4.1. Introduction

Today, in 21st century, world has been facing severe environmental problems, that arises principally due to the evolution of exhaust gases. Chief constituents of exhaust gases are CO, NOx and hydrocarbons. The remedial aspects for the persistence of the environment in hefty condition have been the challenging areas of many researchers. Throughout the recorded history of the oxides of rare earth elements, cerium has been the most important class of compounds, which stand as an indispensable component in catalyst promoters or supporters in the automobile mufflers and for the toxic emission control (e.g., CO, hydrocarbon oxidation and NOx reduction)\(^1\). Nowadays, many researchers have been going on for the better catalytic performance of ceria. Ceria achieved special optical, electrical and magnetic properties that were given by its particular electronic configuration. Vaishak Nair et al\(^2\) reported that CeO\(_2\) can be used as catalyst in the production of guaiacol and its derivatives by fast pyrolysis of alkali lignin. CeO\(_2\) promote the formation of hydroxyl radicals via thermal activation, which then take part in free radical reaction to form guaiacol and its derivatives. Recently ceria materials with nano sized\(^3\), textured\(^4\) and one dimensional\(^5\)–\(^8\) (involving nanotubes, nanowires and nanorods) structures have been prepared by different synthetic routes. Feng Zhang et al\(^9\) prepared narrowly distributed single crystalline CeO\(_2\) nano particles using cerium nitrate and hexamethylenetetramine at room temperature. They established that larger the lattice parameter in nano crystalline ceria makes it to become a more efficient electrolyte material for fuel cell. Tok et al\(^10\)
synthesized nano crystalline CeO₂ from two precursors cerium acetate and cerium hydroxide via hydrothermal route in acidic and basic pH condition. They assayed the effect of duration of reaction on the properties of the resultant specimen CeO₂. Using the amino acid as crystal growth modifiers, mesoporous ceria with hierarchical nano architectures have been synthesized. It has been observed that CeO₂ doped with Ca²⁺ have maximum availability of oxygen because it creates oxygen vacancies with an average spacing close to that of O²⁻. Availability of oxygen vacancies tends to increase the oxygen storage capacity of the oxide. It has been observed that the oxygen storage capacity of CeO₂ can be enhanced up to about 40% with doping of Ca²⁺. Doping of ceria with Pb²⁺ leads to the increment of redox activity of ceria. Miyazako et al prepared CeO₂ nano particle by rapid thermal decomposition by microwave heating of cerium oxalate and concluded that shape of resultant specimen depends on the precursor material shape. Masui et al disclosed excellent redox activity and enhanced thermal stability of CeO₂-ZrO₂ solid solution, prepared from cerium-zirconyl oxalates by means of thermal decomposition in an argon flow at 1273K followed by oxidation at 673-873K in air. Kenji Higashi et al established significant changes in thermal decomposition temperatures of solid solution oxalates of Ce(III) with rare earth elements Yb, Y, La, Nd, Sm and Gd and accounted the contribution of ionic radius of elements in thermal behavior of cerium oxalates. Depending on the ionic radius of doped oxides, the lattice parameter of the oxide also changes. Because of the higher melting point of ceria (2400°C), it has high temperature application such as total oxidation reaction (e.g., natural gas combustion).
There are wide ranges of synthetic methods for the preparation of CeO$_2$\textsuperscript{17-20}. Thermally induced oxidative decomposition of Ce(III) oxalate is an important source for obtaining CeO$_2$ particle with different morphologies. The morphological characteristics of prepared CeO$_2$ vary depending on the particle size and morphology of cerium oxalate. Further, the oxalate powders have better chemical and morphological control over the final product. Particle size, morphology and surface area are the important characteristics responsible for the quality of the functionalities. Oxide solid solution or composite oxide can be prepared from the oxalate precursor at its decomposition temperature under well controlled conditions. Thermal decomposition of cerium oxalate at 600°C for 3h yields porous spherically shaped ceria powders having size of the particle smaller than 100nm\textsuperscript{15}. Decomposition of hydrated cerium oxalate occurs mainly in two stages; the dehydration (of 10 molecules of water around 403K) followed by the decomposition (around 633K) to ceria\textsuperscript{21} as:

\begin{equation}
\text{Ce}_2(\text{C}_2\text{O}_4)_3.10\text{H}_2\text{O} \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3+10\text{H}_2\text{O} \tag{1}
\end{equation}

\begin{equation}
\text{Ce}_2(\text{C}_2\text{O}_4)_3 \rightarrow 2\text{CeO}_2+2\text{CO}_2+4\text{CO} \tag{2}
\end{equation}

The thermal decomposition processes of many of the inorganic solids are significantly controlled by physico-geometrical reaction mechanism\textsuperscript{22–26}. In a thermally induced reaction, surface product layer is formed in the early stages of the reaction. The geometrical constraints occurring between the surface product layer and the inward advancement of the reaction interface generated at the boundary between surface product layer and internal reactant\textsuperscript{27–31}. As the
reaction progresses, the action of surface product layer came in to act. The inhabitation effect of surface product layer on the diffusional removal of gaseous products generated at the internal reaction interface causes the formation of self-generated reaction conditions at the reaction interface. Formation of pores on the surface of solid product is closely related to the formation of a surface product layer at the early stage of the reaction and the subsequent diffusional removal of gaseous products produced by the internal reaction$^{25}$. This occurrence of solid-gas reactions is responsible for the morphological characteristics of the product, metal or metal oxides$^{25}$. Majority of the solid state reactions pass off via crack formation on the surface product layer and the splitting of the reacting particle along a specific crystallographic direction$^{32–34}$.

