5.1. Introduction

Ceria, one of the most promising biomaterial (α = β = γ = 90°, a = b = c = 5.41120 Å, Fm-3m) has possessed multifarious properties which are diverged in catalytic, sensing, solid electrolyte, exhaust gas emission control, medicinal, etc. Most of its properties are raised due to the triggering nature of oxidation state of Ce\(^{3+}/\text{Ce}^{4+}\). Besides its redox nature, oxygen ion vacancies, surface hydroxyl group and radical scavenging ability also contribute towards its diverse applications. Nano ceria can be prepared through variety of methods such as hydrothermal, solvothermal\(^1\), sol-gel\(^3\), micro emulsion\(^4\), thermal decomposition\(^5\), etc. Miyazako et al\(^6\) prepared CeO\(_2\) 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. Preparation of ceria nano particle via solid phase thermal decomposition route has the advantage over other methods such as the use of less chemicals, less impurity (volatile chemicals vaporizes) and time saving process. Hence it is essential to know how much energy is utilized for the formation of nano particle by this solid state conversion. Here the question of kinetic parameters related with the process arises. Therefore the establishment of solid state kinetics of the concerned process is necessary.

Cerium oxalate decomposes into ceria through multistage process\(^7\)-\(^9\). Effect of additives to the precursor salt significantly governs the rate of decomposition. Choose of additives which cause to decrease the \(Ea\) and increase the rate of process and its separation from the product is most considered. Ryusaburo et al\(^10\) studied the effect of
transition metal oxide $\alpha$-Fe$_2$O$_3$ additive on the thermal decomposition of salts of halogen oxoacids, oxalates, azide, permanganate and oxides. The effect of ferro spinel additives on kinetics and mechanism of thermal decomposition of lithium oxalate was studied$^{11}$. John et al$^{12}$ explored the effect of semi conducting metal oxides CuO and TiO$_2$ on the thermal decomposition of sodium oxalate. Also the effect of additives CuO, MnO$_2$ and TiO$_2$ on thermal decomposition kinetics of KIO$_4$ to KIO$_3$ was investigated$^{13}$. Up to now the effect of nano metal oxides of Fe, Co and Ni and nano ferrites of Co and Ni on the kinetic characteristics of formation of ceria nanoparticle from its oxalate precursor is not explored. Fig. 1 represents 2D structure of cerium oxalate.

![2D structure of cerium oxalate](image)

**Fig. 1** 2D structure of Ce(III) oxalates

Oxides of iron (both Fe$_2$O$_3$ & Fe$_3$O$_4$) can perform as the dehydrating agent for the conversion of glycerol to allyl alcohol$^{14}$. Amorphous nanostructured metals, alloys and metal oxides play significant role as catalyst for oxidative process. The conversion of cyclohexanol to cyclohexanone can be catalyzed by amorphous Co$_3$O$_4$$^{15}$. Yang et al$^{16}$ reported that first raw transition metal oxides
especially Fe, Co, Ni and binary oxides have efficient electro catalytic activity for oxygen evolution reaction (OER). Adsorbed OH\(^-\) species becomes much more stable on the surfaces of late transition metal oxides such as Fe, Co and Ni\(^{17}\). Catalytic process with the application of ferrite nanoparticle includes decomposition (in particular photo catalytic decomposition), reactions of dehydrogenation, oxidation, alkylation and C-C coupling among other process. Up to now, ferrite nanoparticle made up of Cu\(^{2+}\), Co\(^{3+}\), Ni\(^{2+}\), Zn\(^{2+}\) and several mixed metal and core shell ferrites have application in the catalytic reaction such as for the synthesis and destruction of organic compound\(^{18}\). Oxides of iron and cobalt and ferrites of Ni and Co have strong ability to reprieve CO by oxidation. Oxidation of CO by ferrites is associated with adsorption and catalytic properties\(^{18–23}\). Use of magnetic metal oxides and ferrites has the advantage is that they can be conveniently recovered from the reaction system using strong magnetic field or magnetic separator, without loss of catalytic activity. The present work aims to synthesize nano metal oxides of Fe, Co and Ni and nano ferrites of Co and Ni via thermal decomposition process. Effect of these nano metal oxides and ferrites (5\%) upon the kinetic characteristics of formation of nano ceria via thermal decomposition of cerium oxalate was established.

