\alpha)$ master plot for estimation of the thermal decomposition reaction mechanism of MgNCs at 15°C/min (c) $z(\alpha)$ master plot for estimation of the thermal decomposition reaction mechanism of MgNCs at 20°C/min.

Figure. 4.5 a shows sinusoidal fluctuation in the activation energy of MgNCs as a conversion function. According to ICTAC rules, apparent activation energy variation should be around $\pm 5\%$ of the average activation energy value [265]. Apparently, our computed activation energy is within this range (0.1-0.9) and very well complies with the recommendations. By visualizing the change in apparent activation energy as a function of conversion, five distinct phases were found to dominate during reaction conversion.

Table 4.1 Activation energy calculated through various models.

<i>Conversion (a).</i>	Activation Energy (E_a)					
	KAS	FWO	Starink	Tang	Vyazovkin	Vyazovkin AIC
<i>0.1</i>	172.9	180.9	173.29	173.3	173.15	164.62
<i>0.2</i>	155.26	164.2	155.62	155.7	155.4	153.41
<i>0.3</i>	197.2	206.85	197.68	198.34	197.5	201.7
<i>0.4</i>	184.77	194.62	185.16	186.5	185	189.7
<i>0.5</i>	162.26	172.33	162.66	165.2	162.54	171.40
<i>0.6</i>	143	153.40	143.4	147	143.38	151.8
<i>0.7</i>	107.9	118.79	108.3	113.8	108.37	117.6
<i>0.8</i>	180.13	191.84	180.6	184.12	180.47	180.2
<i>0.9</i>	106.8	119.99	107.36	115.10	107.4	105.7
<i>Average</i>	156.69	166.99	157.11	159.89	157.02	159.57

In the first phase, for conversion ranging from 0.1 to 0.2, the apparent activation energy decreased from 164.6 to 153.41 kJ/mol. On the contrary, in the second phase, conversion

between 0.2 and 0.3 activation energy increased from 153.41 to 201.7 kJ/mol. In the consecutive third to fifth reaction phases [(0.3 -0.7), (0.7-0.8) and (0.8-0.9)], the apparent activation energy ranged from 201.7 kJ/mol-117.6 kJ/mol ,117.6 kJ/mol-180.2 kJ/mol and 180.2-105.7 kJ/mol, respectively. The sinusoidal trend of apparent activation energy during the reaction progression is mainly due to the development of stable nuclei during the random nucleation process, along with the evolution and absorption of heat in reactions. Additionally, computed apparent activation energy was plotted against reaction progression to ensure the trend of reaction progression and acquire the overlapped activation energies value at each conversion.

The DTG and TGA curve of MgNCs plots temperature against mass loss for all three heating rates, as shown in Figure. 4.7. To avoid undesirable reactions and oxidation of particles, a nitrogen atmosphere was utilized to create inert atmospheres. The DTG peak temperature increased from 592.05→604.15 K with an increment in the heating rate of 10 °C/min → 20 °C /min. It is analyzed that, for different heating rates (10, 15, and 20° C/min), the mass loss rate of MgNCs (71.51% →75.9%) increased with an increase in heating rates. This is probably due to the BSA protein's heterogeneous and intricate nature [266]. Interestingly, an increment in the mass loss and the heat transfer rate is observed at higher heating rates more, due to the termination of the overall resistance barrier inside the MgNCs matrix and enhancement in mass loss[267,268].