The elucidation of the mechanism and kinetics of thermal decomposition would contribute to the evaluation of thermal stability, life time, safe storage and fundamental information for technological applications. Font et al$^{35}$ discussed the correlation model with optimized kinetic parameters with respect to the pyrolysis of olive oil. They correlated dynamic and isothermal runs with same set of parameters and satisfactorily reproduced the experimental results. Researchers established the practical usefulness of the kinetic deconvolution for partially overlapping multistep thermal decomposition process of solids$^{25,26}$. Comparisons were made with experimental deconvolution by thermo analytical techniques and mathematical deconvolution using statistical fitting function. Performance of kinetic deconvolution was evaluated based on
accumulative kinetic equation for the independent process which overlaps partially in views of peak deconvolution and kinetic evaluation\textsuperscript{26}.

In the present work, kinetic and mechanistic features of the synthesis of micro structural rods of CeO\textsubscript{2} \textit{via} the oxidative thermal decomposition of cerium oxalate in air and the effect of dry mixing of 10 mass (%) calcium oxalate with cerium oxalate upon the reaction pathway and mechanism were investigated by thermo analytical techniques under linear non-isothermal condition. The physico-geometrical kinetic behavior of the reaction was illustrated through detailed kinetic analyses using the kinetic deconvolution method. The reaction was traced by thermo analytical measurements and interpreted the kinetic results on the basis of kinetic analysis of thermo analytical curves and complimented the rendition by morphological and structural observations.

4.2. Experimental

4.2.1. Materials

All the reagents were of analytical grade and used without any further purification\textsuperscript{36}. The chemicals used for the study are cerium oxalate decahydrate (99.9\%, Indian Rare Earth Products Ltd, Cochin), CaCO\textsubscript{3} (Sigma-Aldrich), 1M HCl, NH\textsubscript{4}OH and (NH\textsubscript{4})\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (Merck, India).
4.2.2. Preparation of calcium oxalate dihydrate

Calcium chloride is prepared from CaCO₃ and 1M HCl. The oxalate is prepared by using ammonium oxalate as precipitating agent. The precipitate is collected, washed with ethanol and water and dried in an air oven at 60°C.

4.2.3. Preparation of mechanical mixtures of oxalates of cerium and calcium

The particle size of the oxalates of cerium and calcium were fixed in the range 95-105µm. Composition of oxalates of cerium and calcium (CC₂) was prepared by thorough mechanical mixing of cerium oxalate (90 mass (%)) and calcium oxalate (10 mass (%)) in an agate mortar. Cerium oxalate (100 mass (%)) (CC₁) was also sieved through the mesh and fixed the size in the range 95-105µm.

4.2.4. Preparation of pelletized samples

The pure (CC₁) and mixed samples (CC₂) were well-ground and the powdered samples were pressed using the hydraulic pellet press (KP, SR. No. 1718) under a pressure of 50Kg/cm². Thermally heated samples of both CC₁ (623 and 873K) and CC₂ (623 and 953K) were also pelletized using hydraulic press under the same pressure.

4.2.5. Characterization of the sample

Characterization of the samples was done by FT-IR and XRD. The appearance and morphology of the samples were observed using an optical and scanning electron microscopy instrument.
4.2.6. Measurement of thermal behavior

TG measurements were made at four different heating rates, viz. 5, 10, 15 and 20 Kmin\(^{-1}\). Duplicate runs were made under the similar conditions and found that the data overlap with each other, indicating satisfactory reproducibility. The samples heated at 873K (for CC\(_1\)) and 953K (for CC\(_2\)) in flowing atmosphere of air at a heating rate of \(\beta = 5\) K min\(^{-1}\) and kept at a constant temperature for 20 min and measured XRD pattern of each sample immediately after leaving from the furnace. The optical microscopic views of thin pellets of the samples heated at different temperatures were also observed. The optical band gap \((E_g)\) of the decomposed product of each sample was calculated from UV-Visible reflectance which was measured using UV-Vis diffuse reflectance spectrum.