5.2. Experimental

5.2.1. Synthesis of metal oxides

Saturated solution of sodium oxalate (100mL) was added into a flask and stirred at room temperature. Definite amount of FeSO\(_4\)
(NH₄)₂SO₄.6H₂O, Co(NO₃)₂.6H₂O and NiCl₂.4H₂O were taken for the preparation of FeC₂O₄.2H₂O, CoC₂O₄.2H₂O and NiC₂O₄.2H₂O respectively and was dissolved in water and poured into aforementioned sodium oxalate solution under stirring. Appropriate quantities of FeSO₄ (NH₄)₂SO₄.6H₂O, Co(NO₃)₂.6H₂O and NiCl₂.4H₂O were taken for the preparation of CoFe₂(C₂O₄)₃ (Fe: Co; 2:1) and NiFe₂(C₂O₄)₃(Fe: Ni; 2:1). After fifteen minutes later, the precipitate is collected by filtration and washed repeatedly with distilled water and ethanol. Each precipitate of oxalate (except NiC₂O₄.2H₂O) was dried at 60ºC overnight. NiC₂O₄.2H₂O was dried at 80ºC. Metal oxides and ferrites were prepared from corresponding metal oxalates using thermal decomposition strategy. Fe₃O₄, Co₃O₄, CoFe₂O₄ and NiFe₂O₄ were prepared by calcination of the corresponding metal oxalates at 300ºC for 3h. The heating rate was 1ºCmin⁻¹. For the preparation of NiO, the calcination temperature was 350ºC for 3h.

5.2.2. Preparation of mechanical mixture of oxalates of cerium and metal oxides

Particle size of metal oxides, ferrites and cerium oxalates were fixed in the range of 95-105μm. Cerium oxalate decahydrate (A₀), and compositions of oxalates of cerium with 2, 5 and 10m/m (%) each of different metal oxides, Fe₃O₄ (A₁), Co₃O₄ (A₂), NiO (A₃), CoFe₂O₄ (A₄), and NiFe₂O₄ (A₅) were prepared by thorough mechanical mixing in an agate mortar.
5.2.3. Characterization

FT-IR and XRD patterns of the oxides and oxalates were recorded. Average crystal size of metal oxides was calculated by using Scherrer formula. The surface morphology of the oxides and cerium oxalate were observed by scanning electron microscopy instrument. The optical band gap ($E_g$) of electro catalysts were calculated from UV–Vis reflectance which was measured using UV–Vis diffuse reflectance spectrum.

5.2.4. Measurement of thermal behavior

DSC measurements were made on TA instrument at four different heating rates, viz. 5, 10, 15 and 20 K min$^{-1}$. TG measurements were made in N$_2$ atmosphere at a flow rate of 50 mL min$^{-1}$.

5.3. Results and Discussion

XRD and FT-IR spectrum of cerium oxalate decahydrate ($A_0$) are shown in Figs. 2a &b respectively. The reflections from the sample in the XRD pattern indicate that cerium oxalate crystallizes in the monoclinic system (JCPDS. No. 20-0268). The broad band observed at 3080–3433 cm$^{-1}$ (Fig. 2b) associated with water molecules which are removed only at higher temperature$^{24}$. The very strong peak observed at 1633.9 cm$^{-1}$ (Fig. 2b) corresponds to the combined effect of asymmetric bending and stretching of water molecule$^{25}$. The strong peak observed at 1318.4 cm$^{-1}$ represents the asymmetric stretching of CO$_2$ molecule associated with oxalate ligand group$^{25,26}$. The band observed at 523.8 cm$^{-1}$ stands for M-O stretching frequency$^{24,26}$. Fig. 3a
represents the SEM image of the cerium oxalate decahydrate. Figs. 3b & c show the images of ferrites of Co and Ni.

**Fig. 2** XRD pattern (a) and FT-IR spectrum (b) of cerium oxalate decahydrate

**Fig. 3** SEM image of cerium oxalate decahydrate (a), photographic images of oxides of Fe, Co & Ni (b) and ferrites of Co & Ni (c).
Fig. 4 The FT-IR spectra of Fe$_3$O$_4$ (a), Co$_3$O$_4$ (b), NiO (c), CoFe$_2$O$_4$ (d) and NiFe$_2$O$_4$ (e)

Fig. 4a represents FT-IR spectrum of Fe$_3$O$_4$. The band observed at 581.63 cm$^{-1}$ and 439.13 cm$^{-1}$ correspond to Fe-O-Fe stretching frequency. Fig. 4b is attributed to FT-IR spectrum of Co$_3$O$_4$ which displays two strong bands at 572.86 and at 666.03 cm$^{-1}$. The first band at 572.86 cm$^{-1}$ corresponds to OB$_3$ vibration in the spinel lattice, where B denotes Co$^{3+}$ in an octahedral hole, whereas the second band at 666.03 cm$^{-1}$ is associated with ABO$_3$ vibration, where A represents Co$^{2+}$ in a tetrahedral hole. Fig. 4c exhibits FT-IR spectrum corresponding to NiO. The broad bands in 424.28-709.01 cm$^{-1}$ indicate Ni-O stretching frequency. The broadness in absorption band arises due to the presence of nano crystals. Owing to the quantum size effect and spherical nanostructures, FTIR spectrum of NiO particles are blue shifted compared to bulk form$^{27}$. Fig. 4d shows two bands at 433.12 and 585.12 cm$^{-1}$ correspond to Fe-O and Co-O stretching frequency
respectively. Fig. 4e displays FT-IR spectrum of NiFe$_2$O$_4$. The band observed at 411.90 and 593.88cm$^{-1}$ correspond to the intrinsic stretching frequency of M-O at tetrahedral and octahedral sites. These exposed as characteristic features of a spinel ferrite in a single phase$^{28}$.