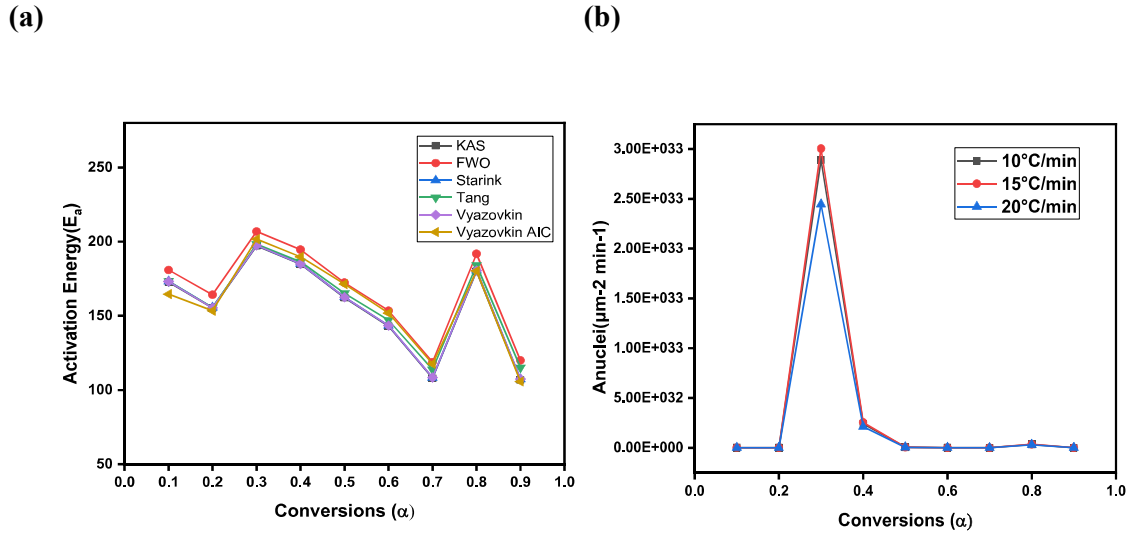


Figure 4.5 (a) Comparison of apparent activation energies at all the conversions obtained from iso conversional models (b) Pre-exponential factor of MgNCs against conversions at all the three heating rates.

4.4.6 Prediction of pre-exponential kinetic factor as a function of conversions

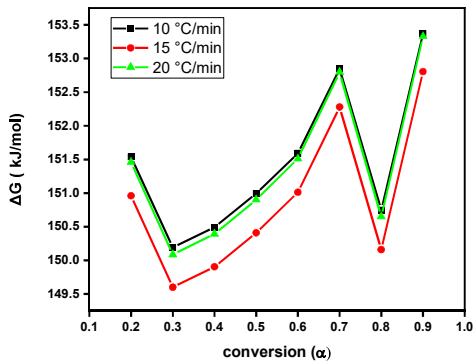
Figure.4.5(b) represents the variation of a pre-exponential factor with the reaction progression. A wide range of variations in the value of the pre-exponential factor suggests the complex and heterogeneous nature of the BSA matrix. Earlier studies have shown that the lower value of the pre-exponential factor ($A_{\alpha} < 10^9 \text{ s}^{-1}$) manifested the less reactive system, and the nucleation process occurs only at the surface of MgNCs. While higher pre-exponential factor ($A_{\alpha} \geq 10^9 \text{ s}^{-1}$) determines a highly reactive system, and the nucleation process occurs both from the core and surface of the MgNCs [139,269].

4.4.7 calculation of thermodynamic parameter against the reaction progression

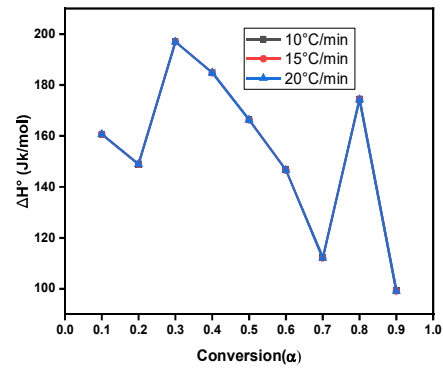
Table. 4.2 represents the value of thermodynamic parameters ΔH , ΔG , and ΔS of MgNCs at all three heating rates, obtained by employing computed Apparent activation energy value (Vyazovkin AIC method). The change in enthalpy (ΔH) signifies the total heat

content associated with the reacting system. The average ΔH value of MgNCs at 10, 15, and 20 °C/min was found to be 154.5 kJ/mol, 154.4 kJ/mol, and 154.3 kJ/mol, respectively, which is almost independent of heating rates; however, the positive value of ΔH revealed endothermic nature of the reaction.

