Non-isothermal decomposition kinetics of Cordierite precursor synthesized through semi-colloidal route from thermo-gravimetric data

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Abstract
A comprehensive study on thermal decomposition kinetics of cordierite precursor powder belonging to multi-component MgO-Al₂O₃-SiO₂ system with variation of heating rates seems absolutely essential for understanding and controlling the course of reaction, the mechanism of thermal decomposition, the optimization of process conditions and the nature of intermediate product. Kinetics of thermal decomposition of cordierite precursor synthesized through semi-colloidal sol-gel route has been studied by thermogravimetric analysis (TG-DTA) in static air using five different heating rates of (5.0, 7.5, 10.0, 12.5 and 15 K min⁻¹) under non-isothermal condition. Isoconversional Flynn-Wall-Ozawa and model free Kissinger method were applied to determine the kinetic parameters like activation energy and pre-exponential factor for the decomposition process. The thermal process of cordierite precursor from room temperature to 1000°C involves the dehydroxylation of the water molecules. Dehydration starts with the loss of physically adsorbed water, inter layer water at around 130°C followed by the removal of hydroxyl groups from its heterogeneous structure at around 405°C which is basically a heterogeneous solid state reaction and mainly governed by the rate of diffusion of formed water molecules through the structure. The average activation energy computed by FWO method for the 2nd peak was 70.57±4.07kJ.mole⁻¹ using fraction conversion from 0.2 to 0.80. Similarly activation energy calculated by modified Coats-Redfern method and Kissinger method are 63.32±3.86 kJ.mole⁻¹ and 62.04 kJ.mole⁻¹ respectively for the dehydroxylation peak are closely consistent and comparable with one another.

Key words: Cordierite, Non-isothermal decomposition, TG-DTA, Kinetic parameters

INTRODUCTION
Cordierite is a magnesium aluminium silicate having the stoichiometric formula (2MgO.2Al₂O₃.5SiO₂) which is the main phase of the MgO-Al₂O₃-SiO₂ system. Cordierite materials have very interesting properties like adequate refractoriness, extremely low thermal expansion; low thermal conductivity, and high mechanical strength, excellent thermal shock resistance and outstanding electrical resistivity. Its multifunctional applications spreads over kiln furniture, moulded honeycomb-like catalyst supports in auto emission reduction devices, thick films, porous ceramics, insulators, high frequency insulators, high performance resistors, special furnace shapes, heating element supports, exhaust catalyst supports, burner tubes, refractory setters and substrates, welding tapes, heaters, thermocouples, and appliance insulators. Cordierite ceramics possess also low values of dielectric constant and dielectric loss which permits its applications in electronic industry as substrates, packaging and multichip module (MCM).

The traditional method for synthesis of cordierite ceramics involves the solid-state sintering of MgO, Al₂O₃ and SiO₂ in ratios corresponding to the stoichiometric chemical composition of cordierite [1-2]. Several methods have been developed to synthesize cordierite over decades such as 1) solid-state reaction of MgO, Al₂O₃ and SiO₂ or their precursors [3-4] and 2) wet chemical methods e.g. sol–gel processes, hydrolysis, hydrothermal spray pyrolysis and combustion synthesis [5-9]. The disadvantages of wet chemical processes include expensive starting materials, low yields and complex processing techniques creating difficulty in large-scale low-cost applications. From the standpoint of cost effectiveness talc, sepiolite, kaolin, silica, gibbsite, and kaolinitic clay were used as starting materials of cordierite and allied products [10-12].
Cordierite phase exists in three polymorphic forms: (i) the high-temperature disorder form known as in diatite (α- or hexagonal-cordierite) which is stable below 1450°C, (ii) β-cordierite, called orthorhombic cordierite stable in between 1450°C and its melting point (1460°C), and (iii) µ-cordierite, called metastable cordierite phase, the low-temperature ordered orthorhombic form [13], which is prepared only under special conditions.

The available literature indicates that upon thermal treatment from room temperature to about 800°C, the cordierite precursor remains more or less non-crystalline. Above 800°C it crystallizes to metastable hexagonal µ-cordierite, which is structurally analogous to “stuffed β-quartz” via partial substitution of Si by Al and Mg entering the structural channels. As the sintering temperature increases, the structure transforms towards hexagonal α-cordierite [14].

