Decomposition of irradiated yttrium oxalate and CuO mixture

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Influence of γ-irradiation, (10-500) KGy on the thermal decomposition of Y₂(C₂O₄)₃ + CuO (10 mol%) mixture has been studied in the temperature range, 603-643 K by gas evolution method. The α-t plots indicate that decomposition of unirradiated and irradiated mixture follows (i) initial gas evolution, (ii) acceleratory period and (iii) decay stage. Irradiation promotes the initial gas evolution, α₀ and decreases the fractional decomposition, α₁ at lower doses up to 50 KGy but the value increases at higher doses without affecting the nature of the isotherms. The data are analysed in the light of theories of various kinetic models and are found to be best fitted to Prout-Tompkins and Contracting Square mechanisms, suggesting that nucleation takes place instantaneously in a chain branching manner. The energy of activation of the acceleratory period is decreased but that of the decay stage is increased by irradiation. Plausible mechanism of decomposition and the effect of irradiation thereon has been discussed.

Due to potential application of precursors in synthesis of high Tₓ superconductors, oxalates of alkaline earth metals as well as of rare earths have drawn the attention of many investigators. Thermal decomposition of oxalates has found its application in the preparation of catalysts and is being successfully applied to low temperature synthesis of oxides, spinel structure AB₂O₄ (ref. 4), Bronzes AByO₂ (ref. 5) and high Tₓ superconductors. Though several workers have reported the role of irradiation and additives on the decomposition of metal oxalates, the effect of transition metal oxides having positive holes in the d-orbital has not received much attention. Hence, the present study, which relates to the simultaneous effect of additive and irradiation on the decomposition process of γ-irradiated yttrium oxalate - CuO mixture, has been undertaken. As these materials are the constituents of high Tₓ superconductors, (Y-Ba-CuO system), the chemistry evolved out of this study may be applied to superconductors.

Experimental

Yttrium oxalate was prepared following the procedure reported earlier and purity of the sample was checked by chemical analysis and IR spectra, establishing the presence of oxalate ions. The Energy Dispersive X-ray Analysis (EDAX) confirmed the presence of Y in the prepared sample. The Energy Dispersive Spectroscopy (EDS) technique is based on the standard material of CuO (10 mol%) was prepared by taking appropriate amounts of the corresponding salts and grinding in an agate mortar. The samples were vacuum sealed and exposed to different doses, 10-500 KGy of 60Co γ-rays at the dose rate of 9 KGy h⁻¹ as determined by Fricke dosimeter. Decomposition study of unirradiated and irradiated crystals was carried out in the temperature range 603-643 K by adopting the procedure reported earlier. Fractional decomposition, α = (p/p₀) was calculated from pressure values, p being the pressure at time t and p₀ the final pressure on completion of the reaction.

Results and discussion

Decomposition isotherms (Fig. 1) of unirradiated and irradiated mixtures indicated that in both the cases, the reaction occurs through (i) initial gas evolution, (ii) acceleratory and (iii) decay periods. The initial gas evolution, α₀ is due to physical desorption of gases from crystal surface or due to release of occluded gases from the interior of the crystals, which increases with increase in radiation dose and time of heating. For example when radiation dose is 0, 10, 50, 100, 250 and 500 KGy, α₀ is 0.145, 0.145, 0.150, 0.155, 0.160 and 0.170 respectively.

The acceleratory period begins just after the initial gas evolution, due to instantaneous nucleation at the surface of the crystal, which is then followed by a decay stage. Data on fractional decomposition, (Table 1) indicate that the α value decreases at lower doses, up to 50 KGy but increases at higher doses and major part of decomposition takes place in the acceleratory period.

Kinetics of decomposition

Decomposition data on unirradiated and irradiated materials are analysed according to different kinetics models and are well fitted to Prout-Tompkins relationship (Fig. 2).
log \( \left( \frac{\alpha}{1-\alpha} \right) = k_{A,D}t + C_1 \) \hspace{1cm} ... (1)

and Contracting square mechanism (Fig. 3)

\[
1-(1-\alpha)^{1/n} = k_{A,D}t + C_2 \quad \text{(n=2)}
\]

... (2)

where \( k_A, k_D \) are the rate constants for the acceleratory and decay stages respectively, \( C_1 \) and \( C_2 \) are constant terms. The ranges of applicability of Eqs (1) and (2) are: \( 0.15 < \alpha < 0.95 \) and \( 0.13 < \alpha < 0.82 \), respectively for irradiated and unirradiated materials.

Fitting of the data to above equations indicate that nucleation takes place in a chain branching manner rapidly at the commencement of the reaction. As a result; the surface of each particle is covered with large amount of product material, \( Y_2O_3 \) which increases in thickness. In crystal faces this leads to sufficient strain to initiate cracks and the reaction proceeds down these cracks. Values of rate constants, calculated by the aforesaid mechanisms are incorporated in Table 2.

