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EFFECT OF RARE EARTH OXIDES ON THE THERMAL DECOMPOSITION OF BARIUM OXALATE

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Abstract

Catalytic activity of rare earth oxides (REO); La_2O_3, Sm_2O_3, Gd_2O_3 and Ce_2O_3 on the isothermal decomposition of barium oxalate has been studied at 723 K. The α–t plots for pure salt as well as mixtures indicate that the process follows: initial gas evolution, a short acceleratory and a long decay stages. The results of the kinetic analysis show that Prout–Tompkins relationship and two-dimensional phase boundary reaction give best fit of the data for both pure salt as well as mixtures. The rate constants of acceleratory and decay periods are enhanced remarkably by adding REO admixtures and their catalytical activity is in the order $La_2O_3 > Sm_2O_3 > Gd_2O_3 > Ce_2O_3$. The plausible mechanism of decomposition and the role of admixture there on has been discussed in the light of electron transfer process.

Keywords: barium oxalate, catalytic activity, rare earth oxides

Introduction

The influence of rare earth oxides on the thermal decomposition of inorganic salts has drawn the interest of many workers [1–4] as these are the important constituents of high T_c superconductors. The rare earth compounds, may attain a variety of chemical and physical properties depending on the position of localized 4f levels which control the transport and optical properties. These oxides are strongly basic in nature and behave as *p*-type semiconductors [1]. The present study has been undertaken with a view to analyse the thermoanalytical data obtained from pure as well as different REO mixture of barium oxalate to understand the role of catalyst on the decomposition process for promoting the desired reactions.

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Experimental

Barium oxalate was prepared by the double decomposition of $(NH_4)_2C_2O_4$ and barium chloride in dilute aqueous solution. The precipitate was filtered under suction, washed several times with hot water, dried at 423.0 K to constant weight and was characterised by IR spectroscopy as well as by thermogravimetry (TG).

Mixtures of the oxalate and rare earth oxides (10 mol%) (La_2O_3, Sm_2O_3, Gd_2O_3 and Ce_2O_3) were prepared taking required amount of both the materials and grinding thoroughly with a pestle in a mortar. Decomposition study was carried out at 723 K with the help of a constant volume pre-evacuated glass apparatus [5]. The fraction decomposed, $\alpha(=p/p_f)$ was calculated from the pressure (p) values at different time interval, t and final pressure (p_f) after complete decomposition of the oxalate to corresponding carbonate.

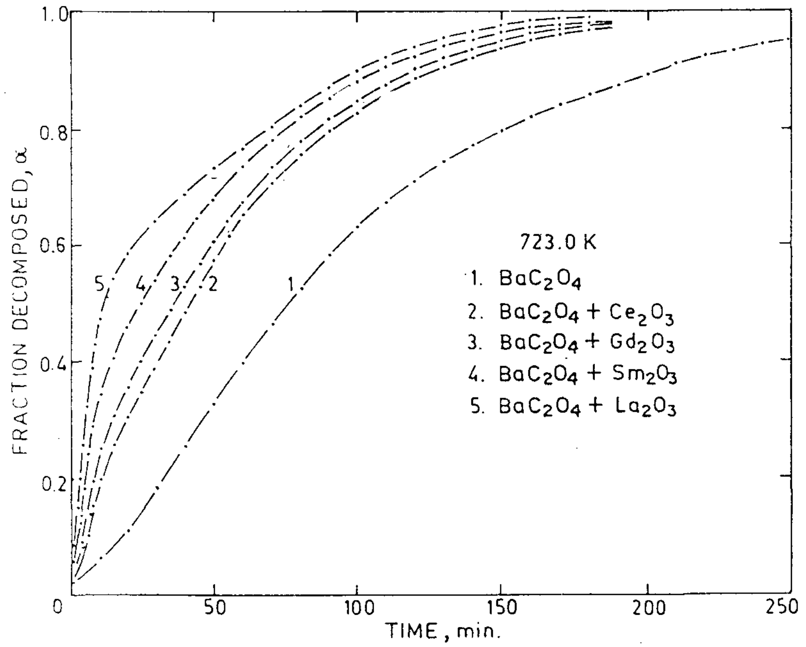


Fig. 1 Thermal decomposition of pure BaC_2O_4 and BaC_2O_4+REOs (10 mol%) at 723 K

Results and discussion

The α-t plots (Fig. 1) of pure as well as mixtures exhibit; initial gas evolution, a short acceleratory and a long decay periods. The initial gas evolution, which is due to release of occluded air from the crystal interior, increases by adding the admixture and completes within the first half minute of the reaction.

Due to instantaneous nucleation at the surface of the crystals acceleratory period begins immediately after the initial gas evolution. Values of fraction decomposed, α at different time intervals for different samples are given in Table 1.