A thorough study of thermal dehydration kinetics of cordierite precursor appears highly essential to understand the course of reaction and estimation of kinetic parameters. Compared to conventional isothermal study, non-isothermal methods for determining kinetic parameters of thermal decomposition have several advantages. A single sample and fewer data are necessary and the kinetics of thermal decomposition can be calculated over an entire temperature range in the continuous manner, although one disadvantage of the non-isothermal data method involves the uncertainty over evaluation of reaction mechanism. Thus the systematic study on the thermal decomposition and the kinetic properties of cordierite precursor employing non-isothermal thermo-gravimetric analysis may accomplish a deep insight into the effect of thermal treatment on the structural changes of the precursor employing non-isothermal TG-DTA analysis for widening the successful application of cordierite ceramics in various fields.

The present work has been designed for computation of kinetic parameters such as activation energy; pre-exponential factor for decomposition of synthetic cordierite precursor powder using TG-DTA technology at five different heating rates from 5-15 K min⁻¹. Non-isothermal kinetics of thermal decomposition of cordierite precursor were examined and correlated by isoconversional Flynn-Wall-Ozawa [15-16], modified Coat-Redfern method [15-16] as well as model free Kissinger [17] methods.

2. METHODS
2.1 Methods of determining dynamic kinetic parameters:
Thermogravimetric analysis is one of the most commonly used techniques to study the primary reaction of dehydration of solid. Weight loss data at a constant temperature are converted to a normalized form called conversion fraction (α). The degree of conversion (α) can be expressed according to the equation (1):

$$\alpha = \frac{m_i - m_t}{m_i - m_f}$$ (1)

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

2.2 Determination of activation energy by Flynn–Wall–Ozawa method [15,16]
Flynn-Wall and Ozawa independently developed an isoconversional calculation method by using Doyle approximation from non isothermal data which is commonly referred to as the FWO method. Rate of solid-state decomposition can be expressed by the following general equation:

$$\frac{da}{dt} = A \cdot e^{-E_a/RT} \cdot f(\alpha)$$ (2)

When heating rate is kept fixed, \(\beta = dT/dt\). Hence, Eqn. 2 can be written as by substituting \(dt\),

$$\frac{da}{dT} = A/\beta \cdot e^{-E_a/RT} \cdot f(\alpha)$$ (3)

Where \(E_a\) is the apparent activation energy, \(A\) is the pre-exponential factor, \(R\) is the universal gas constant, \(f(\alpha)\) is a function of \(\alpha\), which reveals the mechanism of reaction. By a series of transforms, Eq. 3 can be rewritten as

$$\log \beta = [\log E_a/R - \log f(\alpha) - 2.315] - 0.4567 E_a/RT$$ (4)

If \(\alpha\) is a fixed value, then \(\log f(\alpha)\) will be a fixed value, too. The variation of \(\log \beta\) 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 = -0.4567\(E_a/R\)) of the equation irrespective of the \(f(\alpha)\) employed.

2.3 Determination of activation energy and pre-exponential factor by Kissinger method [17]
Kissinger method is a model-free approach, as it does not require any modelistic assumptions to calculate \(E_a\). Moreover, this non-isoconversional method does not calculate \(E_a\) values at progressive \(\alpha\) values but rather assumes a constant \(E_a\) like other methods. Thus, this method cannot detect complexities that occur during the course of the reaction. According to the Kissinger equation (Eq. 5), the activation energy and pre-exponential factor of thermal decomposition reaction can be computed as follows.

$$\ln \beta/T_{max}^2 = -E_a/RT_{max} + \ln AR/E_a$$ (5)

Where \(\beta\) 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 DTA 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 \(\ln(\beta/T^2)\) versus \(1/T\) yields a straight line. Thus, reaction activation energy \(E_a\) can be determined from linear slope \((k = -E/R)\), and the pre-exponential factor \(A\) can be obtained from linear intercept \([h = \ln\left(AR/E_a\right)]\) of the equation.

