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Note

NON-ISOTHERMAL KINETICS IN MIXTURES OF BARIUM CARBONATE AND TITANIUM DIOXIDE (ANATASE)

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A non-isothermal kinetic analysis of the influence of sodium carbonate on the interaction between barium carbonate and anatase is presented.

In a previous note, the results concerning non-isothermal kinetic parameters in the system barium carbonate–rutile were presented [1]. Following our research, this paper deals with the system barium carbonate–anatase, the higher reactivity of the second reactant being already mentioned in the literature [2].

EXPERIMENTAL

The following mixtures were used: (1) $BaCO_3 : TiO_2$ (1 : 1); (2) $BaCO_3 : TiO_2$ (1 : 1) + 1% $Na_2CO_3 \cdot 1.5\ H_2O$; and (3) $BaCO_3 : TiO_2$ (1 : 1) + 5% $Na_2CO_3 \cdot 1.5\ H_2O$.

The heating curves were recorded with a derivatograph MOM Budapest type Paulik–Paulik–Erdey. Samples of 0.1 g were heated between 20 and 1500°C with a heating rate of 7.5 K min^{-1}. In order to establish the phase composition of the mixtures and the mean sizes of the crystallites, a Philips X-ray diffractometer with Cr K_α radiation was used. The mean sizes of the crystallites, calculated with Scherrer's formula [3], were: 328 Å for $BaCO_3$; 415 Å for TiO_2 (anatase); and 4030 Å for $Na_2CO_3 \cdot 1.5\ H_2O$.

The derivatogram corresponding to mixture 1 is given in Fig. 1. Two decomposition steps can be seen.

The first step occurs between 500 and 720°C with a practically constant decomposition rate, followed at higher temperatures by an increase in the rate until a maximum value is reached at 920°C. This first step could be assigned to the partial decomposition of $BaCO_3$. The second decomposition step occurs with a maximum rate at 1100°C and corresponds to the simultaneous decomposition of $BaCO_3$ and reaction of BaO with TiO_2. These assumptions were confirmed by X-ray phase analysis data of the heated mixture at different temperatures. The increase of the decomposition rate in the first step, as well as the rather high decomposition rate in the

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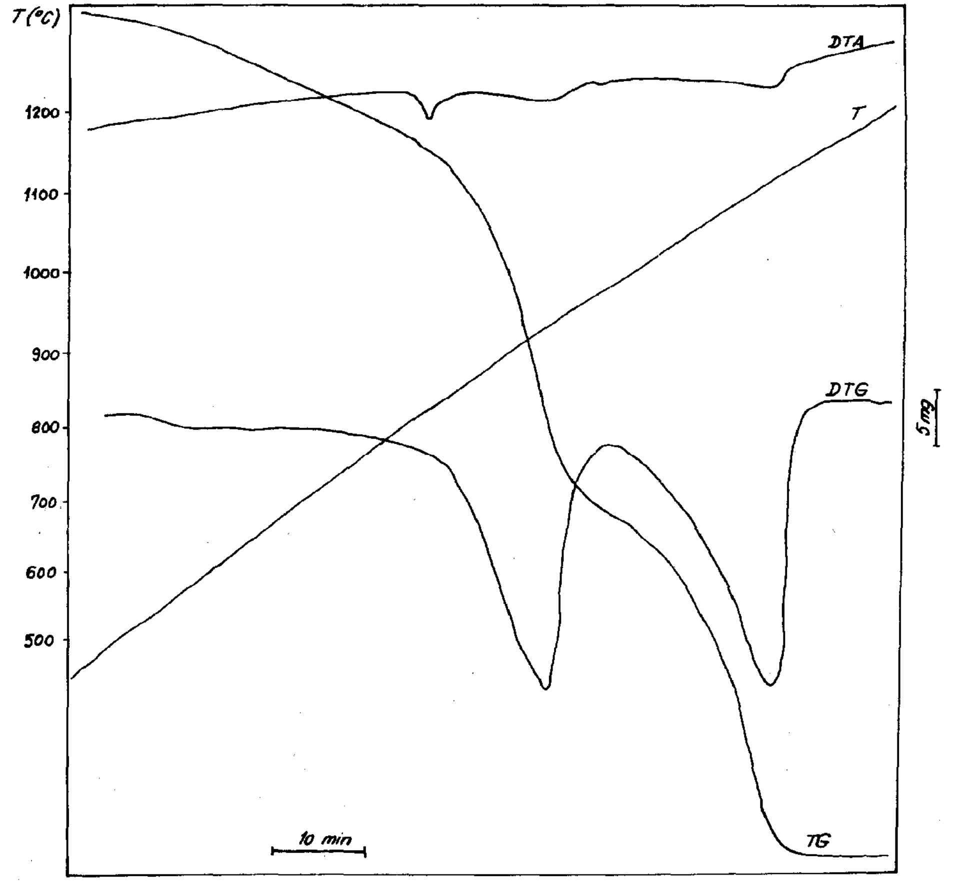

