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KINETICS OF THERMAL DECOMPOSITION OF STRONTIUM ZIRCONYL CARBONATE, $Sr_2Zr_2O_5CO_3$

T. GANGADEVI, M. SUBBA RAO and T.R. NARAYANAN KUTTY

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012 (India)

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ABSTRACT

The decomposition kinetics of the carbonate $Sr_2Zr_2O_5CO_3$ are greatly influenced by thermal effcts during its formation. ($\alpha - t$) curves are found to be sigmoidal and could be analysed on the basis of power law equations followed by first-order decay. The presence of carbon in the vacuum-prepared sample of carbonate has a strong deactivating effect. The carbonate is fairly crystalline and its decomposition leads to the formation of crystalline strontium zirconate.

INTRODUCTION

Carbonates of composition $A_2B_2O_5CO_3$ (A = Ba, Sr, Ca, Pb; B = Ti, Zr) have been identified and isolated as intermediates during the decomposition of titanyl and zirconyl oxalates of alkaline earths and lead [1–6]. Some of these carbonates are crystalline and have been identified as pure phases by X-ray powder diffraction [2,4,5]. All these carbonates decompose further to give the corresponding metatitanates or metazirconates having perovskite structures. We have been interested in studying the kinetics of thermal decomposition of these unusual carbonates. The kinetics of thermal decomposition of $Ba_2Ti_2O_5CO_3$ and $Ba_2Zr_2O_5CO_3$ have been reported in previous communications [7,8]. The present communication deals with the kinetics of decomposition of the carbonate $Sr_2Zr_2O_5CO_3$ (S).

EXPERIMENTAL

Materials

Strontium zirconyl oxalate tetrahydrate, $Sr[ZrO(C_2O_4)_2] \cdot 4H_2O$(SZO), was prepared by the metathesis of strontium acetate and freshly prepared ammonium zirconyl oxalate under controlled pH and reagent concentration [6].

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SZO was heated in air at 673 K for 48 h to produce the compound $Sr_2Zr_2O_5CO_3$ (sample S_1). A portion of S_1 was allowed to age for six months at an ambient temperature around 298 K (sample S_2). A third sample of $Sr_2Zr_2O_5CO_3$ was prepared by heating SZO at 673 K for 48 h in vacuum (sample S_3).

Methods

Kinetic studies were conducted in a constant-volume vacuum manifold [7] which could be evacuated to 10^{-6} Torr. The volume of the system could be varied from 0.5 to 5 l. The increase in carbon dioxide pressure was used to follow the kinetics of decomposition. X-ray powder diffraction patterns were recorded photographically using a Philips Debye–Scherrer camera of 57.3 mm diameter and nickel-filtered copper K_α radiation from a Rich–Seifert X-ray unit.

RESULTS AND DISCUSSION

The compound $Sr_2Zr_2O_5CO_3$ is distinctly crystalline and its identity as a separate phase has been established by its X-ray diffraction pattern [5].

S_1 and S_2 are white flowing powders while S_3 is black because of the presence of elemental carbon deposited on it during its preparation. Because of their different thermal histories, the decomposition kinetics of the three samples show differences both in the temperature range of their decomposition and the magnitude of their activation energies. The detailed kinetic results are presented in Table 1.

TABLE 1

Results of the decomposition kinetics of the carbonate S

	Temp. range of decomposition (K)	α_i	Equation obeyed		Activation energy (kJ mol^{-1})	
			Acceleration	Decay	Acceleration	Decay
S_1	823–848	0.50	$\alpha = k^3(t+t_0)^3$	$-\log(1-\alpha) = kt$	230	198
		0.60	$\log\frac{\alpha}{1-\alpha} = kt$		255	239
S_2	803–823	0.30	$\alpha = k^3(t+t_0)^3$	$-\log(1-\alpha) = kt$	185	170
		0.55	$\log\frac{\alpha}{1-\alpha} = kt$		258	153
S_3	938–958	0.50	$\alpha = k^3(t-t_0)^3$ $0 < \alpha < 0.2$		843	
			$\alpha = k^2(t-t_0)^2$ $0.2 < \alpha < 0.5$	$-\log(1-\alpha) = kt$	745	628
		0.50	$\log\frac{\alpha}{1-\alpha} = kt$		721	433

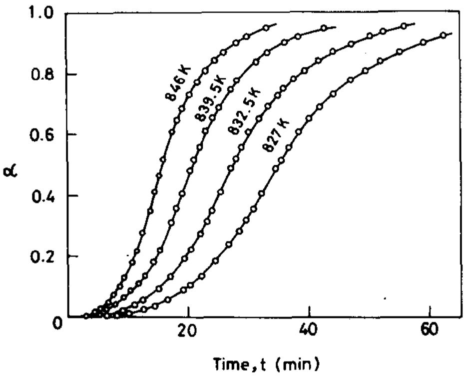

Fig. 1. ($\alpha-t$) plots for S_1.