2.4. Determination of activation energy by modified Coat-Redfern method [15,16]

Coats & Redfern developed the calculation method to determine the kinetic parameters of the dehydration reaction. The equation was given by Coats & Redfern method as follows

\[
\ln\left(\frac{1}{T^2}\right) = \ln\left(\frac{AR}{Ea}\right) - \frac{E}{RT} \tag{6}
\]

\[
\ln\left[-\frac{1}{(1-(\alpha))^{n}}\right] = \ln\left(\frac{AR}{Ea}\right) \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{7}
\]

If it is assumed that the expression

\[
\ln\left(\frac{AR}{Ea}\right) \left(1 - \frac{2RT}{E}\right)
\]

remains constant over the temperature range of decomposition, the Eqns. 6 and 7 assumes a linear forms, then a plot of \(\ln[-\ln\left(\frac{1}{(1-(\alpha))^{n}}\right)]\) vs. \(1/T\) for \(n = 1\) and \(\ln[-\ln\left(\frac{1}{(1-(\alpha))^{n}}\right)]\) vs. \(1/T\) for \(n \neq 1\) gives the value of \(E\) from the slope \((-E/R)\) and the value of \(A\) from the intercept \(\ln\left(\frac{AR}{Ea}\right) \left(1 - \frac{2RT}{E}\right)\). Later this equation has been modified to a generalized as below

\[
\ln\left(\frac{AR}{Ea}\right) \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{8}
\]

Where \(T_{exp}\) is the mean experimental temperature.

Burnham and Barun [18] have transform the model-fitting Coat-Redfern method to an isocoversional method by rearranging Eq. (8) to give,

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Ea}\right) \left(1 - \frac{2RT_{exp}}{Ea}\right) - \frac{E}{RT} \tag{9}
\]

The plot of \(\ln\left(\frac{\beta}{T^2}\right)\) versus \(1/T\) at each \(\alpha\) yields \(E_a\) from the slope for each \(\alpha\) regardless of the model in accordance with

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AeR}{Ea}\right) \left(1 - \frac{2RT_{exp}}{Ea}\right) - \frac{E}{RT} \tag{10}
\]

3. EXPERIMENTAL

3.1 Preparation of Cordierite precursor:

In the investigation, cordierite precursor powder has been chosen as starting material which was synthesized through aqueous phase interaction of ingredients in semi-colloidal route as described below. Finely milled dehydroxylated china clay and precipitated silica was thoroughly dispersed in an aqueous salt solution of Mg(NO\(_3\))\(_2\) followed by hydrolysis and gel formation by addition of 1:1 NH\(_2\)OH and engulfing the dispersion medium. This led to proper distribution of the solid particles in the Mg(OH)\(_2\)gel network. Rajmahal china clay, one of the best varieties of kaolinitic clay available in India was selected which was first purified from the associated impurities and then dehydroxylated at the temperature range of 600°C with 2hrs fixed soaking period. The mole ratio of MgO: Al\(_2\)O\(_3\): SiO\(_2\)was adjusted to stoichiometric composition of cordierite. Formation of coating of Mg(OH)\(_2\) was achieved by hydrolysis of the salt solution with controlled addition of 1:1 ammonia until pH 9.5 was attained. The set gel was filtered and washed with hot water to remove the adhering impurities and dried at 80°Cunder vacuum to minimize formation of agglomerates. The dried precursor was milled to fine state of subdivision. It was then thoroughly dried in an air oven at 110°C for 24 hrs and stored in an incubator maintained at 35+1°C for the thermal study.

3.2. Characterization of the Cordierite precursor powder:

The finely agitated sample was chemically analyzed with respect to chemical constituents following standard procedure of aluminosilicate analysis. Strohlein Area Meter II apparatus was employed to determine its surface area from its low temperature N\(_2\) absorption data using BET principle. Particle size distribution was measured by Malvern Master Sizer, X Ver. 1,2b. Serial No.-6449 in the size range from 0.06 μm to 6 μm. The FTIR absorbance spectra of the samples were recorded in a Perkin-Elmer-783 instrument in KBr phase in the frequency range 4000 - 400 cm\(^{-1}\). The identification of crystalline phases in precursor powder was performed by XRD analysis, using automatic X-ray diffractometer (X’Pert Pro, PW-3071).

