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Note

A THERMOGRAVIMETRIC STUDY OF THE DECOMPOSITION OF BASIC COPPER CARBONATE

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Basic carbonates are appropriate initial compounds for the preparation of highly dispersed metal oxides. For this reason, the kinetics and mechanism of the thermal decomposition of basic copper carbonate have been studied using data from thermogravimetric analyses made under both isothermal and non-isothermal conditions.

An A.R. basic copper carbonate was used for the experiments. The amount of CO_2 in the product, as determined by thermogastitrimetry (TGT), was 19.5% (theoretical amount, 19.2%). Thermogravimetric (TG) measurements were carried out by a Derivatograph-1500 apparatus. The TG curves were obtained under isothermal and non-isothermal conditions using a polyplate sample holder. The heating rate was 5 °C min^{-1}.

Figure 1 shows the DTA, TG and TGT curves of the initial product under non-isothermal conditions. Evidently, the process is one-stage and the decomposition yields no by-products. The data on the decomposition coincide with those given in the literature [1–5].

The decomposition of $CuCO_3 \cdot Cu(OH)_2$ was also investigated by a Q-derivatograph using the same type of crucibles. Figure 2 presents the TG curves obtained under non-isothermal (curve 1) and quasi-isothermal (curve 2) conditions. When the heating proceeds at a constant rate, basic copper carbonate is decomposed at 290–330 °C, while quasi-isothermal decomposition occurs at 240–280 °C. Taking into account the principle of Q-thermal analysis [3], one may say that the shape of curve 2 determines the decomposition process as a non-equilibrium one, occurring with an initial overheating of about 20 °C, the latter being attributed to an intensive nucleation process [4,6].

The data from the non-isothermal TG curve concerning the decomposition degree as a function of temperature were processed using the Coats–Redfern equation [7–9]

$$\log \frac{g(\alpha)}{T^2(1-n)} = \log \frac{ZE}{Rq} - \frac{E}{2.3RT} \qquad (1)$$

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where $g(\alpha)$ is an integral form of the function $f(\alpha)$; T is the absolute temperature (K); Z is the pre-exponential factor in the Arrhenius equation (s^{-1}); R is the gas constant (J mol^{-1} K^{-1}); q is the linear rate of temperature increase; E is the apparent activation energy of the process (J mol^{-1}); and n is a formal reaction order, $n = 0$, 1/2, 2/3 and 3.

For a properly chosen function, $g(\alpha)$, the graphical dependence log $g(\alpha)/T^2$ versus $1/T$ should be a straight line with a slope of $-E/2.3R$.

The non-isothermal curve was analysed using eqn. (1). Various analytical forms of the integral function $g(\alpha)$ describing interface movement (R), nucleation and growth of nuclei (A) and diffusion (D) have been used [10–12].

The graphical dependences of the characteristic functions $g(\alpha)$ are given in Fig. 3. From this figure and the corresponding correlation coefficients, r, it is obvious that the experimental results are well described by equations corresponding to mechanism A (F_1, A_2, A_3 and A_5) over the whole range of decomposition ($0.13 \leqslant \alpha \leqslant 0.95$). The two-dimensional (mechanism F_1) and three-dimensional (mechanism A_5) nucleus growth, during which the number of nuclei does not change, belong to this group of mechanisms. In this case, the rate-limiting stage is the diffusion of the reactant species through the product boundary layer. An analogous case is that of mechanisms A_2 and A_3. However, in this case the chemical incorporation of the reactant species into the phase being formed is rate determining. For mechanisms R (R_2 and R_3) one can say that they are also probable but their linearity is not

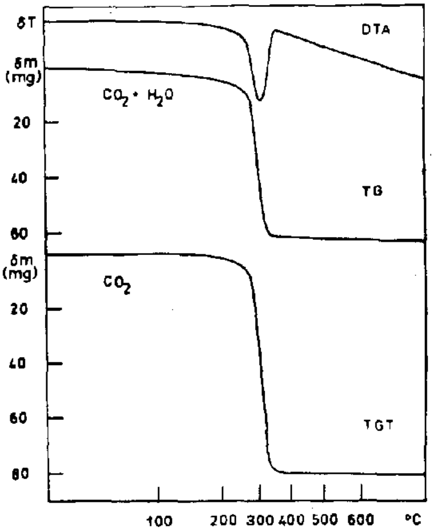


Fig. 1. DTA, TG and TGT decomposition curves of $CuCO_3 \cdot Cu(OH)_2$. Heating rate, 5 °C min^{-1} (in nitrogen).