Fig. 5 represents XRD patterns of oxides of Fe, Co and Ni (Figs. 5a, b & c respectively) and of ferrites of Co and Ni (Figs. 5d & e). All the oxides (except NiO) and ferrites show poor crystalline nature. The average crystal size was estimated by using the Scherrer equation based on the maximum intense peak of XRD pattern. It is listed in Table 1. Oxide of Fe presented is Fe$_3$O$_4$ (JCPDS No. 75-0033) due to brownish-black color of the obtained powder$^{29-31}$. The characteristic peaks of XRD pattern of Co$_3$O$_4$ is well agreed with the reported data [JCPDS 42-1467]. The XRD pattern of nano crystalline NiO is well indexed into cubic lattice structure (JCPDS file No: 47-1049)$^{28}$. Less intense peaks of the synthesized CoFe$_2$O$_4$ Nps are well suited with the JCPDS card No. 77-0426 and that of NiFe$_2$O$_4$ Nps with ASTM 10-325.

**Table 1** Average crystallite size and optical band gap ($E_g$) values of metal oxides and ferrites

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Crystallite size (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>2.3</td>
<td>1.72</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>1.6</td>
<td>1.20</td>
</tr>
<tr>
<td>NiO</td>
<td>8.0</td>
<td>1.54</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>1.4</td>
<td>1.38</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>15.1</td>
<td>1.77</td>
</tr>
</tbody>
</table>
Fig. 5 The XRD patterns of Fe$_3$O$_4$ (a), Co$_3$O$_4$ (b), NiO (c), CoFe$_2$O$_4$ (d) and NiFe$_2$O$_4$ (e)

Fig. 6 represents SEM images of Fe$_3$O$_4$ (Fig. 6a), Co$_3$O$_4$ (Fig. 6b), NiO (Fig. 6c), CoFe$_2$O$_4$ (Fig. 6d) and NiFe$_2$O$_4$ (Fig. 6e). The SEM image of Fe$_3$O$_4$ shows porous flat rod like structure of Fe$_3$O$_4$ which was developed by thermal oxidation of FeC$_2$O$_4$.2H$_2$O. Some shrinkage to the rod was observed from the SEM image. Surface morphological analysis of Co$_3$O$_4$ revealed that it acquired rod like structure. Surface textures of NiO, in which the oxide nano particles are assembled to generate microspheres. SEM image of CoFe$_2$O$_4$ nano particle (Fig. 6d) acquired elliptical multi walled-rod morphology. Some deformations are presented on the surface of the rod related with loss of water molecule and CO upon thermal decomposition of CoFe$_2$C$_2$O$_4$.2H$_2$O at 300°C at a heating rate of 1°Cmin$^{-1}$. Morphology analysis of NiFe$_2$O$_4$ displays the hexagonal shaped rods.
5.3.1. Optical properties of metal oxides

An estimate of the optical band gap, $E_g$ can be obtained from 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. Fig. 7 represents the Tauc-plots of Fe$_3$O$_4$ (Fig. 7a), Co$_3$O$_4$ (Fig. 7b), NiO (Fig. 7c), CoFe$_2$O$_4$ (Fig. 7d) and NiFe$_2$O$_4$ (Fig. 7e). The $(\alpha h\nu)^2$ versus $h\nu$ curve are plotted for Fe$_3$O$_4$, CoFe$_2$O$_4$, Co$_3$O$_4$ and NiO, whereas the
$(\alpha h\nu)^{1/2}$ versus $h\nu$ curve are displayed for NiFe$_2$O$_4$. Lowering the optical band gap ($E_g$), conducting properties of the material increases. The estimated $E_g$ values of metal oxides of Fe, Co and Ni and ferrites of Co and Ni were tabulated (Table 1).

**Fig. 7** Tauc-plots of Fe$_3$O$_4$ (a), Co$_3$O$_4$ (b), NiO (c), CoFe$_2$O$_4$ (d) and NiFe$_2$O$_4$ (e)
5.3.2. Characterization of thermal decomposition behavior

Thermal decomposition behavior of the hydrated cerium oxalate in the presence of metal oxides was studied. Fig. 8a shows the DSC curves of overall thermal decomposition behavior of cerium oxalate decahydrate (A₀) in N₂ atmosphere at different β (5, 10, 15 and 20 K min⁻¹) values. It reflects the multistage of thermal decomposition due to the occurrence of multiple constituent chemical processes that occurs successively during the linear heating program. Each constituent process contributes differently to the overall thermal effect³²–³⁴. Hence, the DSC curves of A₀ sample shows two independent thermal behaviors one at temperature below 550K and one at temperature above 550K. Under the linear non-isothermal condition, a multi-step heat flow process was observed from the DSC curves. A heat flow implying the dehydration of water molecule is remarked in the temperature region of 334-502 K, whereas the decomposition of sample A₀ was occurred in the higher temperature region of 600-752 K. For the lower and higher temperature reaction of A₀ sample, the DSC curves are systematically shifted to higher temperature with increasing the value of β. For the low temperature dehydration of sample A₀, the reaction is arrested at the very beginning at all β values except β = 10 K min⁻¹. Hence it can be stated that dehydration reaction is β dependent.