3.3 Thermal decomposition of cordierite precursor powder

The non-isothermal dehydration kinetics of the precursor powder was measured by thermogravimetric-differential thermal analysis (TG-DTA). The experiments were conducted using a NETZSCH simultaneous thermal analysis apparatus (Model STA 409 PC). Sample of precursor powder was placed in platinum crucible. The instrument was protected from corrosion by a flowing atmosphere of nitrogen of ~20 ml min\(^{-1}\).
The instrument has a maximum heating rate of 50 K min⁻¹ and a fast cooling rate (>30 K min⁻¹) which facilitates the non-isothermal experiment. For conducting thermal study under non-isothermal conditions, the instrument was programmed to heat samples from room temperature to 1000°C at five different heating rates of 5, 7.5, 10, 12.5 and 15 K min⁻¹ in static air. The precursor powder for thermal analysis was taken in the form of loose powder and pure α-alumina powder was used as reference sample.

4. RESULTS AND DISCUSSION

From the chemical analysis (Table 1) of the dried precursor the empirical formula of cordierite was calculated as 2MgO:2Al₂O₃:5SiO₂:8H₂O. This was observed as per with the reacting batch composition taken. It is noted that the water content in the composition resembled with the combination of gel water as well as OH water. Thus the chemical analysis indicated the complete interaction of the ingredients of different nature.

Table 1: Chemical analysis and empirical formula of the ‘as prepared’ cordierite precursor powder

<table>
<thead>
<tr>
<th>Constituents (%)</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>10.46</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.95</td>
</tr>
<tr>
<td>SiO₂</td>
<td>41.1</td>
</tr>
<tr>
<td>H₂O</td>
<td>20.05</td>
</tr>
</tbody>
</table>

The physical properties of the prepared precursor are given in Table 2.

Table 2: Physical properties of the as prepared cordierite precursor powder

<table>
<thead>
<tr>
<th>Property</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loose Bulk density (gm/cc)</td>
<td>0.346</td>
</tr>
<tr>
<td>Surface Area(m²/g)</td>
<td>15.28</td>
</tr>
<tr>
<td>DTA peak Temp.(°C)</td>
<td>130, 405 (Endo), 960 (Exo)</td>
</tr>
</tbody>
</table>

(Table 3) revealed the dispersion of micro-fine kaolinite and silica particles in gel matrix.

Table 3: Particle size analysis of the as prepared cordierite precursor powder

<table>
<thead>
<tr>
<th>Particle size (µm)</th>
<th>% Finer than</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>25.21</td>
</tr>
<tr>
<td>10</td>
<td>39.25</td>
</tr>
<tr>
<td>20</td>
<td>53.09</td>
</tr>
<tr>
<td>30</td>
<td>62.94</td>
</tr>
<tr>
<td>50</td>
<td>77.05</td>
</tr>
<tr>
<td>80</td>
<td>87.64</td>
</tr>
<tr>
<td>100</td>
<td>91.34</td>
</tr>
</tbody>
</table>

The FTIR spectrum of ‘as prepared’ cordierite precursor has been represented in Fig 1. The diagram indicated that individual identity of the ingredient was maintained In the prepared precursor, the content of MgO was as high as 10.46%. Here the appearance of an additional OH stretching peak at 3692 cm⁻¹ corresponds to the presence of loosely bound water. It indicates that surface charge developed was significant in the precursor. The percent absorbance of OH stretching vibrations corresponding to the vibration of the bound OH groups in the precursor became appreciable because of higher surface charge which made the OH bonds relatively strong. The bending vibration of OH groups appeared at 1640 cm⁻¹. Si-O stretching vibration occurred at 1078 cm⁻¹. The appearance of the Al-O stretching vibration was at 803.6 cm⁻¹ while that of Mg-O bond at 464.0 cm⁻¹ [19]. The precursor powder was a mixed phase material and its hydrated nature was reflected from the thermal analysis.

The process of dehydration determines the nature of dehydrated material which undergoes further solid state reactions at elevated temperature. DTA curve [Fig.2] revealed that the initial endothermic peak at 130°C was due to removal of loosely bound gel water followed by dehydroxylation of the hydroxide of Mg²⁺ at 405°C. The exothermic at 960°C might be due to formation of Al-Si spinel from the dehydroxylated clay prior to mullitization. The synthetic Mg(OH)₂ hydrogel forms a thin coating on porous de-hydroxylated clay and silica particles.