(a)



(b)



(c)

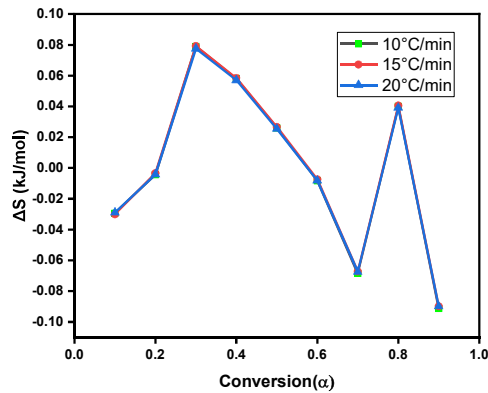


Figure 4.6 (a) Plot between ΔG against Conversion at all three heating rates, (b) Plot between ΔH against Conversion at all three heating rates, (c) Plot between ΔS against Conversion at all three heating rates.

Although it is observed that ΔH strongly depends on reaction progression, especially for conversion 0.1→0.2, yielding an augmented value of ΔH . Whereas from 0.3→0.9 conversions, a sinusoidal pattern similar to activation energy was obtained (Figure. 4.6 b). The slight difference between ΔH and ΔE indicated the formation of the activated complex and also demonstrated the decrease in the endothermic nature of the reacting system as the reaction progressed. The change in Gibbs free energy with conversion at different heating rates is shown in Table 4.2. The change in Gibbs free energy (ΔG) indicated the reaction system's increased energy due to the formation of an activated complex [135]. Although, ΔG at 10, 15, and 20 °C/min was found to be 154.4 kJ/mol, 153.9 kJ/mol, and 154.3 kJ/mol, which is positive, indicating unfavourable conditions for the reaction. The increment in the average value of ΔG (Figure. 4.6 a) concerning heating rates indicated that the reacting process consumes more energy at a high heating rate, whereas the increase of ΔH with reaction progression suggested excess heat supplied to the reacting system [142].

The change in entropy (ΔS) measures a reacting system's randomness [134]. Therefore, its variation as a function of conversion at different heating rates is presented in Table 4.2. The value of ΔS at 10, 15, and 20 °C/min is found to be 1.5×10^{-4} , 7.7×10^{-4} , and 5.5×10^{-5} , respectively. It was observed that ΔS for MgNCs has negative and positive values for the entire reaction course. The lower value of ΔS indicated the physical and chemical changes in MgNCs, bringing them to the state of thermodynamic equilibrium [270]. The graph of ΔS versus conversion is displayed in Figure. 4.6 (c).