The data indicate that \( k_A > k_D \) over the temperature range studied which may arise due to decrease in catalytic activity and reduction of flux of oxalate ion adsorbed on the catalyst surface. Irradiation decreases

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Fractional decomposition, \( \alpha \) & \multicolumn{6}{|c|}{Time (min.)} \\
\hline
& 20 & 40 & 60 & 80 & 100 & \\
\hline
Irr. (KGY) & 0.0 & 0.0 & 0.30 & 0.39 & 0.44 & 0.56 & 0.63 \\
0 & 0.24 & 0.31 & 0.36 & 0.45 & 0.52 & \\
10 & 0.26 & 0.34 & 0.42 & 0.49 & 0.55 & \\
50 & 0.30 & 0.39 & 0.46 & 0.56 & 0.63 & \\
100 & 0.40 & 0.51 & 0.60 & 0.67 & 0.71 & \\
250 & & & & & & \\
500 & & & & & & \\
\hline
\end{tabular}
\caption{Effect of irradiation dose on the thermal decomposition of \( Y_2(C_2O_4)_3 + CuO \) (10 mol %) mixture.}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Thermal decomposition of irradiated (0.25 MGy) \( Y_2(C_2O_4)_3 + CuO \) (10 mol %) mixture at different temperatures.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Prout-Tompkins analysis of the kinetics of the thermal decomposition of irradiated (0.25 MGy) \( Y_2(C_2O_4)_3 + CuO \) (10 mol %) mixture.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Contracting square mechanism of the kinetics of the thermal decomposition of irradiated (0.25 MGy) \( Y_2(C_2O_4)_3 + CuO \) (10 mol %) mixture.}
\end{figure}
the energy of activation of the acceleratory period and increases the same in the decay stage.

**Mechanism of decomposition**

Though several mechanisms are possible for the decomposition of solids\(^{11}\) either in powdered material or in a single crystal, the essential features are: (i) destruction of crystal lattice of the reactants, (ii) breaking and redistribution of chemical bonds, (iii) formation of crystal lattice of reaction product and (iv) the diffusion of one component or the other through the product layer for further propagation of dissociation reaction.

Decomposition of rare earth oxalates follows\(^ {12}\) the paths (3) and (4):

\[
M_2(C_2O_4)_3 \rightarrow M_2(CO_3)_3 + 3CO \quad \ldots (3)
\]

\[
M_2(CO_3)_3 \rightarrow M_2O_3 + 3CO_2 \quad \ldots (4)
\]

leaving behind a homogeneous brown coloured residue which involves some disproportion of CO yielding residual carbon\(^ {13}\).

\[
2CO_{(g)} \rightarrow C_{(s)} + CO_2 \quad \ldots (5)
\]

Decomposition of oxalate\(^ {13}\) occurs when the temperature is reached at which rupture of C-O bond takes place first followed by electronic rearrangement leading to the formation of either CO, CO\(_2\) and O\(_2\) (route-1) or CO and CO\(_3\)^{2-} (route-2) as shown in Scheme 1.

But in the present experimental conditions, decomposition follows route-2; as CO\(_3\)^{2-} is found to be the final product by chemical analysis. It is plausible\(^ {14}\) that the presence of CuO favours the decomposition reaction due to an electron transfer process involved between the C\(_2\)O\(_4\)^{2-} ion and CuO before the cleavage of C-C bond, resulting in the stepwise reduction of Cu\(^ {2+}\) ion as shown in Eqs (6) and (7).

\[
C_2O_4^{2-} + Cu^{2+} \rightarrow 2CO_2 + Cu^0 \quad \ldots (6)
\]

\[
[Cu^{2+} \rightarrow Cu^+ \rightarrow Cu^0] \quad \ldots (7)
\]

CuO, being a \(p\)-type semiconductor favours the electron transfer process due to the presence of positive hole (h\(^ +\)) in the \(d\)-orbital which will be available to accept electron from oxalate ion enhancing the decomposition process.

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**Scheme 1**
Table 2—Temperature dependence of velocity constants on the thermal decomposition of unirradiated and irradiated $Y_2(C_2O_4)_3 + CuO$ (10 mol %) mixture and energy of activation $(E \pm 5 kJ/mol)$

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Prout-Tompkins</th>
<th>Contracting square</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_A$</td>
<td>$E_A$</td>
<td>$k_0$</td>
</tr>
<tr>
<td>603</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>613</td>
<td>9.0</td>
<td>3.0*</td>
</tr>
<tr>
<td>623</td>
<td>14.0</td>
<td>4.0</td>
</tr>
<tr>
<td>633</td>
<td>22.0</td>
<td>4.0</td>
</tr>
<tr>
<td>643</td>
<td>32.0</td>
<td>5.0*</td>
</tr>
</tbody>
</table>

$k_A$ and $k_0 \times 10^2$ min$^{-1}$.

*Values are for irradiated material.

Role of irradiation

Upon exposure of mixture of $Y_2(C_2O_4)_3 + CuO$ to $\gamma$-irradiation, excitation and ionisation followed by rupture of chemical bonds in the anion takes place as the $\gamma$-ray energy, $E_\gamma > C-C$ (3.6 eV), C-O (3.7 eV), C=O (7.7 eV) bond energies. In addition to damaged entities, trapped electrons ($e^-$), holes ($h^+$), excited species, radicals, atoms and ions are generated which constitute decomposition nuclei themselves and may be termed as irradiation nuclei (n), which increase in size and number with increase in radiation dose. These species produce strain in the lattice and favour the decomposition process, consequently decreasing the energy of activation. But the defects and dislocations, introduced into the lattice of $Y_2(C_2O_4)_3$ by CuO get annealed by irradiation thus decreasing the rate of reaction in the acceleratory period. Other contributing factors are trapped electron ($e^-$), CO, etc., generated by irradiation which reduce the catalytic activity of CuO preventing its affinity for favourable electron transfer. The decomposition in the present case is governed by two simultaneous opposite factors, acceleratory effect of CuO and irradiated nuclei and the deceleratory influence of radiation annealing, trapped electrons, CO, etc. At lower doses, the latter effect predominates resulting in decrease in the value of $\alpha$, but at higher doses, the former overpowers the latter favouring the decomposition process.

Acknowledgement

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References