XRD pattern of the cordierite precursor powder dried at 110°C and preheated at 500°C and 800°C respectively are presented in Fig.3.
The cordierite precursor powder obtained by semicolloidal sol-gel route exhibited a number of small characteristic peaks of disordered boehmite (ν Al-OH) and bayerite (α Al(OH)₃) phases. XRD pattern of the precursor powder calcined at 500°C revealed that cryptocrystalline precursor transformed into X-ray amorphous materials during the heat treatment. However the amorphous material crystallized to µ-cordierite at 800°C as evidenced from the existence of its sharp characteristics peak. SEM micrographs (fig. not included) of precursor powder heat treated at 800°C demonstrated that the precursor particles were more or less agglomerated, platy shaped with size distribution from 0.5 to 3μm.
Fig. 3: Powder XRD pattern of a) as prepared cordierite precursor powder b) cordierite precursor powder preheated at 500°C and c) cordierite precursor powder preheated at 800°C

Fig. 4: DTGA thermogram of ‘as prepared’ cordierite precursor powder at a different heating rate

From left to right at heating rates of 5, 7.5, 10, 12.5 and 15 K.min\(^{-1}\) respectively

Fig. 4: DTGA thermogram of ‘as prepared’ cordierite precursor powder at a different heating rate
Mass loss due to removal of water molecules from the biphasic cordierite precursor by thermal activation with the increase of temperature can be defined as dehydration. The differential mass loss with increase of temperature at a given rate was collected from the DTGA data. In this study, the kinetics of thermal decomposition of cordierite precursor for the under non-isothermal condition are analysed from the DTGA data of the sample at five different heating rates of 5, 7.5, 10, 12.5 and 15 K min\(^{-1}\) (Fig.4). With increasing the heating rate, the peak maxima for the dehydroxylation process was gradually shifted towards higher temperature in the DTGA curves of the cordierite precursor. The ratio of the instant mass loss to the total mass upon heat treatment to 1000°C is represented by \(\alpha\).

According to the non-isothermal isoconversional FWO method and modified Coats-Redfern method, the basic data of \(\alpha\) vs temperature was collected from DTGA curves and given in Table 4. From the Eq.4 and 5, the plots of \(\log \beta\) and \(\ln \beta T^2\) vs 1000/T at different fractional conversions (\(\alpha\)) were graphically shown in Fig. 5 and 6 respectively.

Furthermore, employing Kissinger method, a plot of \(\ln \beta /T_{\text{max}}^2\) vs \(1/T_{\text{max}}\) was drawn by a linear regression of least square method and shown in Fig. 7.

Table 4: Correlative data used for drawing plot \(\log \beta\) vs. 1000/T and \(\ln \beta T^2\) vs. 1000/T

<table>
<thead>
<tr>
<th>(\alpha)</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta/\text{K min}^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (T/K)</td>
<td>580</td>
<td>590</td>
<td>597</td>
<td>602</td>
<td>607</td>
<td>613</td>
<td>622</td>
</tr>
<tr>
<td>7.5 (T/K)</td>
<td>596</td>
<td>605</td>
<td>611</td>
<td>616</td>
<td>621</td>
<td>626</td>
<td>635</td>
</tr>
<tr>
<td>10 (T/K)</td>
<td>610</td>
<td>619</td>
<td>625</td>
<td>630</td>
<td>635</td>
<td>640</td>
<td>648</td>
</tr>
<tr>
<td>12.5 (T/K)</td>
<td>622</td>
<td>631</td>
<td>638</td>
<td>643</td>
<td>649</td>
<td>654</td>
<td>662</td>
</tr>
<tr>
<td>15 (T/K)</td>
<td>634</td>
<td>643</td>
<td>648</td>
<td>654</td>
<td>657</td>
<td>663</td>
<td>670</td>
</tr>
</tbody>
</table>

The activation energies calculated from the slope of the straight lines and correlation coefficients (\(r^2\)) from the intercept of straight lines for all \(\alpha\) values from 0.20-0.80 using FWO method and modified Coat-Redfern method were presented in Table 5 and 6. Similarly activation energy calculated by Kissinger equation was presented in Table 7.
Fig. 6: Modified Coats and Redfern analysis for thermal decomposition of the cordierite precursor