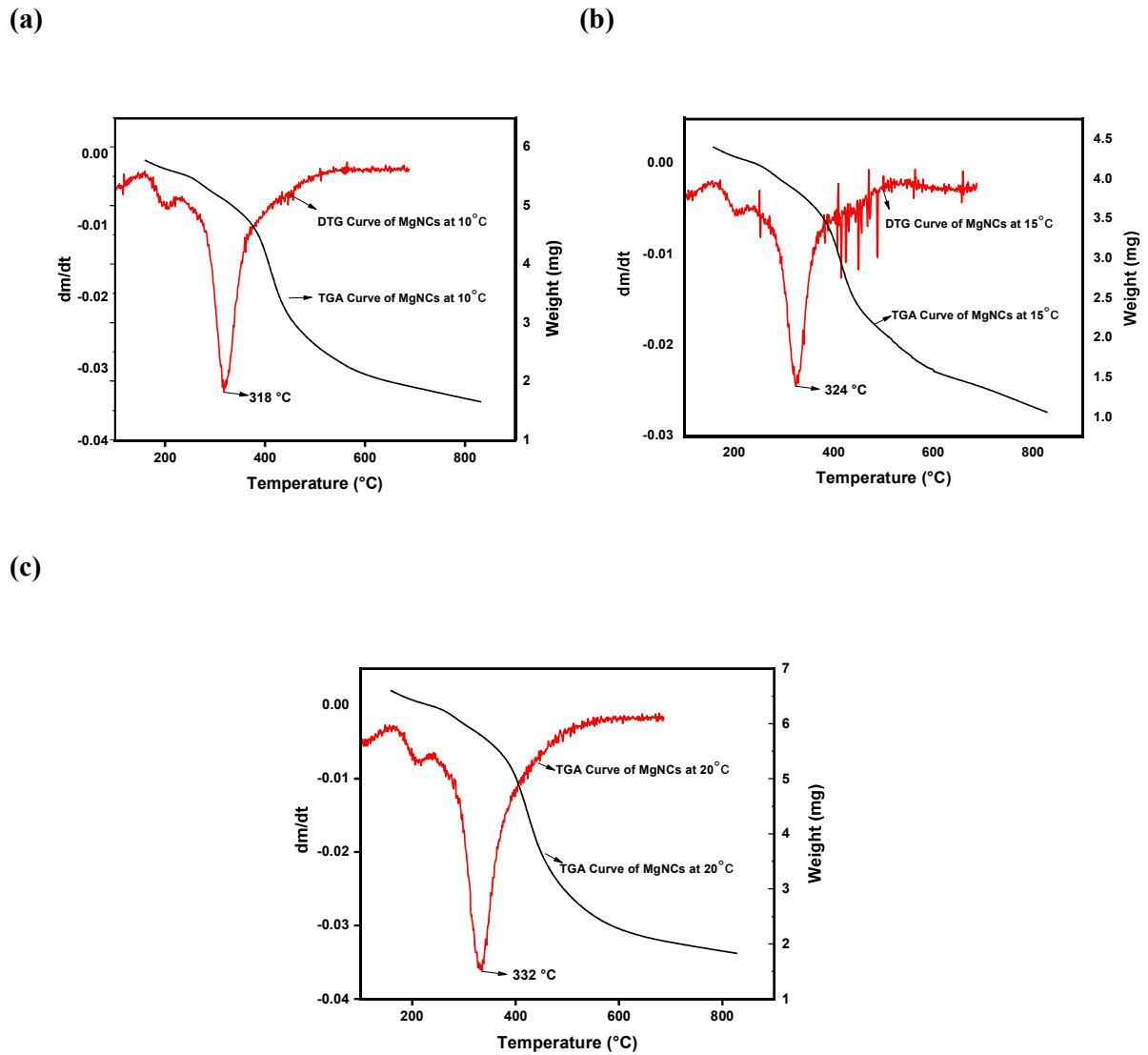


Figure 4.7 (a) TGA and DTG curve of MgNCs at 10 °C/min heating rate (b) TGA and DTG curve of MgNCs at 15 °C/min heating rate (c) TGA and DTG curve of MgNCs at 20 °C/min heating rate.

conversions(α)	Heating rate (10 ° C/min)				Heating rate (15° C/min)				Heating rate (20 ° C/min)			
	A (S ⁻¹)	ΔH (KJ Mol ⁻¹)	ΔG (KJ Mol ⁻¹)	ΔS (KJ Mol ⁻¹)	A (S ⁻¹)	ΔH (KJ Mol ⁻¹)	ΔG (KJ Mol ⁻¹)	ΔS (KJ Mol ⁻¹ K ⁻¹)	A (S ⁻¹)	ΔH (KJ Mol ⁻¹)	ΔG (KJ Mol ⁻¹)	ΔS (KJ Mol ⁻¹ K ⁻¹)
0.1	1.89×10 ¹⁴	160.68	178.05	-0.02933	2.1×10 ¹⁴	160.63	178.63	-0.03014	1.86×10 ¹⁴	160.62	178.13	-0.029
0.2	1.81×10 ¹³	148.98	151.54	-0.00432	2.04×10 ¹³	148.92	150.96	-0.0034	1.86×10 ¹³	148.89	151.46	-0.00424
0.3	4.35×10 ¹⁷	196.98	150.19	0.079039	4.52×10 ¹⁷	196.93	149.60	0.079272	3.67×10 ¹⁷	196.91	150.08	0.077509
0.4	3.61×10 ¹⁶	184.89	150.49	0.058102	3.83×10 ¹⁶	184.83	149.90	0.058494	3.2×10 ¹⁶	184.80	150.39	0.056967
0.5	7.8×10 ¹⁴	166.41	150.99	0.02604	8.54×10 ¹⁴	166.34	150.40	0.026685	7.46×10 ¹⁴	166.31	150.90	0.025503
0.6	1.29×10 ¹³	146.68	151.59	-0.00828	1.46×10 ¹³	146.60	151.01	-0.00738	1.34×10 ¹³	146.56	151.51	-0.00818
0.7	9.63×10 ⁹	112.26	152.84	-0.06855	1.16×10 ¹⁰	112.14	152.27	-0.06721	1.15×10 ¹⁰	112.09	152.79	-0.06736
0.8	4.92×10 ¹⁵	174.42	150.74	0.039995	5.31×10 ¹⁵	174.36	150.16	0.040526	4.54×10 ¹⁵	174.30	150.65	0.039147
0.9	7.79×10 ⁸	99.30	153.37	-0.09133	9.55×10 ⁸	99.15	152.80	-0.08985	9.72×10 ⁸	99.05	153.32	-0.08984
Avg		154.51	154.42	0.000152		154.51	153.97	0.000777		154.39	154.36	5.54×10 ⁻⁵

