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ROLE OF SEMICONDUCTIVE OXIDES IN THE THERMAL DECOMPOSITION OF BARIUM OXALATE

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ABSTRACT

The effect of the semiconductive oxides CuO, TiO_2 and Cr_2O_3 on the isothermal decomposition of barium oxalate has been studied gasometrically. Plots of the fraction decomposed versus time ($\alpha - t$), for pure salt as well as mixtures, indicate an initial gas evolution, a linear period and a sigmoidal regime consisting of acceleratory and decay stages. The data are best fitted to the Prout–Tompkins relationship indicating that nucleation occurs in a chain-branching manner over the entire sigmoidal zone. The oxides CuO and TiO_2, being p- and n-type semiconductors respectively, do not affect the initial gas loss or the linear period but facilitate the acceleratory stage. However, the former decelerates the rate of the decay period whereas the latter does not affect it. Cr_2O_3, a p-type semiconducting oxide, retards the rate in both the stages.

INTRODUCTION

The thermal decomposition of alkaline earth metal oxalates [1,2] have attracted the interest of many workers because the final product, the oxides, possess lattice imperfections and other properties that are necessary for their functions as reactive solids. Although the role of semiconducting oxides in the decomposition of inorganic molecular ions has been reported by many workers [3–5], the alkaline earth metal oxalates, which are superconducting materials, have not received much attention. It is of interest, therefore, to investigate the role of additives (semiconducting oxides) on the thermal decomposition of barium oxalate with a view to increasing the critical temperature (T_c) of the superconducting material [6,7] by applying the results of the present study.

EXPERIMENTAL

Barium oxalate, AR grade, was dried at 380.0 K in a thermostated electric hot-air oven and was stored over phosphorus pentoxide. The metal oxides,

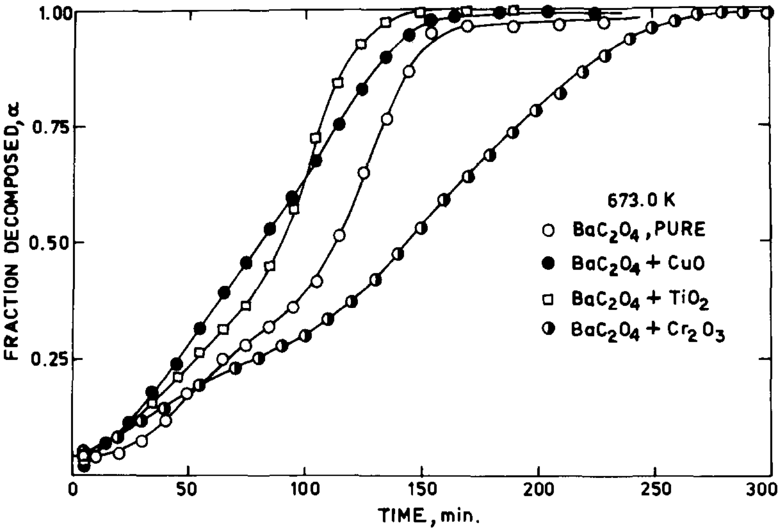

Fig. 1. Role of additives on the isothermal decomposition of barium oxalate at 673.0 K.

CuO, TiO_2 and Cr_2O_3, were BDH laboratory reagent grade. All oxalate–catalyst mixtures were prepared by taking the required proportion (10.0% w/w) of the corresponding salts and grinding them thoroughly in an agate mortar and pestle. The isothermal decomposition study of pure salt and mixtures was undertaken at 673.0 K by measuring the pressure of gas evolved in a constant volume pre-evacuated glass apparatus. The fractional decomposition ($\alpha = p/p_f$) was calculated from the pressure value, p, at any time, t, and p_f, the final pressure on complete decomposition.

