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Rare earth oxide-catalysed decomposition of calcium oxalate

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Abstract

The catalytic activity of rare earth oxides (REOs) on the isothermal decomposition of calcium oxalate has been studied within the temperature range 693–733 K. The fractional decomposition, α, versus time, t, plots for pure salt as well as for mixtures suggest that the process occurs through initial gas evolution, acceleratory and decay stages. Analysing the data in the light of theories of various kinetic models, it is indicated that the two-dimensional phase boundary reaction model gives the best fit of the results. Admixtures enhance the rate of reaction and decrease the energy of activation of both acceleratory and decay stages, the catalytic activity being in the order: $La_2O_3 > Sm_2O_3 > Gd_2O_3$. A plausible mechanism of decomposition and the role of the catalyst in the process have been discussed.

Keywords: Calcium oxalate; Catalyst; Rare earth oxides (REOs); Thermal decomposition

1. Introduction

The thermal analysis and kinetics of thermal decomposition of metal oxalates have been well studied by many workers, [1–6]. Walter-Levy and Laniepce [2] and Mutin and Watelle-Marion [3] have reported the decomposition of various hydrates of barium oxalate. Verdonk and Broersma [4] have carried out the decomposition of this salt in the presence of dry nitrogen and suggested that part of the evolved carbon monoxide disproportionates, leaving carbon behind. A comparative study of the kinetics of decomposition of alkaline earth metal oxalates has been carried out by Tanaka and Koga [5]. Decomposition of γ-irradiated calcium oxalate monohydrate indicates that two-dimensional phase boundary reaction gives the best fit of the data

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[6]. Influence of rare earth oxides on the thermal decomposition of alkaline earth metal oxalates has specially drawn the interest of many workers [7, 8], ever since Bednorz and Müller [9] confirmed the superconductivity of layer cuprate high T_C superconductors. It is of interest, therefore, to study the effect of these oxides on the decomposition of calcium oxalate and to explore the in situ mechanism involved in the process.

2. Experimental

Calcium oxalate (CaC_2O_4) was prepared by hydrolysis of diethyl oxalate with calcium chloride solution at pH 4.7 and the crystals were dehydrated in vacuum at 493 K to constant weight. The purity (99.98%) of the material was verified by IR, TG, and chemical analysis. Calcium was estimated by atomic absorption spectroscopy, and oxalate by titrating with $KMnO_4$ solution.

Physical mixtures of the oxalate with different rare earth oxides; La_2O_3, Sm_2O_3 and Gd_2O_3 (2–10 mol%) were prepared by adding the required amount of these substances and grinding thoroughly in an agate mortar. A ground sample of calcium oxalate as well as the mixtures (300 mesh size) were taken for decomposition study in the temperature range, 693–733 K by adopting the procedure reported earlier [10]. For each run about 50 mg of the sample was taken and the course of the reaction was followed by measuring the pressure of carbon monoxide liberated at different time intervals. The fraction decomposed, $\alpha = (p/p_f)$ was calculated from pressure values, p, the pressure at any time t, and p_f, the final pressure on complete decomposition of the salt to the corresponding carbonate, which was obtained by raising the temperature to 793 K and cooling to the respective temperature of each run. The reported data (Tables 1–3) are means of three determinations.

Table 1

Temperature-dependence of velocity constants in the thermal decomposition of pure calcium oxalate and a mixture of calcium oxalate and lanthanum oxide (La_2O_3) (10 mol%)

Temp. in K	CaC_2O_4		$CaC_2O_4 + La_2O_3$	
	$10^3 k_A$ [a]	$10^3 k_D$	$10^3 k_A$	$10^3 k_D$
693	2.35	1.61	6.25	3.13
703	4.31	2.43	9.88	3.79
713	7.41	3.06	14.29	4.17
723	14.77	4.21	25.71	4.83
733	20.38	5.56	–	–
E_A^{in} kJ mol^{-1}	245.1	127.8	191.3	58.3

[a] k_A, k_D in min^{-1}.

Table 2
Effect of rare earth oxides on the thermal decomposition of calcium oxalate at 703 K

Substance	Fraction decomposed, α		$10^3 k_A$[a]	$10^3 k_D$[a]
	20 min	60 min		
CaC_2O_4	0.165	0.475	4.31	2.43
$CaC_2O_4 + Gd_2O_3$	0.326	0.675	7.14	3.39
$CaC_2O_4 + Sm_2O_3$	0.344	0.724	8.33	3.85
$CaC_2O_4 + La_2O_3$	0.475	0.821	9.88	3.79

[a] k_A, k_D in min^{-1}.