Even though temperature is shifted to lower value for the dehydration reaction at β = 10 than 5 K min⁻¹, the enthalpy change for the process is higher at 10 K min⁻¹. The physico-geometrical constraints have significant role in controlling the multistage thermal behavior.
This occurs due to the changes in reaction conditions as the reaction progresses\textsuperscript{35}. Koga \textit{et al}\textsuperscript{32} put forwarded that the combination of multistep thermal behavior restrained by physico-geometrical features of solid state reaction and successive chemical reaction strategy. During the early stage of reaction, a smooth surface product layer is formed between the reactant and reaction interface. Upon thermal decomposition, this surface product layer come into action \textit{i.e.}, it can impede the diffusional removal of H$_2$O and CO molecule. This causes to increase the internal pressure of the reactant leading to change in the reaction condition at the reaction interface.

![DSC curves](image)

**Fig. 8** The DSC curves of overall thermal decomposition of cerium oxalate decahydrate (a), dehydration reaction (b) and decomposition reaction (c).
Presence of cracks and holes on the surface of the product played as diffusion channel for the removal of gaseous products. In Fig. 8c, the DSC curves of sample A₀ is associated with a shoulder peak. This can be ascribed due to the change in self-generated reaction condition, which arises at the reaction interface as the reaction advances. As the preliminary observation of thermal decomposition of A₀ by each composition (2, 5 & 10 m/m (%)), it was taken into our attention that energy required for lower temperature dehydration of Ce-Ox (A₀) with 5m/m (%) oxides is significantly lowered than 2 & 10 m/m (%). Hence, further studies regarding kinetic analysis has been carried out with samples of 5 m/m (%) oxide mixed A₀.

Figs. 9 & 10 shows the comparison of DSC curves for 2 & 10 m/m (%) oxide mixed samples (A₁, A₂, A₃, A₄ & A₅) with pure Ce-Ox A₀, for the thermal dehydration and decomposition reaction. Fig. 11 shows the comparison of the DSC curves of samples A₀, A₁, A₂, A₃, A₄ & A₅ for the overall as well as independent stages of the reaction i.e., dehydration and decomposition. Both stages of the reaction need uptake of heat energy.

![DSC curves comparison](image)

**Fig. 9** The comparison of DSC curves of pure Ce-Ox, A₀, 2m/m (%) oxides mixed Ce-Ox; A₁, A₂, A₃, A₄ & A₅; dehydration (a) & decomposition (b) at 5 Kmin⁻¹.
Fig. 10 The comparison of DSC curves of pure Ce-Ox, A_0, 10m/m (%) oxides mixed Ce-Ox; A_1, A_2, A_3, A_4 & A_5; dehydration (a) & decomposition (b) at 5 Kmin\(^{-1}\).

Energy required for lower temperature dehydration reaction was found to be higher than higher temperature decomposition reaction. For occurring thermal reaction of the sample A_0 at a heating program of 5Kmin\(^{-1}\), energy required (\(\Delta H\)) for the complete removal of water molecule is about 354.14kJmol\(^{-1}\) and for the formation of nano ceria from it at higher temperature requires energy of 82.35 kJ mol\(^{-1}\). It was noticed that both low temperature and high temperature reactions of the samples with oxides (5m/m (%)) have remarkable shift in temperature to lower value. Among the metal oxides, Fe_3O_4 made comparatively a larger shift of temperature of dehydration to lower value.
Fig. 11 Comparison of the DSC curves of 5 m/m (%) oxide mixed compositions A₀-A₅ at 5Kmin⁻¹; Curves for overall reaction (a), curves for the dehydration (b) and curves for decomposition stages (c).

The value of ΔH calculated for the dehydration from the peak area of DSC curves at a heating rate of 5Kmin⁻¹ in presence of Fe₃O₄, Co₃O₄, NiO, CoFe₂O₄ and NiFe₂O₄ was respectively 295.85, 309.16, 367.94, 345.09 and 332.92kJmol⁻¹. Ascending order of ΔH values for the removal process of water from the sample A₀ is in presence of oxides and ferrites is as follows: Fe₃O₄ < Co₃O₄ < NiFe₂O₄ < CoFe₂O₄ < NiO. NiO requires extra energy 13.80 kJmol⁻¹ for the dehydration than the sample A₀. The shift in temperature of the reaction was
appeared largely at lower $\beta$ value (5Kmin$^{-1}$). There has effect of $\beta$ (heating rate) on the dehydration as well as decomposition reaction of all mixed oxalates of Ce. Moreover, high temperature reaction of samples has constant peak temperature with different contribution of reaction. Existence of lower oxidation state of Ce$^{3+}$ gives certain magnetic behavior to the generated Ce$_2$O$_3$. Hence the system became more rigid and does not increase or decrease the peak temperature of decomposition$^{36}$. In this stage, Co$_3$O$_4$, NiFe$_2$O$_4$ and CoFe$_2$O$_4$ have lower contribution than Fe$_3$O$_4$ and NiO. Hence the system is more stabilized using Fe$_3$O$_4$ and NiO.