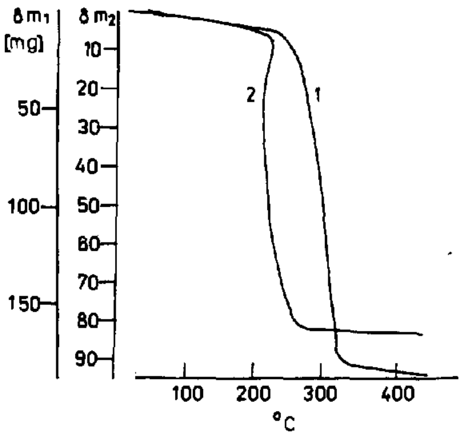
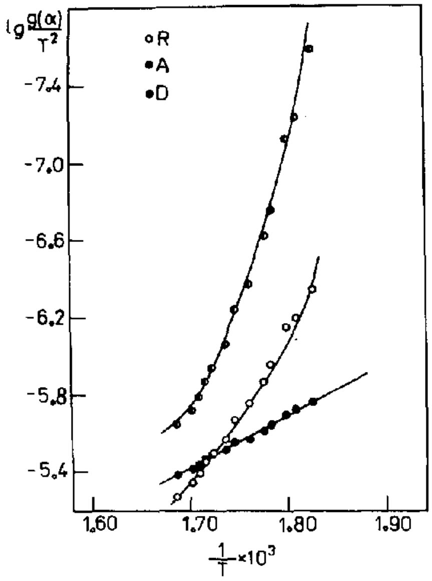


Fig. 2. TG decomposition curves of $CuCO_3 \cdot Cu(OH)_2$. (1) Heating rate, 5 °C min^{-1} (in air); (2) quasi-isothermal heating, decomposition rate, 0.5 mg min^{-1} (in air).



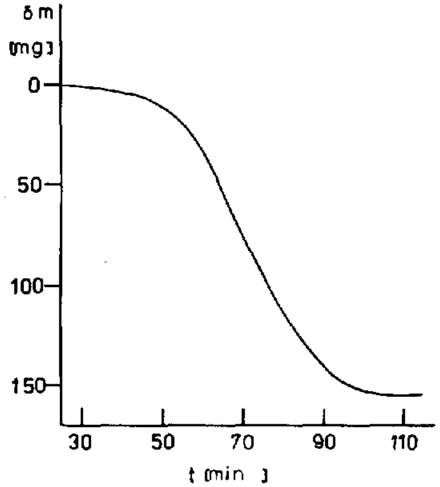
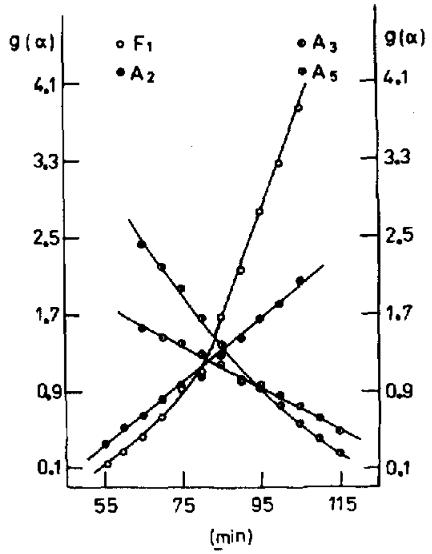


Fig. 3. Data on the decomposition of $CuCO_3 \cdot Cu(OH)_2$ analysed according to mechanisms R ($r = 0.9958$), A ($r = 0.9985$) and D ($r = 0.9893$).