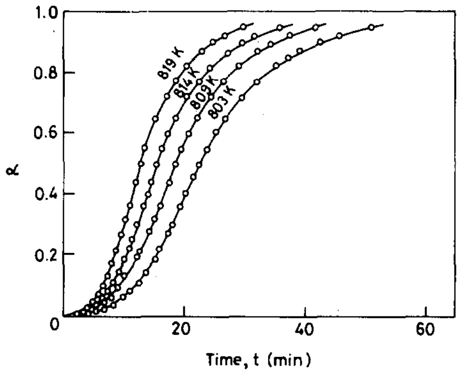

Fig. 2. ($\alpha-t$) plots for S_2.

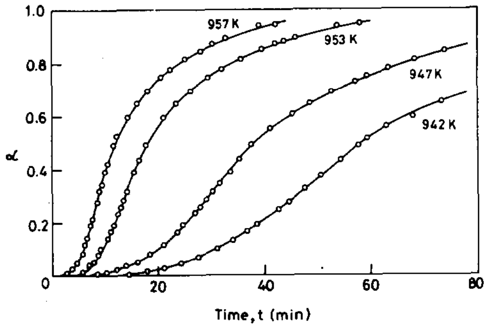

Fig. 3. ($\alpha-t$) plots for S_3.

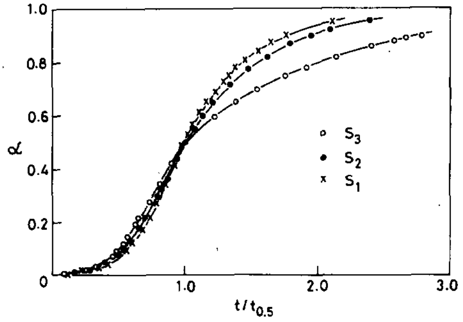

Fig. 4. α vs. $t/t_{0.5}$ plots for S_1, S_2 and S_3.

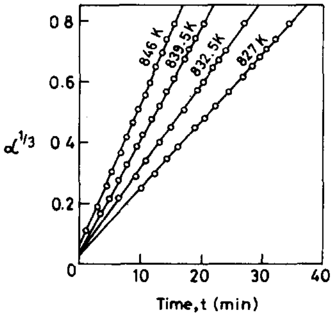

Fig. 5. $\alpha^{1/3}$ vs. t plots for S_1.

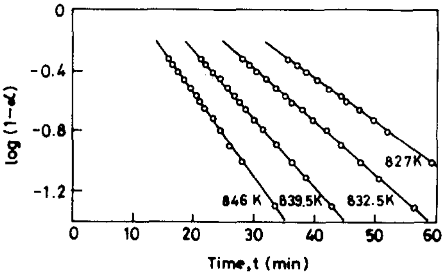

Fig. 6. First-order plots for S_1.

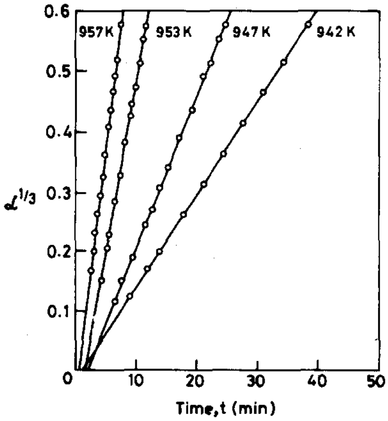

Fig. 7. $\alpha^{1/3}$ vs. t plots for S_3.

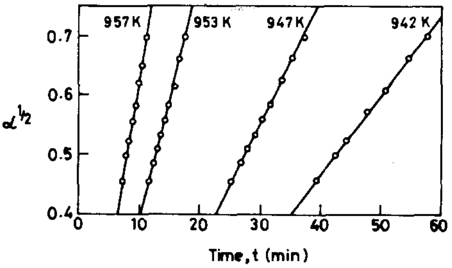

Fig. 8. $\alpha^{1/2}$ vs. t plots for S_3.