RESULTS AND DISCUSSION

Decomposition isotherms, Fig. 1, for pure salt and mixtures, show an initial gas evolution, a slow linear reaction and a sigmoidal regime consisting of acceleratory and decay stages. The initial gas evolution at $\alpha \simeq 0.06$ which is due to the release of occluded air from the accessible interior of the crystal, is not affected by the metal oxides. The linear reaction stage, represented as

$$\alpha = k_1 t + C_1 \tag{1}$$

where k_1 is the rate constant and C_1 is another constant, is also unaffected by additives and may be attributed to surface decomposition caused by the growth of nuclei generated in the initial period. The data for both pure salt and mixtures are well fitted to the Prout–Tompkins relationship (Fig. 2)

$$\log[\alpha/(1-\alpha)] = k_{2,3} t + C_{2,3} \tag{2}$$

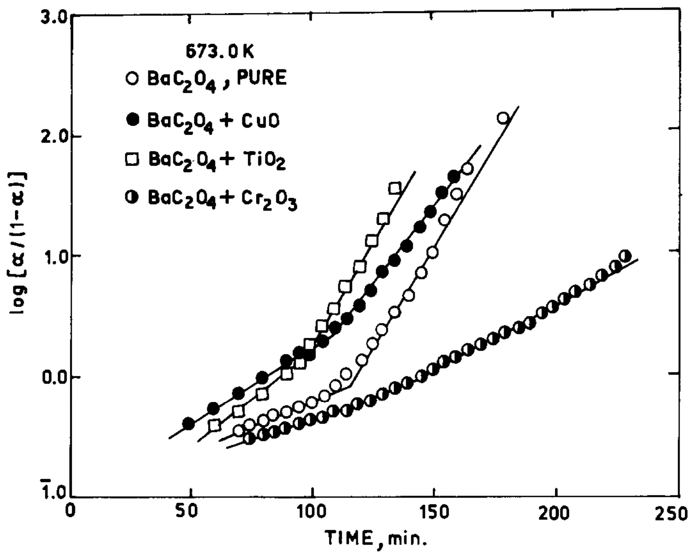

Fig. 2. The Prout–Tompkins relationship in pure and catalyst mixtures of barium oxalate at 673.0 K.

where k_2 and k_3 are the rate constants of the acceleratory and decay periods, indicating that nucleation occurs in a chain-branching manner over the entire sigmoidal regime.

It can be seen that both CuO and TiO_2, being p- and n-type semiconductors respectively, enhance the acceleratory period. However, CuO retards the rate of the decay stage, whereas TiO_2 does not affect it. But Cr_2O_3 decelerates the rate in both stages. In the sigmoidal decomposition region, the rate initially increases with time until a maximum is attained. The enhancement in the rate of decomposition in the acceleratory period may be attributed to the strain exerted by the growing nuclei and the autocatalytic effect of the solid product phase, the oxide generated during decomposition [5,8]. Deceleration in the rate of decomposition possibly occurs due to a decrease in the catalytic activity as decomposition progresses and due to a reduction in the flux of oxalate ions adsorbed on the catalyst surface [9].

MECHANISM OF DECOMPOSITION AND ROLE OF THE CATALYST

Barium oxalate decomposes at 673.0 K

$$BaC_2O_4 \rightarrow BaO + CO_2(+CO) \qquad (3)$$

The chemical properties of its constituents exert some control over the decomposition kinetic behaviour. The reaction mechanism is complex and the CO/CO_2 ratio is temperature dependent but not appreciably so in the temperature range employed in the present study. The initial step is plausibly electron transfer followed by bond redistribution within the anion leading to the evolution of CO_2 [10]. A p-type semiconductor would favour the electron-transfer process because of the presence of positive holes in the d-orbitals [5] which would be available to accept electrons from an adsorbed oxide ion. In n-type oxides, the delocalised electrons in the conduction band contribute to their electrical conductivity. On heating these oxides at high temperature in an oxygen atmosphere, the number of electrons in the conduction band decreases, leading to a lower electrical conductance of the oxide. Thus, an n-type oxide takes up very little oxygen as $O^-_{(ads)}$ compared with a p-type oxide and, hence, is poor catalyst [11].

Although Cr_2O_3, a p-type semiconductor, shows high electrical conductivity, partial or complete electron transfer results in an apparently irreversible change in the oxidation state of the metal ion, which may be oxidised to chromate ($Cr_2O_3 \rightarrow CrO_4^{2-}$) during the process.

The present data are not in agreement with the views of earlier workers [4,12] that p-type semiconductors are good catalysts and that n-type oxides are poor catalysts. In conclusion, the influence of metal oxide catalysts on the decomposition reactions may not be solely based on the semiconductive properties of the oxides but may be the result of the specificity of the catalyst for each reaction.

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