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Note

Kinetics of thermal decomposition of copper basic carbonate

Part I. The analysis of thermogravimetric data

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The kinetic parameters, activation energy (ΔE^*) and reaction order (n), can be determined from the results of thermogravimetric analysis, obtained in the isothermal[1–4] and non-isothermal decomposition[5–7]. In both cases, the common equation for the process of thermal decomposition can be shown in the following manner

$$\text{A(solid)} \rightarrow \text{B(solid)} + \text{C(gas)} \qquad (1)$$

in which B forms at high energy sites in the lattice of A.

The authors have used non-isothermal thermogravimetric analysis to determine the kinetic parameters of thermal decomposition of copper basic carbonate, and the method according to Chatterjee[6] was employed for the evaluation of data. This method is more suitable than other similar methods which can be used for the determination of thermogravimetrical data[2,8], especially in the case when two or more processes are possible to develop in the system investigated.

EXPERIMENTAL

A Netzsch differential thermoanalyzer, Model 409, was used for the DTA measurements, working with thermocouples of Pt-Pt-Rh and the crucibles for the samples were of calcinated alumina.

Thermogravimetric investigations were performed on the Thermic Balance of Netzsch, Model 409, with the holder and a crucible for samples made from calcinated alumina. The thermocouple for measuring the temperature of the stove is of Pt-Pt-Rh, and its peak is positioned in the same level with the surface of the sample being investigated.

The copper basic carbonate powder with a purity of 98% used for these investigations has been synthesized by the Chemical Industry Kemika, Zagreb.

Kinetic method

Chatterjee's method for the evaluation of thermogravimetric data to calculate the kinetic parameters of thermal decomposition used in this work by the authors, requires the performance of two experiments with different initial sample weights, under the same reaction conditions.

The heterogeneous kinetic reaction can be represented by the following general equation for the rate, P:

$$P = -\frac{\mathrm{d}w}{\mathrm{d}t} = K'w^n \tag{2}$$

where K' = constant of the specific rate of reaction, w = the active weight of the reaction material, t = time passed from the beginning of the process, n = pseudo order of reaction.

Mechanisms derived for a heterogeneous reaction from the pseudo order of reaction are of little intrinsic significance and, at best, represent a gross approximation. If K' is expressed in terms of an Arrhenius equation, then

$$K' = A\mathrm{e}^{-\Delta E^{*}/RT} \tag{3}$$

where A = pre-exponential term, ΔE^{*} = activation energy, T = absolute temperature, and R = molar gas constant. Substituting eqn (3) into eqn (2):

$$P = Aw^n\mathrm{e}^{-\Delta E^{*}/RT} \tag{4}$$

or

$$n \log w - \log P = \frac{\Delta E^{*}}{2.303\,RT} - \log A \tag{5}$$

For thermograms obtained for two different initial weigts of the starting substance under similar experimental conditions, eqn (5) gives

$$n \log w_a - \log P_a = \frac{\Delta E^{*}}{2.303\,RT} - c \tag{6}$$

and

$$n \log w_b - \log P_b = \frac{\Delta E^{*}}{2.303\,RT} - c \tag{7}$$

The pseudo order of the reaction, n, can then be determined from the equation

$$n = \frac{\log P_a - \log P_b}{\log w_a - \log w_b}. \tag{8}$$

Usually a series of n values is determined at various temperatures to determine whether n remains constant in the temperature range studied for a particular reaction. The value of ΔE^{*} can be determined by plotting ($n \log w - \log P$) versus $1/T$. The slope of the plot will give the value of $\Delta E^{*}/2.303\,R$.

RESULTS AND DISCUSSION

Figure 1 shows the DTA curve for $CuCO_3Cu(OH)_2$ obtained at a heating rate of 5°C min^{-1} in atmospheric air. From this diagram, it can be observed that the reaction is endothermic and that it is initiated at 220°C and ended at approximately 300°C.

