Chapter Five

EXPERIMENTAL

Starting materials

The raw materials selected for the present study include naturally occurring bauxite rock containing small amounts of impurities and a synthetically prepared alumina hydrate precursors.

5.1.1. Selection of naturally occurring bauxite

The raw bauxite rock was collected in lump form from Sourastra, Gujarat. Gujarat is reputed to be one of the prime bauxite bearing areas producing significant quantity of bauxite of chemical, refractory and abrasive grades. Then bauxite was crushed and ground carefully to powder and sieved using standard sieves to collect the different size fractions viz -20+50, -50+80 and -80+120 meshes (BSS) for conducting thermal analysis. The sieved sample was thoroughly dried in an electric air oven at 105°C, cooled to room temperature and stored in an incubator maintained at constant temperature (35±1°C).

5.1.2. Preparation of synthetic alumina hydrate precursor

5.1.2.1. Raw materials

Analytical reagent grade aluminum isopropoxide $Al(OC_3H_7)_3$ (Merck) and isopropanol C_3H_7OH (Merck) and nitric acid (Merck) were used as starting materials.

5.1.2.2. Procedure

Two liter of 0.1(M) solution of aluminum isopropoxide in isopropanol was taken in a jar and interacted with dropwise addition of 2(N) nitric acid as peptizing agent with

constant stirring in a magnetic stirrer until pH value is changed to 4.0. The mixes was then placed in a thermostat bath at 70°C and subjected to hydrolysis by refluxing for 3 hours. The formed gel was allowed to age for 24 hours. The pH of the gel was measured. Finally the gel filtered through whatman 40 filter paper placing on a beaker with buckner funnel under suction, washed with hot ammoniacal ammonium nitrate solution several times to remove the dissolved electrolyte. The gel precipitate thus obtained was vacuum dried at 70°C, agated to fine gel powder and stored in incubator maintained at 35±1°C.

5.2. Characterization

5.2.1. Chemical analysis of the starting material

Bauxite and synthetically prepared alumina hydrate were analyzed chemically following standard procedure. Both the samples were dissoluted by 2:1 H_2SO_4 digestion. Among the constituents, Al_2O_3 and SiO_2 were determined gravimetrically. CaO and MgO were determined complexometrically by EDTA titration and Fe_2O_3 was estimated by determined by $Hg_2(NO_3)_2$ method, while titania by spectrophotometric method and alkalis by flame photometry.

5.2.2. Specific Surface Area measurement

Specific surface area of submicron ceramic powder is an important tool in predicting the green compaction and sintering characteristics. This is measured by BET method. The BET method (Brunauer, Emmet and Teller) involves adsorbing a monolayer of

liquid nitrogen onto the surface of particles, then measuring the amount of nitrogen that is released when that monolayer is vaporized.

Specific surface area of bauxite and synthetic alumina hydrate powders was determined by the Strohlein Area Meter II instrument. About 0.2-0.3 gm of sample was taken in the sample cell and degassed at 260°C in vacuum up to a maximum of 3 mbar. The sample holder mouth was closed by a stopper. Sample was cooled and the cell was placed in liquid nitrogen bath. The equipment measured the amount of N_2 gas adsorbed on the surface of the sample and the surface area of the sample can be calculated from the BET equation:

$$\frac{1}{V}\left(\frac{x}{1-x}\right)=\frac{c-1}{cV_m}x+\frac{1}{cV_m}$$

V = volume of gas adsorbed, V_m = volume of gas adsorbed at monolayer coverage, x = P/P_o, P = ambient pressure, P_o = total pressure, C, a constant that is related to the heat of adsorption. A plot of (1/V) (x/ (1-x)) versus x gives a straight line with slope, m= (c-1)/ (cV_m), Intercept, b= $1/cV_m$, The value of V_m and c are worked out, V_m = 1/ (slope + intercept). This is normalized by the mass of particles tested to give specific surface area (m^2 gm^{-1}).