Fig. 4. Isothermal TG decomposition curve of $CuCO_3 \cdot Cu(OH)_2$. $t = 240\,^{\circ}C$ (in air).



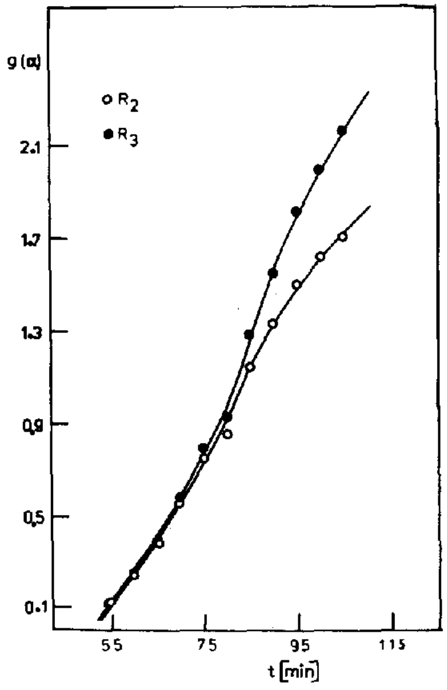


Fig. 5. Data on the isothermal decomposition of $CuCO_3 \cdot Cu(OH)_2$ analysed according to mechanisms F_1 ($r = 0.2312$), A_2 ($r = 0.9979$), A_3 ($r = 0.9984$) and A_5 ($r = 0.9932$).

Fig. 6. Data on the isothermal decomposition of $CuCO_3 \cdot Cu(OH)_2$ analysed according to mechanisms R_2 ($r = 0.9960$) and R_3 ($r = 0.9940$).

so well expressed. These mechanisms correspond to instantaneous surface nucleation leading to the formation of a thin product layer on the particle surface. The process of growth is associated with two-dimensional (mechanism R_2) or three-dimensional (mechanism R_3) movement of the interface to the grain centre.

The application of the integral method to the determination of the decomposition kinetics and mechanism enables one to describe, in many cases, the data from TG curves by more than one equation. This is due to the specificity of the integral methods [13]. For this reason, Criado et al. [8,9] suggested using the fact that the integral kinetic equation, which describes the isothermal decomposition, is a function of time, i.e.

$$g(\alpha) = kt \qquad (2)$$

This means that the dependence $g(\alpha)$ versus t will be linear only when the function $g(\alpha)$ describes the decomposition mechanism well under isothermal conditions.

The TG decomposition curve is given in Fig. 4, whereas Figs. 5 and 6 show the dependences of $g(\alpha)$ on t. The same dependences indicate that the mechanisms A_2 and A_3 are the most probable rate-limiting stages of the decomposition process. The graphical dependences, $\log g(\alpha)/T^2$ versus $1/T$ and $g(\alpha)$ versus t, confirm the results obtained on decomposition under quasi-isothermal conditions.

The method used for the determination of the kinetics and mechanism of thermal decomposition on the basis of TG analysis data gives useful preliminary information on the kinetics of thermal decomposition of basic copper carbonate.

It was established that under definite conditions the process kinetics can be described by the Avrami–Erofeev kinetic equations concerning the volume growth of the new solid-phase nuclei. From the slope of the straight lines in the dependence $\log g(\alpha)/T^2$ versus $1/T$ (Fig. 3) the apparent activation energy of the thermal decomposition process can be determined. For mechanism A_2 it is 79.5 kJ mol^{-1}, whereas an activation energy of 50.2 kJ mol^{-1} corresponds to mechanism A_3. The activation energy values found are close to those obtained by Živković et al. [14,15]. It should be pointed out that mechanism A_2 describes the two-dimensional growth of nuclei with a constant nucleation rate leading to a linearly increasing number of nuclei, which is controlled by the chemical reaction proceeding on the surface of the new solid phase being formed. A more probable mechanism is A_3 which describes an analogous case in which, however, three-dimensional growth of nuclei occurs.

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