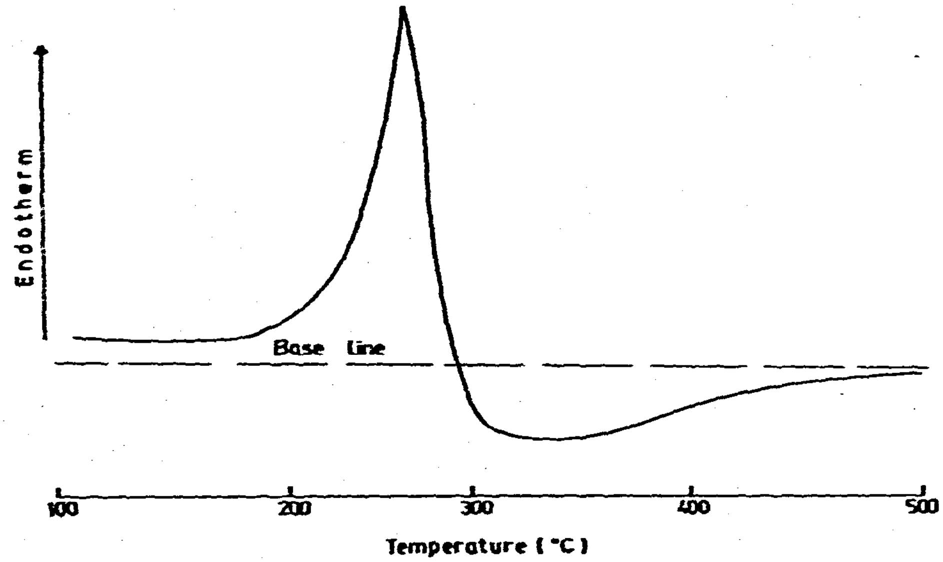

Fig. 1. Differential thermal analysis of $CuCO_3Cu(OH)_2$ in air.

By heating copper basic carbonate on the TG device at a heating rate of 5°C min^{-1} in air, the DTA results have been reproduced.

By means of X-ray difraction and chemical analysis of the sample after thermal decomposition, it was shown that CuO was the product of thermal decomposition of copper basic carbonate. According to this, thermal decomposition of copper basic carbonate is most likely developed according to the following mechanism

$$CuCO_3Cu(OH)_2 \rightarrow 2CuO+CO_2+H_2O \tag{9}$$

According to eqn (9), each 62 mg loss in instantaneous weight due to CO_2 and H_2O is associated with the formation of 162 mg of solid product CuO. In this manner the change of active weight w was calculated as a function of time and temperature. Thermograms in Fig. 2. represent the variation in active weight of $CuCO_3Cu(OH)_2$ with time, for different initial sample weights. The rate of heating was constant in the whole temperature interval of investigation and was 5°C min^{-1}.

The instantaneous decomposition rate, P, as defined by eqn (2), was determined by graphical differentiation of the thermograms in Fig. 2. Thermogravimetric data needed for determining ΔE^* and the kinetic parameter n are contained in Table 1.