5.2.3. Particle size distribution

About 4 mg sample was uniformly dispersed in 10 ml distilled water with magnetic stirring for 2hrs followed by ultrasonication for 10 minutes. The quartz cell was filled up with that suspension and the particle size distribution was measured in ZEN 1600, Malvern Zeta Sizer, USA in the range from 0.06 μm to 6 μm.

5.2.4. Differential thermal (DTA) analysis

It was carried out with an automatic apparatus namely Netzsch simultaneous thermal analyzer (Model 309). 25 mg of the incubated powder sample was taken in each case and the heating rate was maintained at 10°C/min. The experiments were conducted up to 1200°C with α Al_2O_3 as inert reference material.

5.2.5. Dehydration-rehydration study under equilibrium conditions

Unlike differential thermal analysis which is a dynamic method of thermal treatment, samples were equilibrated here at a particular temperature upto the constant loss. For this purpose, 0.5 gm accurately weighed sample in the form of loose powder was taken in a porcelain crucible of 20 ml capacity. This was placed in an electrically operated muffle furnace maintained at specified constant temperature. After three hours, the crucible containing the fraction was taken out, cooled in desiccators and weighed. The temperatures of heat treatment chosen were 100,200,300,400,500,600,700 and 800°C respectively. The mass losses due to dehydration of the samples at different temperatures were recorded.

The rehydration study of the heat treated sample was performed at different relative humidities such as 35, 55, 75 and 100 % respectively. After dehydration, dehydrated samples were placed in the humid chamber successively in the increasing order of humidity. The gain in weight at each stage was determined after equilibrating for 24 hrs. All the dehydration rehydration experiments were carried out taking the fractions equilibrated at 35±1°C.

5.2.6. Fourier Transform Infra-red spectroscopy (FTIR) studies

To provide adequate characterization of hydrated aluminous minerals by infrared spectroscopy, the absorption spectrum was recorded over the range of 4000 to 400 cm^{-1} wave number. A small amount of sample (0.2 gm) was thoroughly mixed with ground KBr in an agate mortar and the thin disk (2.4 mm diameter) was prepared by vacuum pressing at a pressure of 33kg/sq cm. The spectrogram was taken by a Perkin-Elmer-783. The spectroscope used is of dispersive type. In this instrument the detector monitor the intensity of the narrow bandwidth of radiation dispersed by diffraction grating and prism in a monochromator. The operational mode was double beam and was of ratio recording in which the absolute value of the radiation intensity ratio in both reference and sample beam was continuously monitored. The spectroscopy of the sample was observed in video monitor and a graphical representation of the spectra was obtained from the printer. The level was monitored at 100 and the window at 10.

5.2.7. X-Ray Diffraction (XRD) analysis

It was carried out to ascertain the mineralogical and crystallographic characteristic of the starting materials and the crystalline phase changes on heat treatment. For this purpose, powder X-ray diffraction of the bauxite and synthetic hydrated alumina were taken in a Guinier Camera of Phillips diffractometer, X' PERT Pro, PW-3071 with Ni-filtered Cu-K_α radiation at 1.5404 Å at a scanning rate of 2° per minute. All the runs were conducted at 30 KV and 10 mA.

The average crystallite size (D) of the bauxite and synthetic alumina hydrate was calculated from the X-ray line boarding by applying full width half maximum (p) of the characteristic peak (111) to the Debye-Scherrer formulas

$$D_{xrd} = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the incident angle for the (111) plane. The lattice parameters were computed using d-values and the respective (h,k,l) parameters.

5.2.8. Scanning Electron Microscopy (SEM) studies

Scanning electron microscopy studies for bauxite loose powder and synthetically prepared alumina hydrate powder were performed. These studies were carried out using scanning electron microscope, model Quanta 200, FEI, Holland. The photomicrographs were taken at magnification of 6000-10000.

5.2.9. Kinetics of thermal decomposition

In the present investigation, kinetics of the thermal dehydration of the bauxite rock and synthetically prepared alumina hydrate were studied in the form of loose powder. The kinetic study was conducted under both isothermal and non-isothermal condition using thermogravimetric and differential thermogravimetry analysis.