Fig. 7: Kissinger plot for the thermal decomposition of cordierite precursor
Table 5: Activation energies (Ea) and Correlation coefficient ($r^2$) calculated by FWO method

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Decomposition step</th>
<th>$E_a$/KJ mol$^{-1}$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td></td>
<td>66.79</td>
<td>0.9956</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td>68.17</td>
<td>0.9945</td>
</tr>
<tr>
<td>0.4</td>
<td></td>
<td>69.32</td>
<td>0.9967</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>71.17</td>
<td>0.9943</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>70.45</td>
<td>0.9936</td>
</tr>
<tr>
<td>0.7</td>
<td></td>
<td>73.12</td>
<td>0.9950</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>74.95</td>
<td>0.9938</td>
</tr>
<tr>
<td>Average Value</td>
<td></td>
<td>70.57±4.07</td>
<td>0.9948</td>
</tr>
</tbody>
</table>

Table 6: Activation energies (Ea) and Correlation coefficient ($r^2$) calculated by modified Coats and Redfern method

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Decomposition step</th>
<th>$E_a$/KJ mol$^{-1}$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td></td>
<td>59.63</td>
<td>0.9943</td>
</tr>
<tr>
<td>0.3</td>
<td></td>
<td>60.89</td>
<td>0.9921</td>
</tr>
<tr>
<td>0.4</td>
<td></td>
<td>61.96</td>
<td>0.9947</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>63.79</td>
<td>0.9914</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>63.93</td>
<td>0.9876</td>
</tr>
<tr>
<td>0.7</td>
<td></td>
<td>65.65</td>
<td>0.9922</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>67.40</td>
<td>0.9904</td>
</tr>
<tr>
<td>Average Value</td>
<td></td>
<td>63.32±3.86</td>
<td>0.9918</td>
</tr>
</tbody>
</table>

Table 7: Activation energies (Ea) and pre exponential factor ($A$) calculated by Kissinger method

<table>
<thead>
<tr>
<th>Decomposition step</th>
<th>Activation energy, KJ mol$^{-1}$</th>
<th>$\ln A$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62.04</td>
<td>1.13</td>
<td>0.9932</td>
</tr>
</tbody>
</table>
Activation energy (Ea) and correlation coefficient (r²) for the thermal decomposition of cordierite precursor was calculated by using the CurveExpert software. The average activation energy derived was in close proximity for all the methods. The correlation coefficient value also found to tend towards unity.

Based on the available literature, it has been accepted that E_a values are independent of α, when relative error of the slope of the straight lines using FWO and modified Coats-Redfern equation is less than 10%. Nevertheless, in such case, the decomposition may be regarded as a simple reaction [20-22] when the relative error is more than 10%, then the reaction may be interpreted in terms of multi-step reaction mechanism [23, 24]. In this study, variation in the activation energy with respect to α values exceeds 10% and hence, the dehydration of the cordierite precursor proceeds via a multi-step reaction mechanism. The activation energy obtained by FWO method for the dehydroxylation step of the thermal decomposition were 70.57±4.07 kJ.mole⁻¹ with fractional conversion from 0.2 to 0.8. The consistent value of activation energy using the modified Coats-Redfern method and Kissinger method as 63.32±3.86 kJ.mole⁻¹ and 62.04 kJ.mole⁻¹ respectively verifies the credibility of these methods.

The different models yields slight variation in kinetic results using same DTGA data at different heating rates which may be attributed to certain approximation associated with particular model. All the three models are found to evolve satisfactory and comparable values of the kinetic parameters in case of thermal decomposition of synthesized cordierite precursor. This is basically a heterogeneous solid state reaction and mainly governed by the rate of diffusion of evolved water molecules through the heterogeneous structure of multi component precursor.

4. CONCLUSION

1) The thermal treatment of synthesized cordierite precursor from room temperature to 1000°C is accompanied by initial loss of physically adsorbed water; interlayer water at around 130°C followed by the removal of hydroxyl groups from their complex structure at around 405°C.

2) The activation energy estimated for thermal decomposition of cordierite precursor by three different methods under non-isothermal condition was found very close and consistent with one another.

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