Table 4.2 Thermodynamic parameters in all three heating rates.

4.4.8 Dependency of nucleation rate in conversion and temperature

In current scenarios, computation of nucleation rate was limited due to inadequate understanding of kinetic and thermodynamic parameters. Eq. (23) was employed to compute the rate of nucleation at high temperatures, but the kinetic term (J_0) in the equation was considered constant by several scientists [8,147]. However, at high-temperature nucleation rate analysis, the value of J_0 dominated. Hence prediction of J_0 is necessary to obtain an accurate value of nucleation rate [271].

In this study, the kinetic term (J_0) has been computed by utilizing A and Ea , rather than assuming it as a constant value, to predict more accurate nucleation rate values at high temperatures.

Moreover, the value of apparent activation energy and pre-exponential kinetic factor (A) is computed by utilizing Vyazovkin AIC, and KAS derived equation, respectively; furthermore, for a better understanding of the nucleation process, understanding nuclei geometry is crucial [136]. After incorporating the value of nuclei geometry in Eq. (23), This is accomplished by converting activation energy and kinetic factor (A) units into Nuclei $\mu\text{m}^{-2}\text{min}^{-1}$. This results in a significant change of A and J (nucleation rate) values, as nucleus volume and surface area get incorporated into the equation. (Appendix-Table B2)

By visualizing graph 4.8 (b) between J (Nuclei $\mu\text{m}^{-2}\text{min}^{-1}$) and T (K), an increasing trend in nucleation rate as a function of temperature was observed. Additionally, nucleation rate was also computed concerning different heating rates (10, 15, and 20 °C/min) and observed an increasing trend with a rise in heating rate, and this phenomenon is due to a decrease in heat and mass resistance with an increase in temperature. (Appendix- Table B3)

To acquire a relationship of nucleation rate with specific temperature and conversion, a theoretical model was deduced by fitting the experimental data. An exponential model $J = Q_1 \exp\left(\frac{T}{\rho_1}\right) + Y_0$ and $J = Q_2 \exp\left(\frac{\alpha}{\rho_2}\right) + J_0$ were best fitted for the temperature and conversion, respectively, at all three heating rates. Where Q_1 , Q_2 , ρ_1 , and ρ_2 are exponential function constants, their values are shown in Appendix- Table B4. The graph is shown in Figure. 4.8 a, b.