Table 3
Effect of oxide concentration on the thermal decomposition of calcium oxalate at 703 K

Conc. of oxide La_2O_3 in mol%	Fraction decomposed, α		Contracting square	
	10 min	50 min	$10^3 k_A$[a]	$10^3 k_D$[a]
0	0.095	0.422	4.31	2.43
2	0.135	0.529	5.77	2.86
5	0.214	0.639	7.14	3.33
10	0.293	0.767	9.88	3.79

[a] k_A, k_D in min^{-1}.

3. Results and discussion

The decomposition product was slightly grey in colour due to formation of residual carbon during the process [7]. The 'α–t' plots (Figs. 1–3) exhibit three different regions viz., (i) initial gas evolution (initial puff) followed by a sigmoidal regime consisting of (ii) acceleratory and (iii) decay stages. The initial puff of gas is due to release of occluded gases from the accessible interior of the crystal, being completed within the first minute of heating, which increases with addition of the admixture and with increasing temperature. Increase in oxide (REOs) concentration also increases the fractional decomposition, α (Fig. 4); the values are incorporated in Table 3. A marked difference is observed in the catalytic activity of different oxides in the order:

$$La_2O_3 > Sm_2O_3 > Gd_2O_3$$

Admixture with La_2O_3 (10 mol%) enhances the process remarkably; values for the fraction decomposed, α, after 40 min heating at different temperatures are given below:

Temp. in K	693	703	713	723	733
CaC_2O_4	0.191	0.351	0.538	0.779	0.923
$CaC_2O_4 + La_2O_3$ (10 mol%)	0.440	0.689	0.839	0.957	–

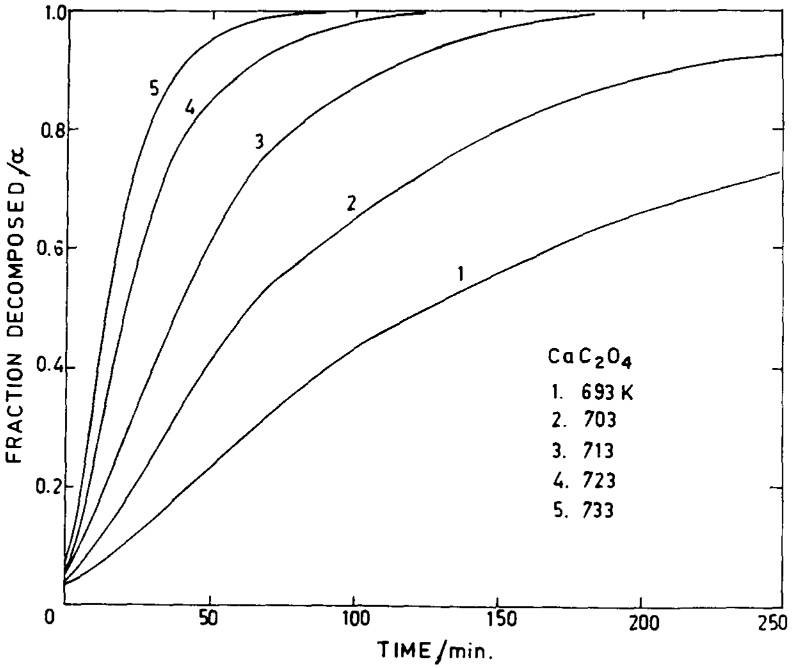


Fig. 1. Thermal decomposition of CaC_2O_4 at different temperatures.