The data indicate that REOs have remarkable effect on the decomposition of barium oxalate. Also a marked difference is observed in the catalytic activity of

Table 1 Fraction decomposed (α) of barium oxalate and barium oxalate+REOs (10 mol%) at 723 K

Material	Fraction decomposed/ α			
	20 min	50 min	100 min	150 min
BaC_2O_4	0.112	0.332	0.630	0.790
$BaC_2O_4+Ce_2O_3$	0.307	0.582	0.837	0.932
$BaC_2O_4+Gd_2O_3$	0.354	0.599	0.846	0.944
$BaC_2O_4+Sm_2O_3$	0.462	0.676	0.880	0.963
$BaC_2O_4+La_2O_3$	0.585	0.731	0.899	0.962

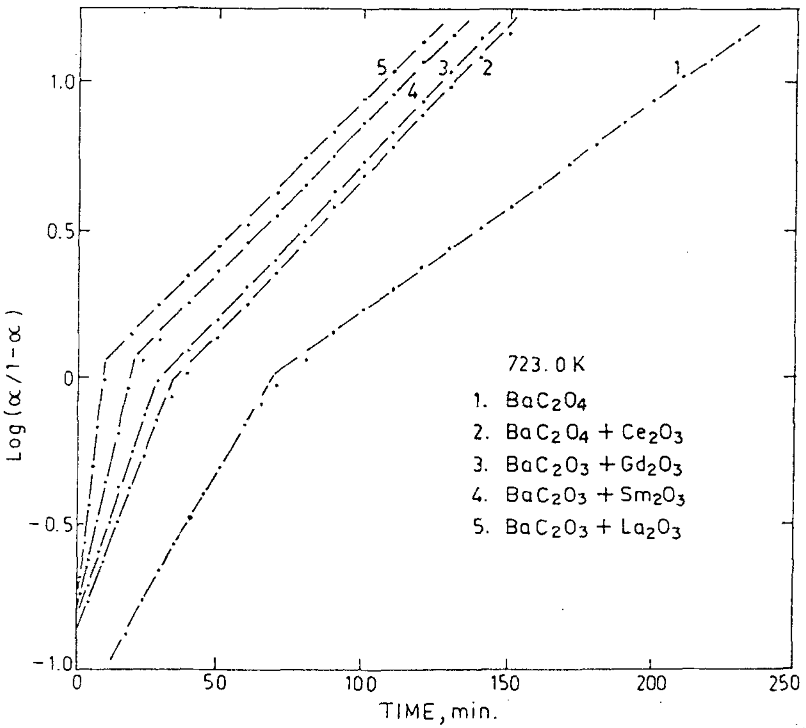


Fig. 2 Prout –Tompkins analysis of the kinetics of thermal decomposition of pure BaC_2O_4 and BaC_2O_4+REOs (10 mol%) at 723 K

various rare earth oxides which follows the order: $La_2O_3 > Sm_2O_3 > Gd_2O_3 > Ce_2O_3$.

The data are analysed according to different kinetic models like Prout–Tompkins relationship [6] (Fig. 2).

$$\log(\alpha/1-\alpha) = k_{A',D'}\,t+C \tag{1}$$

and two dimensional phase boundary condition [7] (Fig. 3).

$$1-(1-\alpha)^{1/2} = k_{A',D'}\,t+C \tag{2}$$

with two different rate constants, for the acceleratory (k_A) and decay (k_D) periods. The ranges of applicability of Eqs 1 and 2 are $0.09 < \alpha < 0.93$ and $0.06 < \alpha < 0.95$, respectively.

Application of the above topochemical models suggest that nucleation occurs in a chain branching manner [2, 6] and is a rapid one, as a result of which the surface of each particle is covered with a layer of product material, barium carbonate.

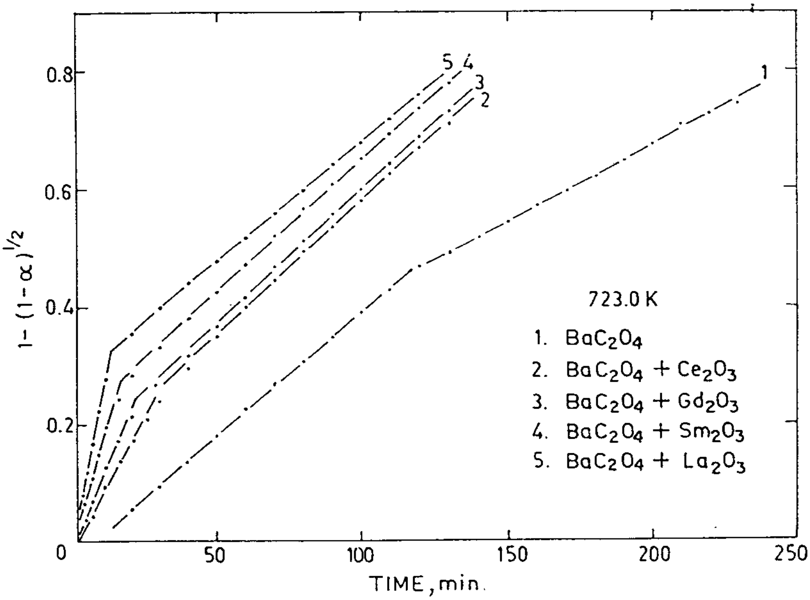


Fig. 3 Phase Boundary analysis of the kinetics of thermal decomposition of pure BaC_2O_4 and BaC_2O_4+REOs (10 mol%) at 723 K