4.4.9 Variation of Interfacial energy with temperature and reaction progression

Determination of interfacial energy of MgNCs in the BSA matrix is a crucial parameter in determining several physical quantities of interest [7]. Until now, numerous experimental techniques have been carried out to determine interfacial energy [28], such as the computation of interfacial energy of copper nanoparticles by using the galvanic cell method for a short range of temperature (750-950 K) [133], calculation of interfacial energy of calcite at room temperature (30-50 mJ/m²) [8,28]. However, no studies has been carried to determine interfacial energy of nanomaterials at high temperature utilizing TGA data. Apart from novel technique, we are very first to interpret interfacial energy of magnesium nanocluster in BSA matrix. In the current case $16\pi/3$ refers constant geometrical factor, derived from the homogeneous nucleation of spherical particles [136]. In contrary, for the heterogeneous nucleation process, $16\pi/3$ is considered as numerical constant instead and facilitate comparison between the interfacial energy in case of homogeneous and heterogeneous nucleation, in place of suggesting spherical nuclei [136]. In our study, it was observed that effective interfacial energy of MgNCs is increase with the rise in temperature, such as 111.75→148.01 mJ/m², 112.8→150.09 mJ/m², 113.03 →151.78 mJ/m² and at 10, 15 and 20 °C/min, respectively. (Appendix-Table B5) Average estimated value of interfacial energy are found to be 125.95 (10 °C/min), 127.07 (15 °C/min) and 127.86 (20

°C/min). This obtained value are in good harmony with previously reported interfacial energy of alkaline earth metal-based nanoparticles [8] . In order to obtain temperature dependent effective interfacial energy, a theoretical model is developed and fitted with experimental data. To understand the mechanistic relation between apparent interfacial energy and temperature a best fitted liner model $Y=a_1T+b_1$ is developed, where a_1 and b_1 are linear function constant and their values are (0.1366, 41.88), (0.1357, 42.25) and (0.1353, 42.62) at 10, 15 and 20 °C/min, respectively. From the above-mentioned model, we deduced that the apparent interfacial energy is independent on heating rates. However, for the graph (Figure. 4.8 c) between interfacial energy versus conversion, suggests a second-order polynomial model ($Y = a_2T^2 - b_2T + R$) at all three heating rates.

The values of a_2 , b_2 , and r at different heating rates 10, 15, and 20 °C/min, are found as (3.47±13.80,36.15±13.45,112.76±3.0),(1.70±13.9,39.0±13.59,113.84±3.03)and(1.00±14.68,41.10±14.31,114.3±3.19),respectively. Analysing this result, we find that as temperature increases, the nucleation rate also increases exponentially, due to increase in the effective value of interfacial energy. Graph displayed in Figure. 4.8 (d).