5.2.9.1. Isothermal kinetics studies

Isothermal kinetic studies of bauxite and synthetic alumina hydrate sample was carried out using thermobalance instrument Model OKAY, Bysakh and Co., India at the

heating rate 10°C min^{-1}. The control of the temperature was within ±0.5°C. In each case, the powdered sample of 0.5 gm was taken and distributed uniformly to the same height in the Pt-crucible. Prior to TG analysis at each temperature the samples were heat treated and equilibrated for 10 seconds. The mass loss were recorded by the thermobalance at 30-120 seconds time interval. The initial mass corresponding to zero time was being taken after 10 seconds insertion of the Pt-crucible with the sample inside the furnace in as to allow the equilibrations at the that isothermal temperature. In each case, the final mass loss was recorded as a function of time until three successive reading at 4 minutes interval were identical.

5.2.9.1.1. Guggenheim method for isothermal kinetics analysis

If the plot of mass loss against time followed exponential behavior in the isothermal dehydration loss measurement of powder sample, then the application of 1st order kinetics appeared to be logical. According to 1st order kinetics, the mass loss of water from the sample at any instant would be proportional to the concentration of the water present in the sample at that time. Now the concentration of the water in the sample would be equal to the weight of water present in it which may be lost at the experimental temperature divided by the volume of the sample. Therefore, if the weight and the volume of the initial sample are kept fixed, the concentration terms may be replaced by the relevant weight. Thus, at a given temperature, if L = mass loss at time t, and L_∞ = total mass loss at infinite time, then L_∞ is equivalent to the initial concentration of water (dehydration at the experimental temperature) in the sample, and

(L_∞-L) is equivalent to the concentration of water remaining in the sample at time t. Thus, according to the first order kinetics, the rate of loss water will be given by

$$\frac{dL}{dt} = k_1(L_\infty - L) \quad \text{or,} \quad \log\frac{[(L_\infty - L)]}{L_\infty} = -\frac{k_1 t}{2.303} \tag{1}$$

Eqn. (1) permits the evaluation of the rate constant for dehydration (k_1) at the initial stage from the slope of the line obtained by plotting log [(L_∞ -L)/ L_∞] against t, provided the value of L_∞ is known. As the first order reaction can never go to completion theoretically, any direct experimental determination of L_∞ would be in accurate and was not attempted. Instead, the method initially suggested by Guggenheim and later followed by Murray and White[169], Mitra *et al*[170], Bhattacharya *et al*[171] and also by Maitra *et al*[172] was adopted for evaluation of both L_∞ and k_1.

Let $L_1, L_2 \ldots\ldots L_n$ be the mass losses at times $t_1, t_2 \ldots\ldots t_n$ and $L_1^{'}$, $L_2^{'} \ldots\ldots L_n^{'}$ be the losses at time $t_1+\Delta t$, $t_2+\Delta t, \ldots t_n+\Delta t$, i.e., at constant time interval Δt after the previous set. Then using Eqn. (1) we can write,

$$L_\infty - L_1 = L_\infty e^{-k_1 t} \quad \text{and} \quad L_\infty - L_1^{'} = L_\infty e^{-k_1(t+\Delta t)} \tag{2}$$

Subtracting, $L_1^{'} - L_1 = L_\infty e^{-k_1 t}\left(1 - e^{-k_1 \Delta t}\right)$

Taking logarithm and putting ΔL for $L_1^{'} - L_1$ terms, the equation takes the general form,

$$\log(\Delta L) = -\frac{k_1 t}{2.303} + \log\left[L_\infty \left\{1 - e^{-(k_1 \Delta t)}\right\}\right] \tag{3}$$

Eqn.(3) is known as the Guggenheim equation where ΔL is the differences between the mass loss at ($t+\Delta t$) and that at times t. The time interval Δt between the two set of

readings being kept fixed at values greater than twice the time for 50% dehydration. Using Eqn.(3) the rate constant (k_1) can be calculated from the slope of the straight line obtained by plotting log (ΔL) against t. L_∞ is determined from the intercept of the line on the logΔL axis by knowing Δt and rate constant (k_1) values.