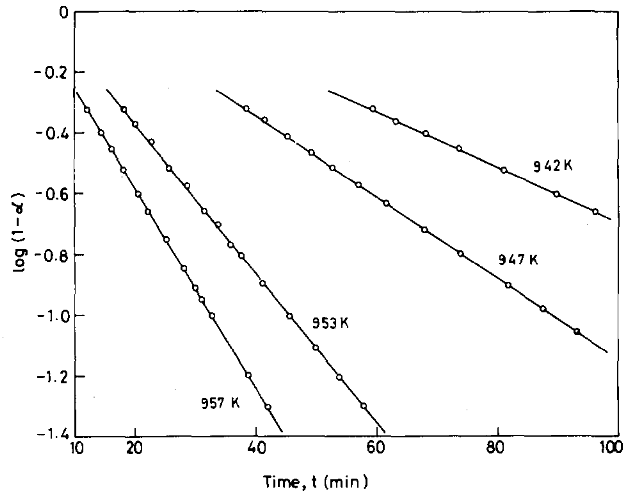

Fig. 9. First-order plots for S_3.

Typical (α–t) plots for S_1, S_2 and S_3 are shown in Figs. 1–3, respectively. The plots for S_2 are similar to those of S_1. Figure 4 shows a reduced time plot of the same data, which do not overlap one another, indicating different decomposition mechanisms for the three samples. Samples S_1 and S_2 obey a cube law, $\alpha = k^3(t + t_0)^3$, in the acceleratory period and a first-order law in the decay period (Figs. 5 and 6). For S_1 the acceleratory period is more pronounced, the inflection point being 0.5α, whereas for S_2 it is 0.3α. S_3 obeys a cube law in the region $0 < \alpha < 0.2$ and the rest of the acceleratory period can be described by a square law. The inflection point α_i is again 0.5α. The decay period obeys a first-order law (Figs. 7–9). Activation energies are calculated from an Arrhenius plot (Fig. 10).

Two factors come to light during this kinetic investigation: (i) the kinetics are affected by the thermal histories of the materials and (ii) the decomposi-

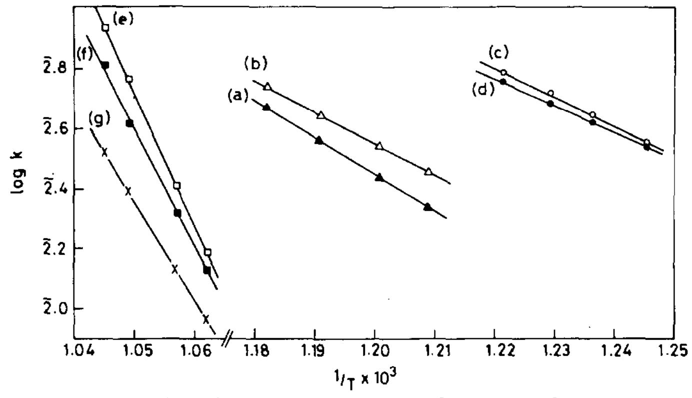

Fig. 10. Arrhenius plots: (a), (b) S_1; (c), (d) S_2; (e), (f), (g) S_3.

tion is inhibited by the presence of a foreign material; the fine deposit of carbon in sample S_3 retards the decomposition both by physical interference and by poisoning the centres of reactivity.

The difference in the kinetic behaviour of the three samples can be explained on the basis of their conditions of preparation, as has been done for the decomposition kinetics of $Ba_2Ti_2O_5CO_3$ [7]. During the preparation of S_1, by heating SZO in air, the exothermicity of the oxalate decomposition causes thermal strain and induces extensive nucleation. Thus, during the acceleratory period for S_1, obedience of a cube law implies instantaneous nucleation and three-dimensional growth. During the formation of S_3, the decomposition of oxalate is endothermic and, hence, during the kinetics of decomposition of S_3, nucleation becomes kinetically important. Therefore, the initial cube law obedience implies a nucleation step followed by two-dimensional growth. The higher temperature range of decomposition and the high activation energies for S_3 are attributed to the deactivating effect of the carbon deposit.

The kinetic data were also analysed employing the Prout–Tompkins equation but the fit of the experimental data was not as good as with the power laws followed by the first-order decay law.

The final product, strontium zirconate, isolated at any stage of decomposition is found to be distinctly crystalline. This suggests the carbonate $Sr_2Zr_2O_5CO_3$ (which is also crystalline) and the product $SrZrO_3$ may be topotactically related.

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