Values of rate constants for different periods, calculated in accordance with aforesaid models are given in Table 2. It is clearly evident from the data that the rate constant of the acceleratory period in the case of mixtures increase in the

Table 2 Effect of REO admixtures (10 mol%) on the velocity constants in the thermal decomposition of barium oxalate at 723 K

Material	Prout-Tompkins		Phase Boundary	
	k_A	k_D	$k_{A'}$	$k_{D'}$
BaC_2O_4	1.75	0.75	0.42	0.26
$BaC_2O_4+Ce_2O_3$	2.48	1.05	0.88	0.46
$BaC_2O_4+Gd_2O_3$	2.86	1.10	1.15	0.45
$BaC_2O_4+Sm_2O_3$	4.42	1.01	1.58	0.45
$BaC_2O_4+La_2O_3$	8.57	1.02	2.33	0.42

k_A, k_D, $k_{A'}$, $k_{D'}$ in 10^2 min^{-1}

order: La > Sm > Gd > Ce and that for the decay period remains almost same, though in all cases, k_A and k_D are facilitated by the admixture as compared to that of pure salt.

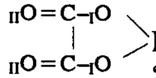
Mechanism

Barium oxalate decomposes as:

$$BaC_2O_4 \rightarrow BaCO_3 + CO \tag{3}$$

Data on pure salt as well as mixture fit same topochemical models, equations 1 and 2, indicating that REOs enhance the rate of the reaction without affecting the mechanism of the process.

Decomposition of metal oxalate [8, 9]



M occurs when a temperature is reached at which rupture of the '$M–O_I$' link is possible or at which rupture of '$C–O_I$' bond occurs. It has been reported [10] from IR studies that as '$M–O_I$' bond becomes stronger, '$C–O_I$' bond is lengthened and '$C–O_{II}$' bond is shortened. It is proposed that thermolysis of ionic metal oxalates involves the initial rupture of the '$C–O_I$' bonds.

The catalytic activity of rare earth oxides on the decomposition of barium oxalate may possibly be explained in the light of electron transfer mechanism. These oxides behave as *p*-type semiconductors [1] and are strongly basic in nature [11] thus donate electrons to satisfy the electron requirement of '$C=O_{II}$' weakening the '$C–O_I$' bond and favouring the decomposition process. Hence, the catalytic activity depends upon the basicity, or the ease with which the REO can donate electron which is also supported by the present experimentally obtained catalytic activity sequence: $La_2O_3 > Sm_2O_3 > Gd_2O_3 > Ce_2O_3$, same as the basicity order reported earlier [11].

When an appreciable amount of carbonate ion is formed in the acceleratory period, it gets deposited over the remaining undecomposed oxalate ion acting as a barrier for further decomposition to proceed resulting deceleration which is evident form the fact that for a given sample, $k_A > k_D$. Well fitting of the data to Eq. (2) also supports the above view.

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Zusammenfassung — Bei 723.0 K wurde die katalytische Aktivität von Seltenerdenoxiden (REO) La_2O_3, Sm_2O_3, Gd_2O_3 und Ce_2O_3 bei der isothermischen Zersetzung von Bariumoxalat untersucht. α-t-Diagramme für Reinstoffe und auch Gemische zeigen den folgenden Prozeßablauf: anfängliche Gasfreisetzung, kurze Prozeßbeschleunigung und lange Ausklangsphase. Die kinetische Analyse ergab sowohl für reine Substanzen als auch für Gemische, daß die experimentellen Angaben am besten mit der Prout-Tompkins-Beziehung und einer zweidimensionalen Grenzphasenreaktion nachvollzogen werden können. Die Geschwindigkeitskonstanten sowohl für die Beschleunigungs- als auch für die Ausklangsphase werden durch Zusatz von REO-Mischungen außergewöhnlich erhöht, die katalytische Aktivität sinkt in der Reihenfolge $La_2O_3 > Sm_2O_3 > Gd_2O_3 > Ce_2O_3$. Ein plausibler Zersetzungsmechanismus und der Einfluß der Gemische darauf wurde unter dem Aspekt von Elektronentransferprozessen diskutiert.