**Fig. 12** Comparison of $\alpha$-$T$ curves (a) and the TG curves (b) of the overall thermal decomposition of oxide mixed (5 m/m (%)) samples (A$_1$-A$_5$) and parent sample A$_0$.

Progress of the overall thermal decomposition of each oxide mixed samples (A$_1$-A$_5$) as a function of temperature was compared with parent sample A$_0$ (Fig. 12a). It was noticed that reaction follows multistep kinetic behavior. Sample A$_1$ undergoes dehydration reaction at lower progress of reaction (0.017 $\leq$ $\alpha$ $\leq$ 0.424) whereas other
samples undergo with $\alpha > 0.424$. Experimental mass loss up to the formation of oxide nano particle for each composition is depicted in Table 2. Fig. 12b shows the TG curves of all samples (A₀-A₅) from room temperature to 820K in N₂ atmosphere.

**Table 2** Experimental mass loss obtained from the TG curves of each composition at 5Kmin⁻¹

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀</td>
<td>50.04</td>
</tr>
<tr>
<td>A₁</td>
<td>61.23</td>
</tr>
<tr>
<td>A₂</td>
<td>52.85</td>
</tr>
<tr>
<td>A₃</td>
<td>53.75</td>
</tr>
<tr>
<td>A₄</td>
<td>63.40</td>
</tr>
<tr>
<td>A₅</td>
<td>61.94</td>
</tr>
</tbody>
</table>

*Theoretical mass loss for the sample A₀ is 52.48%

**5.3.3. Kinetic Analysis**

Heat flow (dQ/dt) by the reaction and overall heat of reaction obtained from the experimentally resolved DSC curve after subtracting the baseline. The overall reaction rate can be expressed as

$$\frac{d\alpha}{dt} = \left(\frac{dQ}{dt}\right) \frac{1}{Q}$$

(1)

Where $\alpha$ is the progress of the overall reaction. DSC curves for the thermal decomposition of cerium oxalate decahydrate are assumed to occur from the dehydration and decomposition to Ce₂O₃, the overall
reaction rate recorded using DSC is the sum of these two kinetic processes\(^{32}\) (Fig. 13). Hence

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

\[ (2) \]

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 step and contribution ratio of each reaction step to the overall process while \(A, E_a\) and \(f(\alpha)\) are Arrhenius parameter, activation energy and kinetic model function in different forms respectively.

**Fig. 13** The deconvoluted DSC curves of sample \(A_0\) (a) and \(A_1\) (b)

The contribution \(c_{\text{endo}}\) and \(c_{\text{exo}}\) can be defined as

\[ c_{\text{endo}} = \frac{Q_{\text{endo}}}{Q} < 0 \quad \text{and} \quad c_{\text{exo}} = \frac{Q_{\text{exo}}}{Q} > 0 \]

\[ (3) \]
where $Q_{\text{endo}}$ and $Q_{\text{exo}}$ are the heats of endothermic and exothermic process respectively. Due to the experimental inconvenience of separately tracking the component process, deconvolution of overall kinetic information into reaction component is the only possible way for interpreting the reaction scheme of the successive processes. Low temperature dehydration reaction ($< 550\text{K}$) of incorporated water molecule and high temperature decomposition reaction ($> 550\text{K}$) are kinetically independent process. Therefore the aforementioned cumulative kinetic equation (Eq. 2) can be applied to the overall reaction under linear non-isothermal condition$^{35,37-46}$. All the kinetic parameters of each component process of overall reaction can be optimized by using non-linear least square analysis. Empirical kinetic model function such as modified Sestak Berggren SB ($m,n$) was employed for finding the mechanistic features, $f_i(\alpha_i)$ of each reaction process$^{47-49}$.

$$\text{SB}(m,n): f(\alpha) = \alpha^m (1-\alpha)^n$$

(4)

where $m$ and $n$ are kinetic exponent.