4.3. Results and discussions

4.3.1. Sample characterization

Fig. 1a shows the typical microscopic image of thin pellets of cerium oxalate, the surface of cerium oxalate crystals consists of rod-like crystals (Fig. 1b) having thickness in the range 1.71-2.01\(\mu\)m. Fig. 1c shows the microscopic image of thin pellets of cerium-calcium oxalate crystals and the SEM image (Fig. 1d) shows slight change in the rod-like crystals of cerium oxalate due to the addition of calcium oxalate. Calcium oxalate exist as separate crystals, covering the surface of cerium oxalate rods, which causes the breakdown of the rods due to the strain experienced on the surface of the rods.
Fig. 1 Microscopic images of cerium oxalate and mixture of cerium and calcium oxalate; Optical microscopic image of cerium oxalate thin pellet (a), SEM image of anhydrous cerium oxalate heated at 623K (b), optical image of cerium-calcium oxalate thin pellet (c) and SEM image of anhydrous cerium-calcium oxalate heated at 623K (d).

FT-IR spectra and XRD patterns of the samples are shown in Fig. 2. Fig. 2a represents characteristic XRD pattern of cerium oxalate decahydrate with significant reflections at 2θ values of 20.94, 25.29, 26.12, 32.14, 32.75, 34.24, 39.58, 42.17, 44.24 and 46.18°. The reflections from the sample indicate that cerium oxalate crystallizes in the monoclinic system (JCPDS. No. 20-0268). The characteristic XRD pattern of calcium oxalate dihydrate, shown in Fig. 2b, exhibit major reflections at 2θ values of 24.23, 32.51, 35.82 and 43.39° (JCPDS. ASTM File No. 15-762). The powder X-ray diffraction patterns of the samples reveal good crystalline nature of calcium oxalate than cerium
oxalate. In the FT-IR spectra, the broad band observed at 3080-3433 cm\(^{-1}\) corresponds to water molecules in hydrated samples which are removed only at higher temperature\(^{37}\). The very strong peak observed at 1633.9 (Fig. 2c) and 1622.45 cm\(^{-1}\) (Fig. 2d) is attributed to combined effect of asymmetric stretching and bending of water molecules\(^{38}\). The strong peak observed at 1318.39 (Fig. 2c) and 1317.01 cm\(^{-1}\) (Fig. 2d) correspond to the asymmetric stretching of CO\(_2\) molecule associated with oxalate ligand group\(^{38,39}\). The band observed at 523.8 (Fig. 2c) and 514.4 cm\(^{-1}\) (Fig. 2d) corresponds to the M-O stretching frequency\(^{37,40}\).

![Fig. 2](image)

**Fig. 2** The XRD patterns of cerium oxalate decahydrate (a) and calcium oxalate dihydrate (b) and the FT-IR spectra of cerium oxalate decahydrate (c) and calcium oxalate dihydrate (d).

### 4.3.2. Characterization of thermal decomposition behavior

Fig. 3 shows the results of TG measurements with two samples, CC\(_1\) and CC\(_2\), at different \(\beta\) values. The oxidative thermal decomposition reaction of the solids composed of multiple constituent chemical processes that occurs successively and each constituent reaction provide differently to the overall thermal effect (to be either
exothermic or endothermic). Therefore, the TG curves of the sample CC₁ shows two distinguishable mass loss processes, one at temperature below 575 K and one at temperature above 575 K. A mass loss accompanying the dehydration of water molecules is observed over the temperature region of 325-445 K, prior to the thermal decomposition of cerium oxalate in the higher temperature region of 600-760 K. The mass loss value for the overall thermal decomposition process for the sample CC₁ is 52.12%, which is in good agreement with the ideal reaction pathway for the formation of ceria from cerium oxalate decahydrate (52.48%). In Fig. 3b there exists a third mass loss step with small amplitude at 873K due to the decomposition of calcium carbonate. Hence for the sample CC₂, the overall mass loss value was increased to 55.45% due to the contribution from the thermal decomposition of calcium oxalate along with cerium oxalate. The TG curves of CC₂ sample is systematically shifted to higher temperature with increase in the value of β, whereas the TG curves of the sample S₀ show anomaly with β = 10 and 20 K min⁻¹.

The processes of multistep mass loss behavior are controlled by physico-geometrical constraints which may occur due to the changes in reaction conditions as the reaction advances. Fig. 3b shows partially overlapping multistep process which would reflect in complex reaction pathway. Koga et al. stated that complex reaction proceeds in a combination of multistep behavior controlled by physico-geometrical features of solid state reactions and successive chemical reaction schemes.
The TG curves for the thermal decomposition of samples (m₀ = 10mg) in flowing air (100mLmin⁻¹) at different β values; CC₁ (a) and CC₂ (b).

Fig. 4 shows DTG curves for the thermal decomposition process of the two samples, CC₁ and CC₂. The DTG curves indicate multistep process for the thermal decomposition of cerium oxalate, CC₁ (Figs. 4a, b and c) and partially overlapped multistep reaction for cerium-calcium mixed oxalate, CC₂ (Figs. 4d, e and f). The reaction process of the sample CC₁, at both lower and higher temperature, are arrested at the very beginning when the sample is heated at a β value of 10 and 20 K min⁻¹, whereas the ratio of mass loss was found to be higher at these heating rates. Moreover at these heating rates, the curves exhibited sigmoidal shape for the lower temperature reaction.
Fig. 4 The DTG curves of CC$_1$ and CC$_2$: overall thermal decomposition of CC$_1$ (a), first (b) and second (c) stage of CC$_1$, overall thermal decomposition of CC$_2$ (d), first (e) and second (f) stages of CC$_2$.