Fig. 1. Heating curves for mixture 1.

second step, are probably due to the phase transitions from orthorhombic to hexagonal (810°C) and hexagonal to cubic (980°C) undergone by barium carbonate. Thus, the reactivity is increased through the Hedvall effect [4]. The kinetic parameters of these decomposition steps evaluated by the Coats–Redfern method [5] are, respectively: $n = 0$, $E = 41$ kcal mol^{-1} and $A = 5.5 \times 10^4$ s^{-1} for the first step; and $n = 0$, $E = 61$ kcal mol^{-1} and $A = 0.5 \times 10^6$ s^{-1} for the second step.

The derivatogram corresponding to mixture 2 (Fig. 2) exhibits three decomposition steps, the weight ratios of the evolved CO_2 being 1 : 4 : 2.

During the first step, which occurs between 540 and 730°C, the decomposition of $BaCO_3$ is initiated. The X-ray diffractogram of a sample heated at 600°C exhibits the following compounds: $BaCO_3$, TiO_2, BaO_2 and BaO. The second step occurs between 730 and 950°C. The X-ray diffractogram exhibits the following phases: $BaTiO_3$, $BaCO_3$ and TiO_2. The high decom-

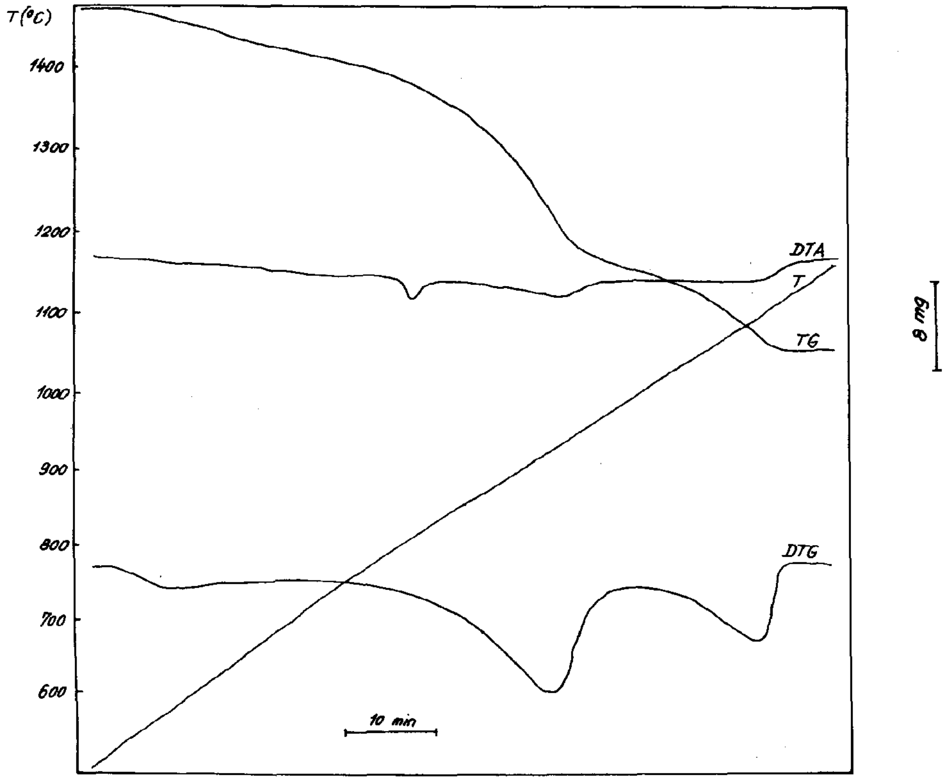

Fig. 2. Heating curves for mixture 2.