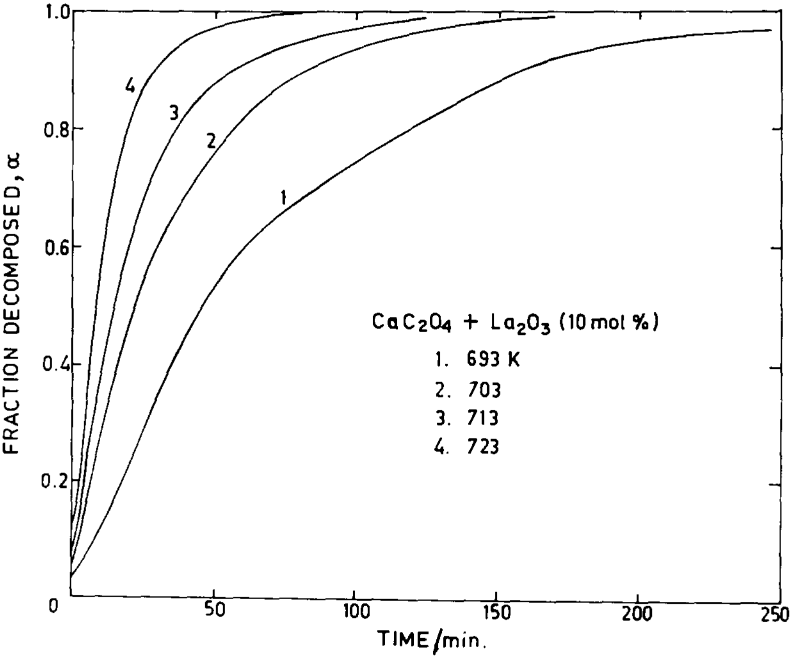


Fig. 2. Thermal decomposition of $CaC_2O_4 + La_2O_3$ (10 mol%) at different temperatures.

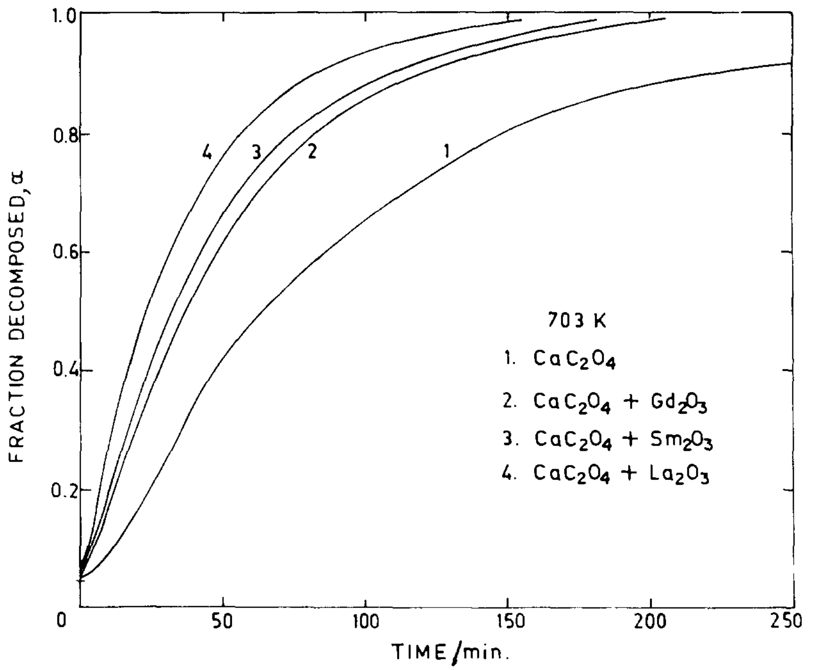


Fig. 3. Thermal decomposition of CaC_2O_4 and of CaC_2O_4 + REOs (10 mol%) at 703 K.