It has been reported that both the reaction time and temperature have significant influence on the crystallographic orientation of the ceria particles formed$^{16,41}$. Hence the $\beta$ value of 10 and 20Kmin$^{-1}$ have marked influence on thermal decomposition of cerium oxalate, which make different shape to the DTG curve compared with other heating rates. The observed changes in the shape of mass loss curve with $\beta$ certainly indicate a change in the mechanistic features of the reaction. The addition of calcium oxalate to cerium oxalate cause a shift in the temperature range of the reaction process, both at lower and higher temperature, to the higher values, $i.e.$, to 340-485 and 645-790 K respectively.

For both higher and lower temperature processes of the sample CC$_2$, it has been observed a shift in the DTG curves to the higher
values with increasing the value of $\beta$. However, with decreasing $\beta$ value, there occurs increase in mass loss ratio for both high and low temperature process for the sample CC$_2$. In the DTG curves of the sample CC$_2$ (Figs. 4d, e and f) the shoulder peaks observed is associated with the dehydration and oxidative process. This can be ascribed due to the change in the self-generated reaction condition, which is generated at the reaction interface as the reaction progresses. The sample CC$_2$, a mixture of cerium oxalate and calcium oxalate, upon thermal treatment under controlled condition, there occurs thermal decomposition of calcium oxalate along with cerium oxalate leading to partial overlapping of the reaction which brings changes in the self-generated reaction condition produced by cerium oxalate$^{23}$ and therefore, the shape of the DTG curves is altered.

![DTG Curve](image)

**Fig. 5** The powder XRD patterns of the thermally treated samples of CC$_1$ and CC$_2$; sample CC$_1$ at 873 (a) and CC$_2$ at 953 K (b).

The changes of XRD patterns of these samples which are calcined at 873 (for CC$_1$) and 953K (for CC$_2$) were represented in Figs.
5a and b respectively. In Fig. 5b, there exists an additional peak at 2θ value 29.15° and this confirms that the sample CC₂ at 953K forms mixed oxides of cerium and calcium. Masui et al.¹⁴ reported that oxidative process induces a lattice contraction and hence all peaks in Figs. 5a and b are shifted to higher angle compared to those in Fig. 2a. The redox reactions in pure and mixed oxalates of cerium are associated with Ce³⁺/Ce⁴⁺ couple¹⁴ and the contraction of the lattice is therefore due to the oxidation from Ce³⁺ (0.633nm) to Ce⁴⁺ (0.55 nm).

The XRD pattern of CeO₂ confirms that ceria crystallizes in cubic fluorite structure. In cubic structure, the mobility of oxygen and desorption were strongly favored than tetragonal structure¹⁴ and hence lower energy is required for the thermal decomposition. Since Ca²⁺ does not incorporated into the lattice of ceria frame work (Fig. 5b), the lattice strain was absent to the fluorite structure of ceria. This confirms that ceria retains its cubic structure in mixed oxides. The average crystallite size of CeO₂ calculated using the Scherrer equation from XRD pattern is 9.026nm. The cubic fluorite structure of ceria gives isolated peaks which confirm the poly crystalline nature of CeO₂ nanoparticle³⁶.

The FT-IR spectra of the samples treated at 873K (for CC₁) (Fig. 6a) and 953K (for CC₂) (Fig. 6b) were used for the characterization of thermal behavior. The band corresponds to 3028-30680 cm⁻¹ is due to -O-H stretching of the adsorbed water molecules on the surface of the oxide. This hydroxyl group is eliminated only at higher temperature⁴². The absorption band in the region of 862.8cm⁻¹ in Fig. 6a is associated with δ (Ce-O) bond⁴⁰ which undergoes blue
shift to 876.98 cm$^{-1}$ in the sample CC$_2$ (Fig. 6b). This occurs due to the strengthening of $\delta$ (Ce-O) bond due to the interaction of Ca$^{2+}$ with oxygen atom of carbonyl group during the early stages of the reaction. But the band observed at 424.73 cm$^{-1}$ represents Ce-O stretching frequency of the product formed, CeO$_2$ (Fig. 6a)$^{36,40,43}$ which undergo red shift to 413.19 cm$^{-1}$ (Fig. 6b). This can be attributed to the interaction of Ca$^{2+}$ with the unpaired electrons situated in the oxygen atom of the -O-Ce-O- bond during thermal decomposition process. The sharp band observed at 714.9 cm$^{-1}$ corresponds to the Ca-O stretching frequency$^{37}$.

For the determination of optical band gap, the samples were heated at higher temperature and for the successive interpretation of thermal behavior of the mixed cerium oxalate; the UV-Vis diffuse reflectance spectrum was measured. Fig. 7a shows the UV-Vis diffuse reflectance spectra of the samples CC$_1$ and CC$_2$ heated at 873 and 953K respectively and it shows obvious shift towards lower wavelength, *i.e.*, blue shift, due to the presence of Ca$^{2+}$. The presence of Ca$^{2+}$ cause a decrease in the particle size of CeO$_2$ rods$^{44,45}$ *via* the breaking down of rods due to the strain experienced on the surface of the rods.
Fig. 6 The FT-IR spectra of CC$_1$ at 873 (a) and CC$_2$ at 953K (b).