The initial values of the kinetic parameters are obtained by the kinetic deconvolution of DSC curves. Kinetic parameters for each component step are analyzed by assuming single stage kinetic analysis. Appropriate $f_i(\alpha_i)$ is obtained by merely adjusting the parameters $c$, $m$ and $n$ in Eq. 5 and such an equation fits every kinetic model proposed for solid state reactions, and also scores for the deviations of ideal kinetic model due to for example, particle inhomogeneity in size and shape$^{47}$. 
\[
\ln \left[ \frac{d\alpha}{dt} \bigg/ \left( 1 - \alpha \right)^n (\alpha)^m \right] = cA - \frac{Ea}{RT} \tag{5}
\]

Pearson linear correlation coefficient between left hand sides of the equation with inverse of temperature is set as an objective of optimization. The Kissinger method, which was utilized to determine the apparent activation energy for the overall reaction from the DSC curves recorded at different \(\beta\).

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left[ - \frac{f(\alpha_p)}{d\alpha} \frac{AR}{Ea} \right] - \frac{Ea}{RT_p} \tag{6}
\]

where \(T_p\) is the peak maximum temperature characteristics for the overall reaction. For the reaction of cerium oxalate decahydrate crystalline particle, the change in \(T_p\) in the DSC curves with \(\beta\) can be analyzed for the Kissinger plot. It is possible to apply the Kissinger plot to the reaction of \(A_0\) and mixed samples \(A_1-A_5\): the four subsequent endothermic peak maximum. The Kissinger plots \(\ln (\beta/T_p^2)\) versus \(T_p^{-1}\) for samples \(A_0\) and \(A_1\) are represented in Figs.14a & b respectively.

![Kissinger plots for each peak of samples A0 (a) and A1 (b).](image-url)
After setting all of the initial values of kinetic parameters for each step, a parameter optimization was executed in order to minimize the squares of the residue \( F \) when fitting the calculated curve \((d\alpha/dt)_{cal}\) versus time to the experimental curve \((d\alpha/dt)_{exp}\) versus time.

\[
F = \sum_{j=1}^{n} \left( \frac{d\alpha}{dt}_{exp,j} - \left( \frac{d\alpha}{dt}_{cal,j} \right) \right)^2
\]

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

**Fig. 15** The Friedman plots for each stage of decomposition of Ce-Ox in presence of iron oxide \( A_1 \); first (a), second (b), third (c) and fourth stages (d).
For finding the $Ea$ values of each stage of thermal decomposition of Ce-Ox in presence of oxides, Friedman method and Kissinger methods were used. For the estimating the values of $Ea$ of $A_1$, $A_2$ & $A_4$, Friedman method was best fitted (Figs. 15, 16&17), whereas for $A_3$ & $A_5$, Kissinger method (Fig. 18) was best suited than Friedman plots. Due to the occurrence of partially overlapped reaction, the distributed $\alpha$ value of each stage are merged with other stages. Fig. 15 shows the Friedman plots of each stage of $A_1$.

![Friedman Plots](image)

**Fig. 16** The Friedman plots for each stage of decomposition of Ce-Ox in presence of $\text{Co}_3\text{O}_4$ $A_2$; first (a), second (b), third (c) and fourth stages (d).

Thermal decomposition of cerium oxalate crystalline particle is significantly influenced by the self-generated reaction condition.
Change in the internal gaseous pressure in the oxalate crystalline particle during heating play a predominant role in regulating the kinetic behavior in the early stages of the reaction. But the change in the internal gaseous pressure cannot be traced during the reaction. Hence, it is a challenge to reveal how kinetic characteristic of the reaction behave with reaction condition by tracking the heat flow process under systematically altering reaction condition. Thermal decomposition stage of cerium oxalate decahydrate in N\textsubscript{2} atmosphere occurs through following mechanism. Theoretical mass loss corresponding to the formation of ceria (Ce\textsubscript{2}O\textsubscript{3}) from cerium oxalate is 55.06\%. The experimental mass loss of the decomposition of the sample A\textsubscript{0} from the TG curve (Fig. 12b) was found to be 50.04\%. The mass loss (%) for other samples is listed in Table 2.

Fig. 17 The Friedman plots for each stage of decomposition of Ce-Ox in presence of CoFe\textsubscript{2}O\textsubscript{4}, A\textsubscript{4}; first (a), second (b), third (c) and fourth stages (d).
Fig. 18 Kissinger plots for each peak of samples A₃ (a) and A₅ (b).

\[
\begin{align*}
\text{Ce}_2(\text{C}_2\text{O}_4)_3.10\text{H}_2\text{O} & \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3.3\text{H}_2\text{O} + 7\text{H}_2\text{O} \quad (8) \\
\text{Ce}_2(\text{C}_2\text{O}_4)_3.3\text{H}_2\text{O} & \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O} \quad (9) \\
\text{Ce}_2(\text{C}_2\text{O}_4)_3 & \rightarrow \text{Ce}_2\text{O}_2\cdot\text{CO}_3 + 4\text{CO}_2 + \text{CO} \quad (10) \\
2\text{CO} & \rightarrow \text{C} + \text{CO}_2 \quad (11) \\
\text{Ce}_2\text{O}_2\cdot\text{CO}_3 & \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2 \quad (12)
\end{align*}
\]

For the parent and mixed sample, the overall heat absorbing process of thermal decomposition is empirically resolved into four stages as evident from Fig. 19. Fig. 19 shows kinetic deconvolution of the thermal decomposition of the samples A₀–A₅ in inert atmosphere, which was based on the Eq. 2. The first low temperature reaction of all samples is considered as dehydration reaction. Each sample goes through two overlapping stages for the dehydration reaction. Similarly, the higher temperature decomposition of each sample to Ce₂O₃ under
vacuum is composed of two partially overlapping reaction steps due to the formation of an intermediate cerium oxy carbonate Ce$_2$O$_2$.CO$_3$.