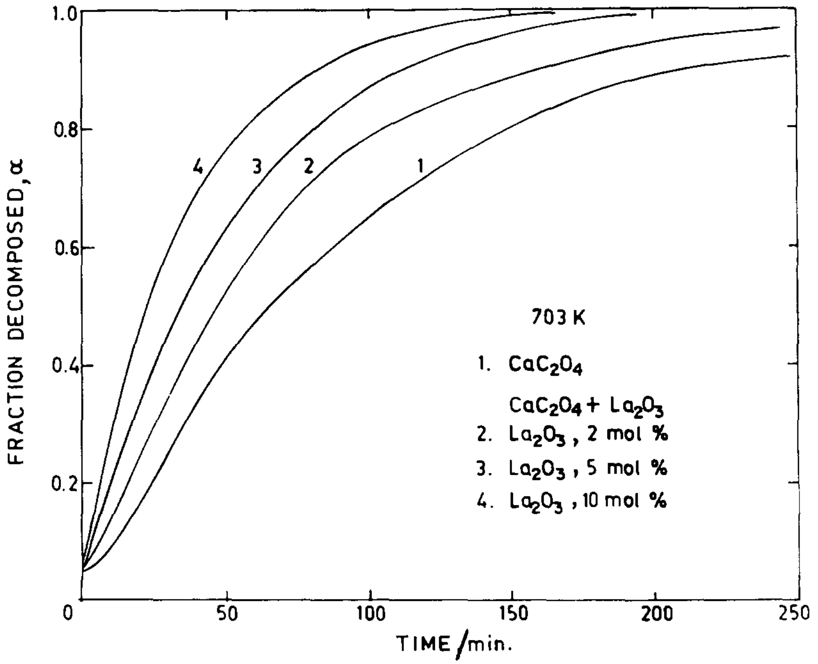


Fig. 4. Effect of concentration of admixture Ln_2O_3 on the thermal decomposition of calcium oxalate

Due to instantaneous nucleation at the surface of the crystals, the acceleratory period begins just after initial gas evolution, the duration of which is increased but that of the decay stage is decreased by the admixture. The sigmoidal regime consisting of acceleratory and decay stages are well analysed according to contracting square kinetics [11] (Figs. 5 and 6)

$$1-(1-\alpha)^{1/2} = k_{A,D}t + C \tag{1}$$

with two different rate constants, k_A and k_D respectively for the acceleratory and decay stages. The ranges of applicability of Eq. (1) being $0.065 < \alpha < 0.98$, which remains almost unaffected by the admixture. At a given temperature, $k_A > k_D$, and both increase with increasing temperature and with increasing concentration of the rare earth oxide. The admixture remarkably decreases the energy of activation E(± 10 kJ mol^{-1}) (Table 1).

3.1. Chemistry of decomposition

Under the present experimental conditions, decomposition of calcium oxalate occurs as:

$$CaC_2O_4 \longrightarrow CaCO_3 + CO \tag{2(a)}$$

$$2CO \rightleftharpoons CO_2 + C \tag{2(b)}$$

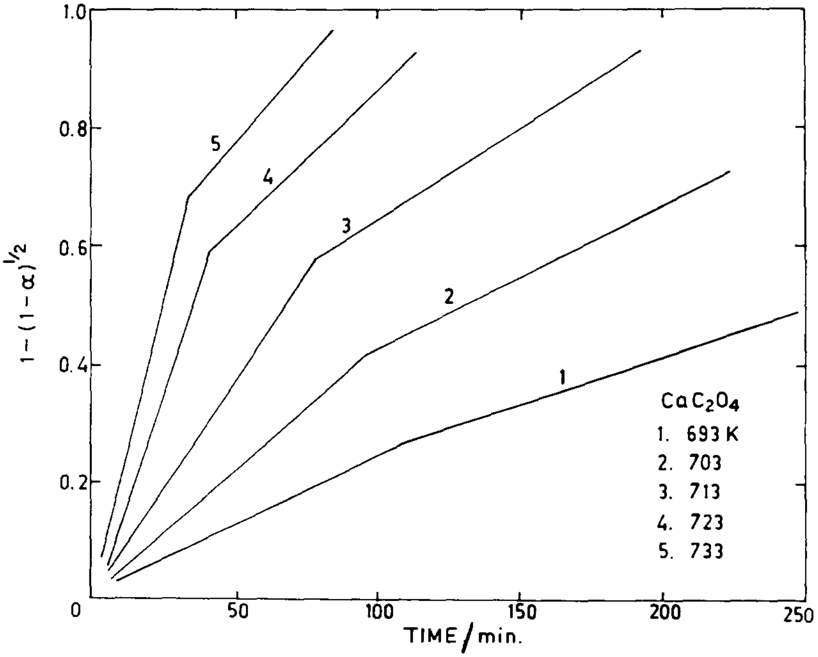


Fig. 5. Phase boundary analysis of the kinetics of thermal decomposition of calcium oxalate.