An estimate of the optical band gap, $E_g$, can be determined by the Tauc-equation $(\alpha h\nu)^n = B(h\nu-E_g)$ where $h\nu$ is the photon energy, $\alpha$ is the absorption coefficient, $B$ is a constant relative to the material and $n$ is either 2 for direct transition, or 1/2 for an indirect transition. The $(\alpha h\nu)^2$ versus $h\nu$ curves (Tauc-plots) is shown in Figs. 7b and 7c, which reveals that the band gap increases from 1.546 to 2.05eV supporting the blue shift. The reported value of $E_g$ corresponding to bulk CeO$_2$ is 1.82 eV$^{46}$. The increase in the value of $E_g$ of a material reflects the decrease of conducting properties. It has been reported that electron donors accelerate thermal mass-loss process and electron acceptors retard the thermal process$^{47,48}$. The findings in the UV-Vis diffuse reflectance spectra and Tauc-plots of thermally treated samples at higher temperatures indicate possible contribution of Ca$^{2+}$ to impede thermal decomposition process of cerium oxalate. Therefore, the presence of CaO along with ceria causes a decrease in the conducting properties of CeO$_2$. Hence it can be stated that the presence of Ca$^{2+}$ cause to retard the thermal decomposition of cerium oxalate, whereas increases its thermal stability.
Fig. 7 The UV-Vis diffuse reflectance spectra of the samples CC₁ and CC₂ (a), Tauc-plot of the sample CC₁ heated at 873K (b) and Tauc-plot of the sample CC₂ heated at 953K(c).

4.3.3. Morphological characterization

The SEM and optical microscopic observation of each sample at different stages of decomposition reaction were performed in order to correlate the complex reaction pathways with the physico-geometrical characteristics of the reaction. Microstructure of precursor and resultant specimen are exhibited in Figs. 8b & d. All resultant specimens acquired rod shape and formed secondary particles along with aggregated particles. Average grain size of primary and secondary particles of aggregated CeO₂ is 662.42nm and 305.94nm respectively. Hence SEM image of ceria depicted that polycrystalline
CeO$_2$ nanoparticles are aggregated to form micro structural rods of ceria$^{36}$. Fig. 8a shows some deformations present in the surface of the sample CC$_1$ which can be related to the loss of water molecules. Fig. 8b shows the surface textures of the sample CC$_1$, which is dehydrated during the first stage of decomposition reaction (Fig. 4b). It shows significant boundaries between the rods, which are accompanied by the holes. This is possibly served as the diffusion channels for the removal of H$_2$O molecules and at this stage the cerium oxalate possess rods of smooth surfaces. Upon thermal decomposition, this smooth surface product layer of cerium oxalate gradually impedes the diffusional removal of CO$_2$ which is generated by the internal reaction. Therefore, this inhabitation of CO$_2$ release causes for the change in the self-generated reaction condition. At the end of reaction, CO$_2$ is diffused through the channels created by the internal pressure in the surface product layer. Fig. 8c shows the optical image of solid film of CeO$_2$. The surface product layer of CeO$_2$ is then divided into rods (Fig. 8d). These CeO$_2$ particles are sintered gradually and which form smooth surfaces.

Figs. 9a and b shows the optical images of thin pellet of the sample CC$_2$ heated at 590 and 683K respectively. These images show change in the color indicating the reaction progress. Fig. 9c shows SEM image of the sample CC$_2$ heated at 573K, at this temperature, the loss of water molecules are completed. This image reveals that cerium oxalate rods are covered with calcium oxalate. Hence the smoothness of rods of cerium oxalate is lost. Since the occurrence of strain on the
rods, some of the rods are broken into small pieces. Further increase in the temperature makes the system more complex and creates the holes and cracks for the diffusive removal of gaseous products. Fig. 9d discloses that the sample CC$_2$ treated at 723K consists of heterogeneous reaction products, which indicate complexity of the reaction at this temperature. Both optical and SEM images show more complex pathway for the decomposition reaction of cerium oxalate in the presence of calcium oxalate.

**Fig. 8** The optical microscopic image of thin pellet of the sample CC$_1$ at 603K (a), the SEM image of the sample CC$_1$ at 573K (b), the optical image of thin pellet of CeO$_2$ (c) and the SEM image of CeO$_2$ (d).
Fig. 9e shows the SEM image of mixed oxides of ceria and calcium with disturbed shapes of rods. The optical image of thin pellet of mixed oxides is shown in Fig. 9f, exhibiting composite oxides.

![SEM and Optical Images](image)

**Fig. 9** The optical images of CC$_2$ at 590 (a) and 683K (b), SEM image of CC$_2$ at 573K (c), optical image of CC$_2$ at 723K (d), SEM image of CC$_2$ at 953K (e) and optical image of CC$_2$ at 953K (f).