5.3.4. Effect of Fe$_3$O$_4$, Co$_3$O$_4$ and NiO on the removal of water of crystallization of Ce-Ox

Oxides of Fe and Co have strong affinity for the adsorption of water vapor$^{50-52}$. These oxides act as dehydrating agent$^{14,15}$. Heat of adsorption of water for NiO is comparatively lower than other oxides. Therefore NiO chemisorb water vapor weakly$^{53}$. In the concerned work, Fe$_3$O$_4$ & Co$_3$O$_4$ facilitate the dehydration of Ce-Ox requiring lower $E_a$ value but NiO can’t facilitate the dehydration reaction. The average optimized kinetic parameters for different $\beta$ values are listed in Table 3. For the entire sample, the optimized kinetic parameters for first, second, third and fourth reaction step was not much deviated from those parameters which were determined previously. The optimized $E_a$ value for the dehydration of sample A$_0$ comes in the range of 73 to 93 kJ mol$^{-1}$, whereas in presence of Fe$_3$O$_4$ $E_a$ value of 35 to 36 kJ mol$^{-1}$ is needed. The $E_a$ value of A$_2$ requires activation energy of 73-74 kJ mol$^{-1}$. 
Fig. 19 The results of kinetic deconvolution analysis for the thermal decomposition of the samples $A_0(a)$, $A_1(b)$, $A_2(c)$, $A_3(d)$, $A_4(e)$ and $A_5(f)$ under linear non-isothermal condition at $\beta = 5 \text{ Kmin}^{-1}$ in $\text{N}_2$ atmosphere.
5.3.5. Effect of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ on the removal of water of crystallization of Ce-Ox

Both CoFe$_2$O$_4$ and NiFe$_2$O$_4$ have strong affinity to adsorb water vapour$^{54,55}$. Therefore water vapor comes out during the dehydration of Ce-Ox, can be adsorbing by these ferrites. Hence these ferrites facilitate the process. From the Table 3, it was shown that the Ea value required by CoFe$_2$O$_4$ and NiFe$_2$O$_4$ are 43-74 and 73-74 kJ mol$^{-1}$ respectively.