The reaction rate constants (k_2) at the final stage of dehydration was determined from the slope of mass loss vs. time curves at the point of termination of the first order kinetics, using relation

$$k_2 = \frac{\left(\frac{dL}{dt}\right)}{(L_\infty - L)} \tag{4}$$

where, dL/dt is the slope of the mass loss versus time curve at the point of dehydration beyond which 1st order law is not followed and L is the actual loss at that point.

The activation energies of initial (E_1) and final (E_2) stage dehydration are calculated from rate constant values using Arrhenius equation,

$$\log k = \log A - \frac{E}{RT} \tag{5}$$

and from the slope of the plots log k vs 1/T respectively, E can be calculated where 'A' is the constant known as frequency factor. The activation energy E is actually the height of energy barrier to the dehydration reaction and that must be surmounted by thermal excitation.

5.2.9.1.2. Integral isoconversional method recommended by kinetic committee[173]

The dehydration of bauxite is a solid state dehydration reaction, rate of which can be expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{6}$$

where k is the rate constant, T is the absolute temperature, $f(\alpha)$ is the reaction model function and α is the fractional conversion.

$$\alpha = \frac{(w_i - w_t)}{(w_i - w_f)} \tag{7}$$

where w_i, w_f and w_t are the initial, final and current sample mass at the moment t during thermogravimetric analysis, respectively.

Under constant temperature condition, Eqn. (6) can be integrated to

$$g(\alpha) = kt \tag{8}$$

where g (α) is the integral form of reaction model. The temperature dependence of the rate constant k is usually described by the classical Arrhenius relation

$$k = A\exp^{-\frac{E}{RT}} \tag{9}$$

where A is the pre-exponential factor, E is the activation energy and R is the universal gas constant.

Combining Eqns. (8) and (9) gives

$$g(\alpha) = A \exp^{-\frac{E}{RT}} t \qquad (10)$$

Applying the isoconversional principle and rearrangement in Eqn. (10), ICTAC kinetic committee recommended Eqn. (11) of integral isoconversional method can be derived.

$$\ln t_{\alpha,i} = \ln\left[\frac{g(\alpha)}{A_\alpha}\right] + \frac{E_\alpha}{RT_i} \qquad (11)$$

where $t_{\alpha,i}$ is the time to reach a given reaction extent at different isothermal temperature T_i. The reaction extent dependent activation energy can be calculated from the slope of the plot ln $t_{\alpha,i}$ vs $1/T_i$ without applying an actual model.

5.2.9.2. Non isothermal kinetic studies

The Non-isothermal kinetic study was examined by thermogravimetric-differential thermal (TG-DTA) analysis. Thermogravimetric analyses (TGA) of the bauxite and synthetically prepared alumina hydrate samples were conducted using high temperature NETZSCH simultaneous thermal analyzer STA 449 /F/3. The specifications of the equipment are: measurement range from 5 g to 10 g, sensitivity 0.1 μg, maximum temperature (P = 1 bar) 1600 °C, maximum heating rate 50 K/min. The 4-mg samples were put into an alumina holder and pyrolysed in the argon atmosphere at flow rate of 50 ml/min. Prior to heating, the system was vacuumized three times to eliminate oxygen. Mass loss against temperature data were taken under non-isothermal operating conditions. The samples were subjected to differential thermogravimetric analysis from room temperature to 1200°C at heating rates 5, 7.5 and 10 $Kmin^{-1}$ respectively.

Mass loss data at a constant temperature are converted to a normalized form called conversion fraction (α). The reaction rate can be expressed by the degree of conversion (α) according to the formula:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{12}$$

Where: m_i, m_f and m_t are the initial, final and current sample mass at the moment t during thermogravimetric analysis, respectively.

5.2.9.2.1. Determination of activation energy by Flynn–Wall–Ozawa method[30-31]

Flynn-Wall and Ozawa independently developed an isoconversional calculation method by using Doyle approximation for nonisothermal data which is commonly referred to as the FWO method.