### 4.3.4. Kinetic behaviour

Prior to conducting a detailed kinetic characterization of each mass loss step of the reaction, a formal kinetic analysis was performed
by assuming a single step reaction for the overall reaction using the fundamental kinetic equation

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)
\]  

(3)

where \(t\) is time, \(T\) the temperature, \(R\) the ideal gas constant, \(A\) the apparent Arrhenius pre-exponential factor, \(E_a\) the apparent activation energy and \(f(\alpha)\) the apparent kinetic model function used to describe the physico-geometrical reaction mechanism as a function of the fractional reaction, \(\alpha\). Based on Eq. 3, plots of \(\ln(\alpha/dt)\) vs \(T^{-1}\) at different \(\alpha\) for the series of kinetic data recorded under linear non-isothermal condition, known as the Friedman plot\(^{50-52}\), were examined for determining the values of \(E_a\) for different \(\alpha\) and for evaluating variations in \(E_a\) with respect to \(\alpha\).

**Fig. 10** The \(\alpha\)-T curves for the sample CC\(_1\) (a) and CC\(_2\) (b) at 5, 10, 15 & 20Kmin\(^{-1}\).
Fig. 11 The Friedman plots at different $\alpha$ values (from 0.1 to 0.9) for the sample $CC_2$ (a) and the values of $Ea$ at different $\alpha$ for the sample $CC_1$ (b) and $CC_2$ (c).

Fig. 10 shows $\alpha$-$T$ curves for the pure cerium oxalate decahydrate (Fig. 10a) and Ca(II) cerium oxalate decahydrate (Fig. 10b). These curve shows multistage thermal decomposition of $CC_1$ and $CC_2$. For $CC_1$ there was not observed a general trend with increasing heating rate, but for sample $CC_2$, there was observed a general trend; with increasing heating rate ($\beta$), the completion of each stage was occurred more fastly than at lower values of $\beta$. Fig. 11 shows the
results of the isoconversional kinetic analysis for thermal decomposition of the samples CC\textsubscript{1} and CC\textsubscript{2} using a series of kinetic data under linear non-isothermal condition. The slopes of the plots show significant variation with \( \alpha \) (Fig. 11a). This appears in the observed \( \alpha \)-dependent variation of \( Ea \) (Figs. 11b and c). The variation of \( Ea \) with \( \alpha \) (Fig. 11b) is segmented majorly into two \( \alpha \)– regions \( i.e., \), \( 0.04 \leq \alpha \leq 0.44 \) and \( 0.45 \leq \alpha \leq 0.99 \) recalling the low temperature dehydration of incorporated water molecules (\(<575 \text{K}\)) and high temperature oxidative thermal decomposition (\(>575 \text{K}\)) reactions of sample CC\textsubscript{1}. Similar division of \( \alpha \)–regions is also exhibited for sample CC\textsubscript{2} (Fig. 11c). For both samples, \( Ea \) values continuously varied with \( \alpha \). The sample CC\textsubscript{1} shows a minimum value of approximately 40 kJmol\(^{-1}\) at \( \alpha = 0.23 \) and a maximum value of approximately 169.5 kJmol\(^{-1}\) at \( \alpha = 0.84 \), whereas the sample CC\textsubscript{2} passes through a minimum value of approximately 54.6 kJmol\(^{-1}\) at \( \alpha = 0.19 \) and a maximum value of approximately 315.9 kJmol\(^{-1}\) at \( \alpha = 0.899 \).

Since the thermal dehydration of incorporated water and the oxidative decomposition are the independent kinetic processes, the following cumulative kinetic equation can be applied to the overall reaction under linear non-isothermal conditions\textsuperscript{22-26, 34, 53-57}.}

\[
\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i A_i \exp \left( \frac{-E_{a,i}}{RT} \right) f_i(\alpha_i) 
\]

(4)

with \( \sum_{i=1}^{n} c_i = 1 \) and \( \sum_{i=1}^{n} c_i \alpha_i = \alpha \)
where \( n \) and \( c \) are the number of component steps and the contribution ratio of each reaction step to the overall process, respectively and the subscript \( i \) denotes each component reaction step. \( A_i \) and \( E_{a_i} \) are the Arrhenius pre-exponential factor and the apparent activation energy, respectively, of process \( i \). The kinetics of each component process of the overall reaction can be characterized by optimizing all the kinetic parameters in Eq. 4 using nonlinear least-square analysis. Empirical kinetic model functions such as Sestak-Berggren\(^{34,58}\) SB \((m,n)\) and phase-boundary-controlled model RO \((n)\)\(^{59}\) were employed for \( f_i(\alpha_i) \) in Eq. 4 in order to accommodate any possible mechanistic feature of each reaction process\(^{60-62}\).