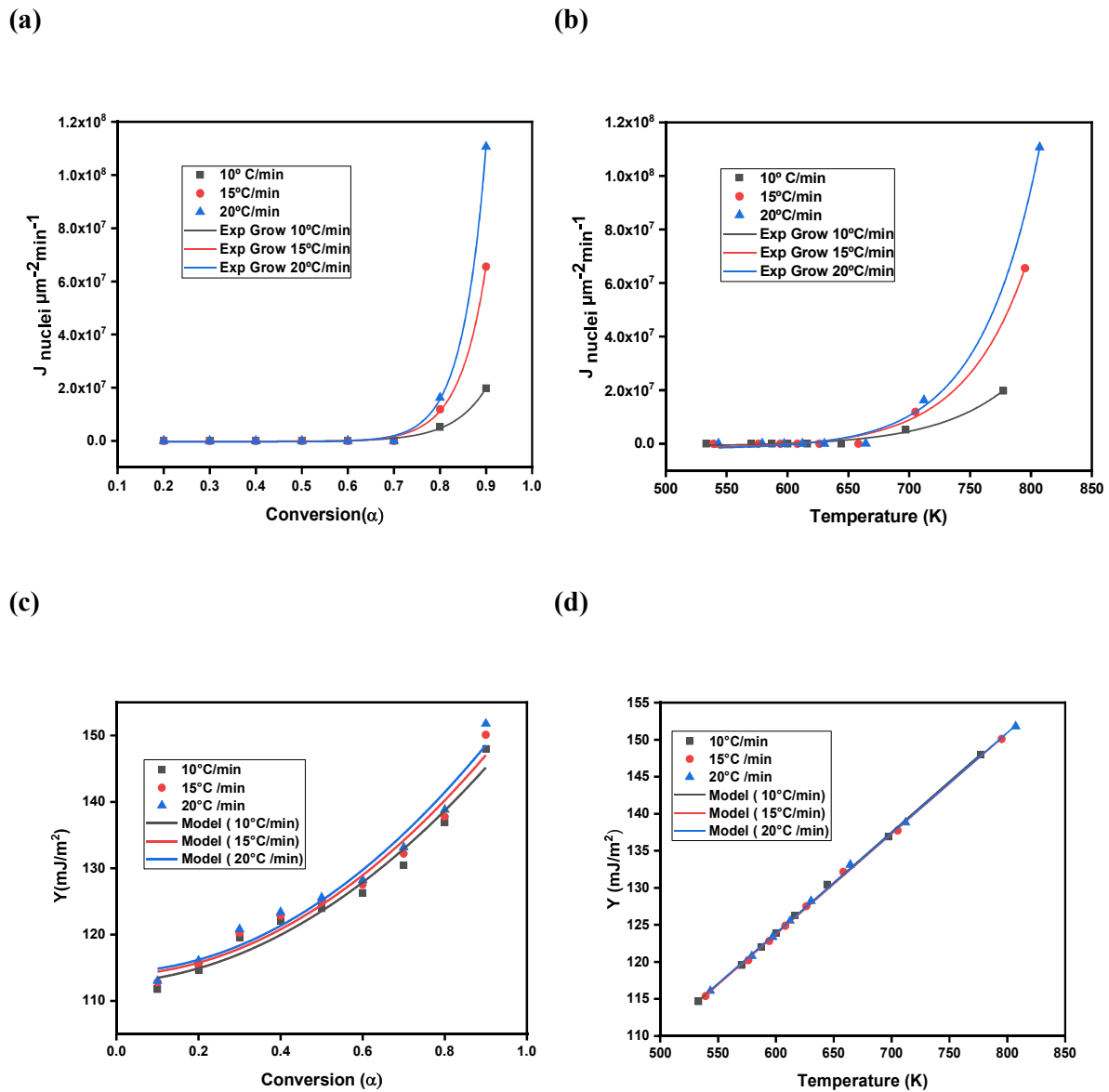


Figure 4.8 (a) Plot between nucleation rate and conversion(α) (b) Plot between nucleation rate and Temperature(K) (c) Plot between interfacial energy and conversion(α) (d) Plot between interfacial energy and Temperature (K).

4.5 Conclusion

The thermogravimetric analysis of metallic magnesium nanoclusters was carried out using TGA analyser at 10, 15 and 20 °C/min heating rates, under nitrogen atmosphere. Apparent activation energy (E_a), pre-exponential kinetic factor (A), nucleation rate (J), interfacial energy (Y) and thermodynamic parameters (ΔH , ΔG and ΔS) of ultrasmall MgNCs in BSA matrix were computed using most appropriate and accurate technique at high temperature. Furthermore, the differential function $f(\alpha)$ and integral form $g(\alpha)$ was found to vary as $(1-\alpha)^3$ and $[(1-\alpha)^2-1]/2$ respectively, upon monitoring $Z(\alpha)$ master plot against experimental value. Moreover, the apparent value of activation energy calculated using the most accurate Vyazovkin AIC method was found to be 159.56 kJ/mol and further utilized to compute thermodynamic parameters. The lesser value of activation energy revealed the suitability in reaction progression, whereas the value of ΔH at different conversion points suggested the easier reaction progression via activated complex formation. The negative value of ΔS at some conversional points revealed that both chemical and physical changes in material are extended to reach thermodynamic equilibrium.

Further, the pre-exponential kinetic factor was also determined by utilizing KAS derived equation to obtain the nucleation rate at high temperature and specific conversions. For the first time, the Nucleation rate of MgNCs was investigated at found to be governed by $J = Q_1 \exp\left(\frac{T}{\rho_1}\right) + Y_0$ and $J = Q_2 \exp\left(\frac{\alpha}{\rho_2}\right) + J_0$ models against high temperature and specific conversion, respectively. Additionally, interfacial energy for the MgNCs was also computed by utilizing a thermodynamic barrier and was governed by $Y = a_1T + b_1$ and $Y = a_2T^2 - b_2T + R$ models at specific temperatures and conversions, respectively.