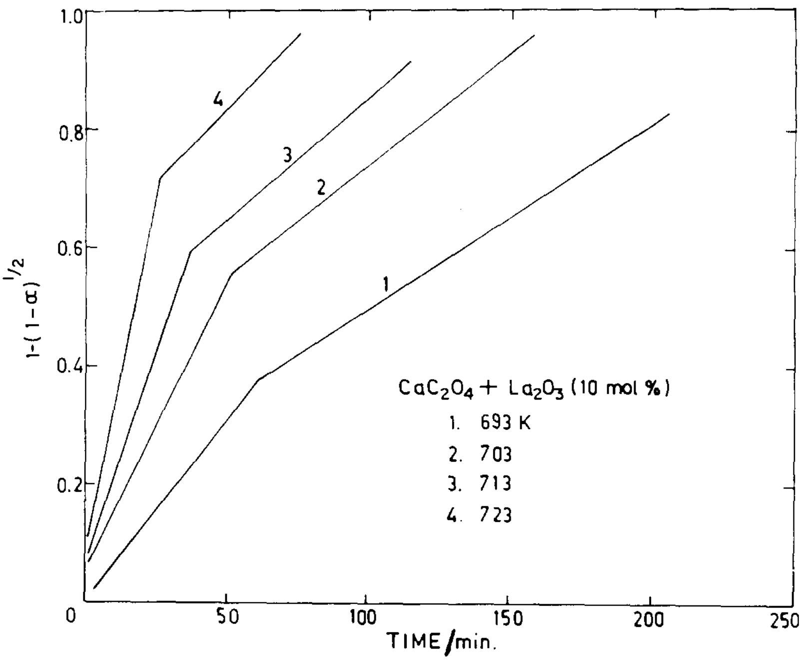


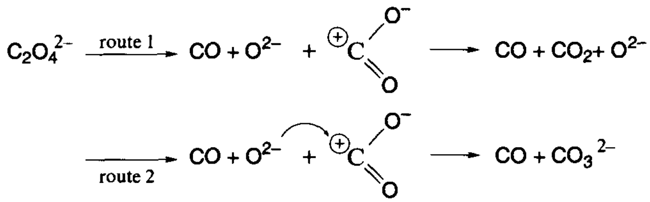
Fig. 6. Phase boundary analysis of the kinetics of thermal decomposition of $CaC_2O_4 + La_2O_3$ mixture.

the disproportionation reaction, Eq. 2(b) is catalysed by the solid product, $CaCO_3$ formed in the first step.

In the sigmoidal regime, the rate initially increases with time until a maximum is attained; this may be ascribed to formation of additional nuclei due to the strain exerted by the growing nuclei [12] and the autocatalytic effect of the solid product phase, $CaCO_3$ [13, 14] formed during decomposition. The data are well fitted to contracting square kinetics indicating that overlapping of the nuclei takes place in a two dimensional fashion. Since the data on both pure salt as well as mixture follow Eq. (1), it is concluded that the admixture enhances the rate of the reaction without altering the mechanism of the process.

In oxalates of bivalent metals, the extent to which the M–O bond is covalent depends on the electronegativity of the metal [15]. Decomposition takes place at a temperature at which rupture of the M–O bond or rupture of the C–O bond takes place. As the metal–O bond becomes stronger, the carbon–O bond is lengthened and breaks first, followed by rupture of the other metal–O bond to yield metal oxide and equimolecular quantities of CO and CO_2. When simultaneous rupture of the M–O bonds takes place, the products are metal and two moles of CO_2. Thus, the reaction depends upon the nature of the cation.

According to Kahwa and Mulokozi [16, 17], the decomposition of oxalates follows a mechanism in which the C–O bond ruptures first, followed by electronic rearrangement leading to formation of either CO, CO_2 and O^{2-} (route 1) CO and CO_3^{2-} (route 2)



In the case of oxalates whose decomposition temperatures vary considerably from those of the corresponding carbonates, as in the present study, the breakdown mechanism follows route 2, which is also supported by the analysis of the end product obtained in the present study.

The catalytic activity of rare earth oxides on the decomposition process may be explained in the light of an electron transfer mechanism. These oxides are strongly basic in nature [18] and donate electrons to satisfy the electronic requirements of the C=O bond weakening to the C–O bond, thus favouring the reaction. Hence, the catalytic activity depends upon the degree of basicity or the ease with which they can donate electrons. This view is also in agreement with the present experimental data, i.e., the rare earth oxides catalyse the process in the order:

$$La_2O_3 > Sm_2O_3 > Gd_2O_3$$

the same as their order of basicity [18].

Though the reaction proceeds with rapid nucleation in the initial period, after a certain time interval the appreciable amount of carbonate generated during the acceleratory period gets deposited over the remaining oxalate ion acting as a barrier to further decomposition, thus slowing down the reaction and resulting in the decay stage. The decrease in activation energy resulting from the admixture may be ascribed to a favourable electron transfer process involved in the decomposition mechanism.

Acknowledgements

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