Rate of reaction of solid-state decomposition can be expressed by the following general equation

$$\frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}.f(\alpha) \tag{13}$$

When heating rate is kept fixed, β = dT/dt. Hence Eqn. 13 can be rewritten as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-\frac{Ea}{RT}}.f(\alpha) \tag{14}$$

Where E_a is the apparent activation energy, A is the pre-exponential factor, R is the universal gas constant, f (α) is a function of α, which reveals the mechanism of reaction. By a series of transforms, Eqn. 14 can be rewritten as

$$\log\beta = \left[\log\frac{E_a}{R} - \log g(\alpha) - 2.315\right] - 0.4567\frac{E_a}{RT} \tag{15}$$

If α is a fixed value, then log g(α) is a fixed value, too. The variation of log β against 1/T must give rise to a straight line. Thus activation energy E_a of the reaction can be obtained from linear slope ($k = -0.4567E_a/R$), irrespective of the $g(\alpha)$ employed.

5.2.9.2.2. Determination of activation energy and pre-exponential factor by Kissinger method[32]

Kissinger method is a model-free approach as it does not require any modelistic assumptions to calculate E_a. However, it is not an isoconversional method because it does not calculate E_a values at progressive α values but rather assumes a constant E_a, like other methods. Thus this method can not detect reaction complexities over the course of the reaction.

According to the Kissinger equation (Eqn.16), the activation energy and pre-exponential factor of thermal decomposition reaction can be computed as follows.

$$\ln\frac{\beta}{T_{\max}^2} = -\frac{E_a}{RT_{\max}} + \ln\frac{AR}{E_a} \qquad (16)$$

where β is the heating rate (K min^{-1}), T_{max} is the most rapidly decomposing temperature corresponding to maximum reaction rate(that is, peak temperature on DTGA curve, in K), E_a is the activation energy (kJ mol^{-1}) of thermal decomposition, R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), and A is the pre-exponential factor. The plot of $\ln \beta/T_{max}^2$ against $1/T_{max}$ must give rise to a straight line. Thus, reaction activation energy E_a can be determined from linear slope ($k = -E_a/R$), and the pre-exponential factor A can be obtained from linear intercept [$h = \ln (AR/E_a)$].

5.2.9.2.3. Determination of activation energy by modified Coats-Redfern[28-29] method

The decomposition reaction based on the nth order reaction kinetics can be written as:

$$-d\alpha/dt = k\,(1-\alpha)^n \qquad (17)$$

i.e, the rate of reaction is proportional to the nth power of undecomposed part of the sample. n the order of the reaction , k the specific reaction rate constant.

The rate constant which is a function of temperature can be expressed by Arrhenius equation,

$$k = A\,e^{-E/RT} \qquad (18)$$

where, E the activation energy of the reaction, A the pre-exponential factor, R the gas constant, T the temperature in absolute scale.

Substituting k from Eqn.18 into the Eqn. 17 gives

$$-d\alpha/dt = A\,e^{-E/RT}\,(1-\alpha)^n \qquad (19)$$

After separating variables from Eqn. 19 results in

$$-d\alpha/(1-\alpha)^n = A\,e^{-E/RT}\,dt \qquad (20)$$

Again, the rate of heating $\beta = dT/dt$ or, $dt = dT/\beta$ (21)

Putting the expression of dt in Eqn. 20 and integrating between temperature limits T_1 and T_2 and fractional decomposition α (increasing from 0 to1of the solid reactant during course of reaction), the following equation is obtained.

$$-\int_0^{\alpha}\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T1}^{T2} e^{-\frac{E}{RT}}dT \qquad (22)$$

But the integration at the right hand side $\frac{A}{\beta}\int_{T1}^{T2} e^{-\frac{E}{RT}}dT$ has no analytical solution.