position rate in this step can be assigned to a double Hedvall effect due to the phase transition from orthorhombic to hexagonal of $BaCO_3$ and to the melting of Na_2CO_3. At higher temperatures, a third decomposition step extended to 1120°C is seen. The kinetic parameters for these three steps are, respectively: $n = 1$, $E = 25.4$ kcal mol^{-1} and $A = 2.1 \times 10^2$ s^{-1} for the first step; $n = 0$, $E = 36.1$ kcal mol^{-1} and $A = 5 \times 10^3$ s^{-1} for the second step; and $n = 0$, $E = 41.6$ kcal mol^{-1} and $A = 5 \times 10^3$ s^{-1} for the third step.

The derivatogram of mixture 3 also exhibits three decomposition steps, the weight ratios of the evolved CO_2 being 5 : 10 : 1 (Fig. 3).

For the first step (decomposition of $BaCO_3$) and the second step (decomposition of $BaCO_3$ and reaction of BaO with TiO_2), the kinetic parameters are, respectively: $n = 0$, $E = 25.8$ kcal mol^{-1} and $A = 2.7 \times 10^3$ s^{-1}; and $n = 1$, $E = 50.0$ kcal mol^{-1} and $A = 2.0 \times 10^7$ s^{-1}.

The kinetic parameters for the third step of decomposition were not determined, due to the small amount of CO_2 evolved in this step, resulting in errors in the experimental data.

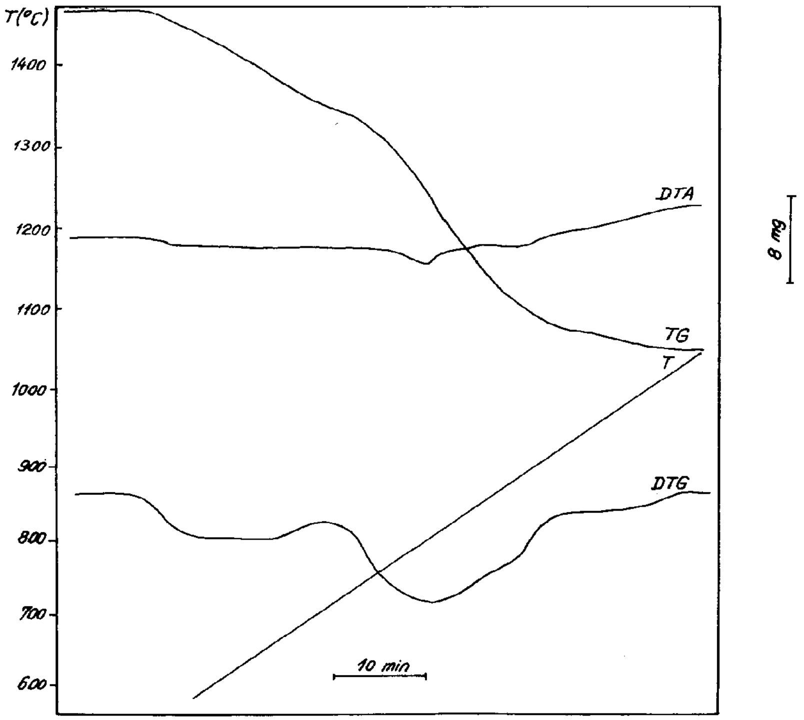

Fig. 3. Heating curves for mixture 3.

From the above data it can be concluded that sodium carbonate has a significant influence on the number of steps involved in the interaction between barium carbonate and anatase, as well as on the kinetic stability of this system.

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