SB\((m,n)\): 
\[
 f(\alpha) = \alpha^m (1-\alpha)^n 
\]  
(5)

RO \((n)\): 
\[
 f(\alpha) = n(1-\alpha)^{1/n} 
\]  
(6)

In the present work, the initial values of the kinetic parameters were determined through a formal kinetic analysis of the kinetic data, first subjected to mathematical deconvolution using a statistical function (Weibull). The number of component steps for both samples are obtained through kinetic deconvolution of DTG-peaks. After setting all of the initial values of kinetic parameters, a parameter optimization was carried out to minimize the squares of the residues (F) when fitting the calculated curve \((d\alpha/dt)_{cal}\) versus time to the experimental curve \((d\alpha/dt)_{exp}\) versus time.
\[
F = \sum_{j=1}^{n} \left[ \left( \frac{d\alpha}{dt} \right)_{\text{exp},j} - \left( \frac{d\alpha}{dt} \right)_{\text{cal},j} \right]^2
\]  

(7)

where \( n \) is the number of data points.

Fig. 12 shows the Friedman plots for the sample CC\(_1\), which was used for the calculation of \( Ea \) for the first stage (Fig. 12a), second stage (Fig. 12b), third stage (Fig. 12c) and fourth stage (Fig. 12d). Fig. 13 shows the same plot for finding the \( Ea \) value of respective stage first (Fig. 13a), second (Fig. 13b), third (Fig. 13c), fourth (Fig. 13d) and overlapped stages of fifth, sixth and seventh stages of the reaction. Due to the partially overlapping of each stages with other stages, the extent of conversion \( \alpha \) is also mingled with other stages.

Fig. 14 shows kinetic deconvolution of the oxidative thermal decomposition of the samples CC\(_1\) and CC\(_2\), attempted on the basis of Eq. 4 after the preliminary determination of the initial values through mathematical deconvolution and the subsequent formal kinetic analysis of each resolved reaction step. For the sample CC\(_1\), the overall mass loss process is empirically separated in to four steps (Fig. 14a) and that of sample CC\(_2\) into seven partially overlapping mass loss steps (Fig. 14b).
The first low temperature reaction observed is considered as the dehydration reaction. The sample CC₁ takes two overlapping processes for the removal of water molecule whereas the sample CC₂ goes on through three overlapping processes since the dehydration of calcium oxalate occurs along with cerium oxalate. For the higher temperature reaction, the oxidative decomposition of CC₁ to CeO₂ is composed of two partially overlapping reaction steps due to the formation of an intermediate cerium oxy carbonate Ce₂O₂CO₃. The sample CC₂ goes through more complex reaction pathways during the decomposition reaction. The average values of the optimized kinetic
parameters are listed in Table 1. The values of Ea calculated for each reaction step are in good agreement with that determined from the Friedman plot.

**Fig. 13** The Friedman plots for the sample CC2 for the first (a), second (b), third (c), fourth (d) and fifth, sixth and seventh (e) stages.
The oxidative decomposition given in Eqs. 1 and 2 can be further divided into five stages as:\(^\text{38}\):

\[
\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O} + 7\text{H}_2\text{O} \quad (8)
\]

\[
\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O} \quad (9)
\]

\[
\text{Ce}_2(\text{C}_2\text{O}_4)_3 \rightarrow \text{Ce}_2\text{O}_2\cdot\text{CO}_3 + 4\text{CO}_2 + \text{CO} \quad (10)
\]

\[
\text{Ce}_2\text{O}_2\cdot\text{CO}_3 \rightarrow 2\text{CeO}_2 + \text{CO} \quad (11)
\]

\[
\text{CO} + (1/2) \text{O}_2 \rightarrow \text{CO}_2 \quad (12)
\]

Even though there exists complex reaction pathways for the decomposition of \(\text{CC}_2\), the rate of decomposition reaction occurs with higher rate similar to the rate of mass loss shown in the DTG curves (Fig. 4). In Fig. 14b, the sixth and seventh step of mass loss corresponds to the decomposition reaction of calcium oxalate to \(\text{CaO}\) via \(\text{CaCO}_3\) as the intermediate phase. The XRD curve (Fig. 5b) indicates the formation of mixture of \(\text{CeO}_2\) and \(\text{CaO}\) as the end product of decomposition reaction, which occur during the seventh stage.

The temperature is shifted to higher temperature region due to the increase in the internal gaseous pressure and the interaction of \(\text{Ca}^{2+}\) with oxygen atom of cerium oxalate, which arrests the reaction. But at the characteristic temperature, the rate of decomposition was found to be higher due to the ease of diffusional removal of gaseous products. The reaction rate behavior of each overlapping mass-loss steps of both low temperature and high temperature reaction process of sample \(\text{CC}_1\)
has been best described with phase-boundary-controlled model (given in Eq. 6).