5.3.6. Effect of Fe$_3$O$_4$, Co$_3$O$_4$ and NiO on the formation of ceria nanoparticle by decomposition

Thermal decomposition of Ce-Ox to the formation of ceria releases CO. Co$_3$O$_4$ surface has strong CO oxidizing ability than Fe$_3$O$_4$ and NiO$^{20,23,56}$. Hence any additives having capacity to oxidize these evolving CO can promote the reaction$^{11}$. Therefore CO evolved from the Ce-Ox diffuses to the surface of Co$_3$O$_4$, CO react with oxygen on the surface of the catalyst giving CO$_2$$^{23}$. Non-reducible metal supported Fe$_3$O$_4$ has strong CO oxidizing ability than Fe$_3$O$_4$ alone$^{20}$. Also interface of NiO with other metal/metal oxide has strong ability to convert CO to CO$_2$$^{56}$. The activation energy needed for the sample A$_0$ for the decomposition stage comes in the range of 172-175 kJmol$^{-1}$. The increasing order of $Ea$ (kJmol$^{-1}$) for the samples A$_2$, A$_3$ and A$_4$ follows as: A$_3$ (163-164) < A$_2$ (169-175) < A$_4$ (187-192).
Table 3 Average values of optimized kinetic parameter for each reaction step of thermal decomposition of cerium oxalate decahydrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>i</th>
<th>$Ea_i$ (kJ mol$^{-1}$)</th>
<th>$A_i$ (sec$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_0$</td>
<td>1</td>
<td>93.21 ± 0.05</td>
<td>(2.49 ± 0.01)× 10$^7$</td>
<td>0.9985</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>73.68 ± 0.09</td>
<td>(4.23 ± 0.00)× 10$^4$</td>
<td>0.9496</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>172.20 ± 0.20</td>
<td>(1.50 ± 0.03)× 10$^{14}$</td>
<td>0.9205</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>175.50 ± 0.20</td>
<td>(1.80 ± 0.05)× 10$^{14}$</td>
<td>0.9325</td>
</tr>
<tr>
<td>A$_1$</td>
<td>1</td>
<td>35.75 ± 0.05</td>
<td>(4.70 ± 0.05)× 10$^5$</td>
<td>0.9639</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36.84 ± 0.04</td>
<td>(2.30 ± 0.06)× 10$^5$</td>
<td>0.9484</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>169.20 ± 0.40</td>
<td>(7.94 ± 0.03)× 10$^{13}$</td>
<td>0.9543</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>175.69 ± 0.50</td>
<td>(2.16 ± 0.10)× 10$^{14}$</td>
<td>0.9483</td>
</tr>
<tr>
<td>A$_2$</td>
<td>1</td>
<td>74.270 ± 0.20</td>
<td>(4.62 ± 0.03)× 10$^4$</td>
<td>0.9376</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>73.520 ± 0.12</td>
<td>(2.48 ± 0.04)× 10$^4$</td>
<td>0.9101</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>163.90 ± 0.23</td>
<td>(8.64 ± 0.02)× 10$^7$</td>
<td>0.9838</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>164.46 ± 0.08</td>
<td>(1.88 ± 0.03)× 10$^8$</td>
<td>0.9319</td>
</tr>
<tr>
<td>A$_3$</td>
<td>1</td>
<td>112.41 ± 0.03</td>
<td>(4.18 ± 0.02)× 10$^9$</td>
<td>0.9243</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>115.00 ± 0.02</td>
<td>(2.63 ± 0.01)× 10$^9$</td>
<td>0.9720</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>187.50 ± 0.01</td>
<td>(2.94 ± 0.02)× 10$^{15}$</td>
<td>0.9688</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>192.60 ± 0.03</td>
<td>(3.54 ± 0.11)× 10$^{15}$</td>
<td>0.9765</td>
</tr>
<tr>
<td>A$_4$</td>
<td>1</td>
<td>78.67 ± 0.03</td>
<td>(3.72 ± 0.05)× 10$^5$</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>43.20 ± 0.05</td>
<td>(6.56 ± 0.04)× 10$^4$</td>
<td>0.9692</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>163.20 ± 0.02</td>
<td>(7.80 ± 0.10)× 10$^8$</td>
<td>0.9966</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>164.60 ± 0.01</td>
<td>(3.48 ± 0.04)× 10$^8$</td>
<td>0.9603</td>
</tr>
<tr>
<td>A$_5$</td>
<td>1</td>
<td>73.40 ± 0.30</td>
<td>(1.41 ± 0.01)× 10$^2$</td>
<td>0.9525</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>74.30 ± 0.40</td>
<td>(5.30 ± 0.10)× 10$^1$</td>
<td>0.9479</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>167.30 ± 0.30</td>
<td>(2.19 ± 0.12)× 10$^{13}$</td>
<td>0.9793</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>165.40 ± 0.00</td>
<td>(4.24 ± 0.06)× 10$^{13}$</td>
<td>0.9816</td>
</tr>
</tbody>
</table>

5.3.7. Effect of CoFe$_2$O$_4$ and NiFe$_2$O$_4$ on the formation of ceria nanoparticle by decomposition

Ferrites of Ni and Co have strong affinity to adsorb CO and to oxidize it to CO$_2$\textsuperscript{21, 22}. Hence releasing CO during the reaction diffused to surface of ferrite. $Ea$ needed for the process by A$_4$ and A$_5$
respectively are 163-164 and 165-167 kJmol\(^{-1}\). Fig. 20 illustrates the mechanism of thermal decomposition of cerium oxalate decahydrate in presence of ferrites. It was noticed from the Table 3 that higher difference in the values of \(A\) for initial \((i = 1 \text{ and } 2)\) and final stages \((i = 3 \text{ and } 4)\) of each sample was high, indicating higher lags of reaction time and temperature. \(Ea\) needed by the sample A\(_3\) is higher for dehydration and decomposition due to less catalyzing effect of NiO.

**Fig. 20** Schematic representation of the mechanism of thermal decomposition of cerium oxalate decahydrate in presence of ferrites

### 5.4. Conclusion

Semi conducting magnetic nano metal oxides, Fe\(_3\)O\(_4\), Co\(_3\)O\(_4\), NiO, CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) were synthesized by thermal decomposition of their oxalate precursor. Characterization techniques used for the synthesized oxides were FT-IR, XRD, SEM and UV-DRS. Synthesized oxides except NiO are amorphous in nature. Effects of
nano metal oxides on thermal decomposition stages of cerium oxalate decahydrate up to the formation of ceria were studied and predicted the thermal events which were occurred during the reaction process. Using the method of kinetic deconvolution, kinetic analysis of each resolved stage was performed. It was explored that nano Fe$_3$O$_4$ facilitates the dehydration stages requiring less $Ea$ value of 35-36 kJmol$^{-1}$. Nano Co$_3$O$_4$, CoFe$_2$O$_4$ and NiFe$_2$O$_4$ promoted the dehydration as well as decomposition stages of cerium oxalate decahydrate by decreasing the $Ea$ value. Nano NiO has shown retarding effect on both the dehydration as well as decomposition stages.
5.5. References


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