Therefore, the solution advanced by Coats & Redfern is used to determine the kinetic parameters of the dehydration reaction. The approximate solution as given by Coats & Redfern method is as follows

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E}\left[\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{(for n =1)} \qquad (23)$$

$$\ln\left[-\ln\left\{\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right\}\right] = \ln\frac{AR}{\beta E}\left[\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{(for n≠1)} \qquad (24)$$

If it is assumed that the expression $\ln\frac{AR}{\beta E}\left[\left(1-\frac{2RT}{E}\right)\right]$ remains constant over the temperature range of decompostion, then the Eqns. 23 and 24 assumes a linear forms, then a plot of $\ln[-\ln(1-\alpha)/T^2]$ vs.1/T for n=1 and $\ln[-\ln\{1-(1-\alpha)^{1-n}\}/(1-n)T^2$ vs. 1/T for n≠1 gives the value of E from the slope (-E/R) and the value of A from the intercept $\ln\frac{AR}{\beta E}\left[\left(1-\frac{2RT}{E}\right)\right]$. The equation 23 and 24 is known as Coats and Redfern equation which was derived assuming a first-order model ($g(\alpha) = -\ln(\ln(1-\alpha)$. Later this equation has been generalized to other reaction models. Generalized equation is given as

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E_a}\left[1-\left(\frac{2RT_{\exp}}{E_a}\right)\right]\right) - \frac{E_a}{RT} \qquad (25)$$

Where T_{exp} is the mean experimental temperature.

Burnham and Barun[ref] have transformed the model-fitting Coats-Redfern method to an isoconversional method by rearranging Eq. (25) to give,

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{AR}{E_a g(\alpha)}\left[1-\left(\frac{2RT_{exp}}{E_a}\right)\right]\right) - \frac{E_a}{RT} \qquad (26)$$

A plot of $\ln\frac{\beta}{T^2}$ versus 1/T at each α yields E_a from the slope for each α regardless of the model according to:

$$\ln\left(\frac{\beta}{T^2}\right)_\alpha = \ln\left(\frac{A_\alpha R}{E_{a\alpha} g(\alpha)}\left[1-\left(\frac{2RT_{exp}}{E_{a\alpha}}\right)\right]\right) - \frac{E_{a\alpha}}{RT} \qquad (26)$$

5.2.9.3. Thermal Dehydration mechanism by non-isothermal methods

The indepth evaluation of underlying exact mechanism of thermal decomposition for aluminous materials under non-isothermal condition is absolutely essential for controlling and optimization of the course of reaction, actual energy consumption for thermal decomposition process and the nature of the product derived.

The classification of kinetic models based on *f(α)* values (Eqn.14) to determine the reaction mechanism for solid state decomposition reaction can be found out per table 2.

Table 2: Solid-state rate expressions for different reaction models

Model	Differential form $f(\alpha)=1/k\ d\alpha/dt$	Integral form $g(\alpha)=kt$
Power law(P2)	$2\ \alpha^{(1/2)}$	$\alpha(1/2)$
Power law(P3)	$3\ \alpha^{(2/3)}$	$\alpha(1/3)$
Power law(P4)	$4\ \alpha^{(3/4)}$	$\alpha(1/4)$
Avarami-Erofeyev(A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avarami-Erofeyev(A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avarami-Erofeyev(A4)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Geometrical contraction models		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Contracting volume(R3)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
Diffusion models		
1-D Diffusion (D1)	$1/(2\alpha)$	α^2
2-D Diffusion (D2)	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3-D Diffusion-Jander (D3)	$[3(1-\alpha)^{2/3}] / 2[1-(1-\alpha)^{1/3}]^2$	$[1-(1-\alpha)^{1/3}]^2$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order (F3)	$(1-\alpha)^3$	$0.5\ [(1-\alpha)^{-2}-1]$

Determination of decomposition mechanism by Malek method[33-34]

The Malek method is used to determine the most probable mechanism of decomposition reaction where the standard curve equation of mechanism function is depicted by:

$$y(\alpha) = \frac{f(\alpha)F(\alpha)}{f(0.5)F(0.5)} \tag{28}$$

Experimental curve equation can be written as:

$$y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2 \left[\frac{\left(\frac{d\alpha}{dT}\right)}{\left(\frac{d\alpha}{dT}\right)^{0.5}}\right] \tag{29}$$

Where $F(\alpha)$ and $f(\alpha)$ are the reaction models and $d\alpha/dT$ is obtained from TG curve. When experimental curve and standard curve overlaps in plot of y(α) versus α curves, the corresponding $F(\alpha)$ or $f(\alpha)$ is being taken as the most probable mechanism function.