For the sample CC₂, each overlapping mass-loss steps of both low temperature dehydration and high temperature oxidation process have been empirically described by Sestak-Berggren SB \((m, n, 0)\): \(\alpha^m(1-\alpha)^n\). The empirical SB \((m, n, p)\) kinetic model function can be applicable to any type of solid state reactions. The change in mechanism exists due to the change in self-generated reaction condition due to the interaction of Ca\(^{2+}\) and partial overlapping with neighboring reaction interfaces. For the low temperature dehydration reaction of CC₁, the required value of \(E_a\) is 42 ± 0.0977 kJmol\(^{-1}\) (for \(i = 1\)) and 56.5 ± 0.157 kJmol\(^{-1}\) (\(i = 2\)). The higher temperature oxidative decomposition to CeO₂ passes off via two steps. The required value of \(E_a\) is 140 ± 0.96 kJmol\(^{-1}\) (\(i = 3\)) and 169.2 ± 0.08 kJmol\(^{-1}\) for the succeeding step (\(i = 4\)).

The sample CC₂ undergoes thermal decomposition under multistep kinetics through seven steps. The lower temperature dehydration reaction proceeds through three steps. The average value of energy needed for the respective steps are 67.42 ± 0.008 (\(i = 1\)), 68.09 ± 0.007 (\(i = 2\)) and 128.10 ± 0.0044kJmol\(^{-1}\) (\(i = 3\)).
The higher temperature reaction of the sample CC\textsubscript{2} comes about in four steps producing mixed oxides of cerium and calcium. The average value of energy needed for the respective steps are 239.5 (i = 4), 236.3 ± 0.02 (i = 5), 277.8 ± 0.09 (i = 6) and 290.8 ± 0.06 kJmol\textsuperscript{-1} (i = 7). It should also be noted that difference in the values of A for the initial stages (i = 1 and 2) and final stages of CC\textsubscript{2} was high, indicating the higher lags of the reaction time and temperature. This difference can be attributable to the higher impedance effect on the internal
reaction due to the presence of both the surface product layer of cerium-calcium oxalate and the \textit{in situ} \( \text{Ca}^{2+} \) interaction with lone pair of electron on the oxygen atom of cerium oxalate. When the characteristic temperature is reached, destruction of surface product layers occur and the interaction of \( \text{Ca}^{2+} \) tend to increase the rate of oxidative decomposition. The findings of present study reveal that \( \text{Ca}^{2+} \) interaction during thermal decomposition of cerium oxalate produces thermally stable excellent redox active material.

\textbf{Table 1} The average values of kinetic parameters optimized for each reaction step of oxidative thermal decomposition of the samples CC\textsubscript{1} and CC\textsubscript{2}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( i )</th>
<th>( E_{a_i} ) (kJmol(^{-1}))</th>
<th>( A_i ) (sec(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC\textsubscript{1}</td>
<td>1</td>
<td>42.000 ± 0.097</td>
<td>(6.94 ± 0.006)( \times 10^5 )</td>
<td>0.9926</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>56.500 ± 0.570</td>
<td>(1.51 ± 0.58)( \times 10^6 )</td>
<td>0.9925</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>140.000 ± 0.960</td>
<td>(8.63 ± 0.15)( \times 10^{12} )</td>
<td>0.9375</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>169.200 ± 0.087</td>
<td>(3.29 ± 0.005)( \times 10^{13} )</td>
<td>0.9964</td>
</tr>
<tr>
<td>CC\textsubscript{2}</td>
<td>1</td>
<td>67.420 ± 0.008</td>
<td>(2.54 ± 0.008)( \times 10^8 )</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>68.090 ± 0.007</td>
<td>(2.78 ± 0.0013)( \times 10^8 )</td>
<td>0.9756</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>128.100 ± 0.004</td>
<td>(1.30 ± 2.01)( \times 10^9 )</td>
<td>0.9467</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>239.500 ± 0.000</td>
<td>(1.77 ± 0.003)( \times 10^{16} )</td>
<td>0.9356</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>236.300 ± 0.005</td>
<td>(1.62 ± 0.05)( \times 10^{16} )</td>
<td>0.9876</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>277.800 ± 0.097</td>
<td>(1.66 ± 0.03)( \times 10^{18} )</td>
<td>0.9666</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>290.800 ± 0.060</td>
<td>(2.24 ± 0.005)( \times 10^{22} )</td>
<td>0.9768</td>
</tr>
</tbody>
</table>
4.5. Conclusion

Thermally induced oxidative decomposition of cerium oxalate decahydrate and mixed cerium oxalate with 10 mass (%) calcium oxalate in flowing air was studied. Overall kinetics of the formation of micro structural rods of CeO$_2$ and its mixed oxide with CaO was regulated by physico-geometrical constraints. The complexity of the reaction was found to be increased with the introduction of calcium oxalate. Even though both samples show multistep kinetic behavior, mixed cerium oxalate passes through more complex reaction pathways. The reaction stages are distinguished by the ease of diffusional removal of gaseous products formed by the internal reaction. Mixed cerium oxalate (CC$_2$) sample undergoes reaction with higher rate even if the temperature of the reaction shifted to higher region. Optical band gap measurement indicated higher value of $E_g$ for the sample CC$_2$ due to the $\textit{in situ}$ interaction of Ca$^{2+}$ with the lone pair of electrons on the oxygen atom of cerium oxalate. Both the surface product layer of the decomposing cerium-calcium oxalate and the interaction of the Ca$^{2+}$ can impede the diffusional removal of gaseous products.
4.6. References