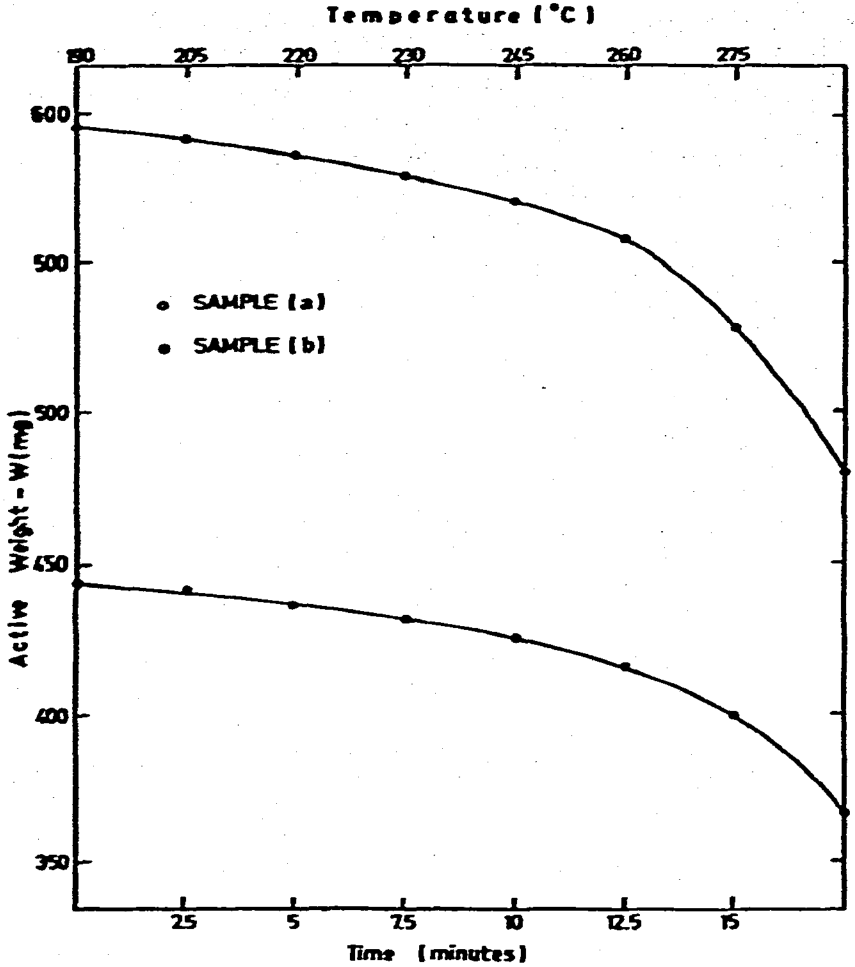

Fig. 2. Variation of active weight of $CuCO_3Cu(OH)_2$ with both time and temperature.

Reaction order, n, was calculated from eqn (8) at 190, 205, 220, 230, 245, 260 and 275°C, and was found to be 1.31 ± 0.5.

A plot of ($n \log w - \log P$) versus the reciprocal absolute temperature is shown in Fig. 3. From the slope of this curve (eqn (5)), the activation energy is estimated to be 17.1 ± 6.5 kcal mol^{-1}.

The rate of $CuCO_3Cu(OH)_2$ thermal decomposition in air and at constant heating rate (5°C min^{-1}) can be described by the equation

$$n \log w - \log P = \frac{3733}{T} - 4.85$$

where $n = 1$ the order the reaction, w = active weight of the reactant, and $P = -dw/dt$ thermal decomposition rate.

TABLE 1

THERMOGRAVIMETRIC DATA FOR CALCULATING THE KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF $CuCO_3Cu(OH)_2$ IN AIR

Time (min)	Temp. (°C)	Sample number	Instantaneous Weight W_t (mg)	Active Weight W (mg)	$P = -\frac{dW}{dt}$ (mg·min^{-1})	log W	log P	Reaction order n	1000/T (°K^{-1})	log W − log P
0	190	a	614.7	594.5	—	2.774	—		2.16	—
		b	458.3	443.0	—	2.646	—			—
2.5	205	a	613.6	590.5	1.74	2.771	0.240	0.74	2.09	2.531
		b.	457.2	440.9	1.40	2.644	0.146			2.498
5	220	a	612.5	585.8	2.36	2.767	0.372	1.23	2.03	2.395
		b.	456.1	436.0	1.64	2.639	0.214			2.425
7.5	230	a	610.3	578.7	3.09	2.762	0.480	1.75	1.99	2.282
		b.	454.9	432.7	1.82	2.636	0.260			2.376
10	245	a	608.0	570.7	4.40	2.756	0.643	1.54	1.93	2.113
		b	453.3	426.9	2.80	2.626	0.447			2.182
12.5	260	a	604.1	556.7	8.42	2.745	0.925	1.98	1.88	1.820
		b	451.0	418.7	4.78	2.621	0.679			1.942
15	275	a	596.3	528.6	11.84	2.723	1.073	0.61	1.82	1.650
		b	446.6	403.0	10.02	2.605	1.0008			1.664

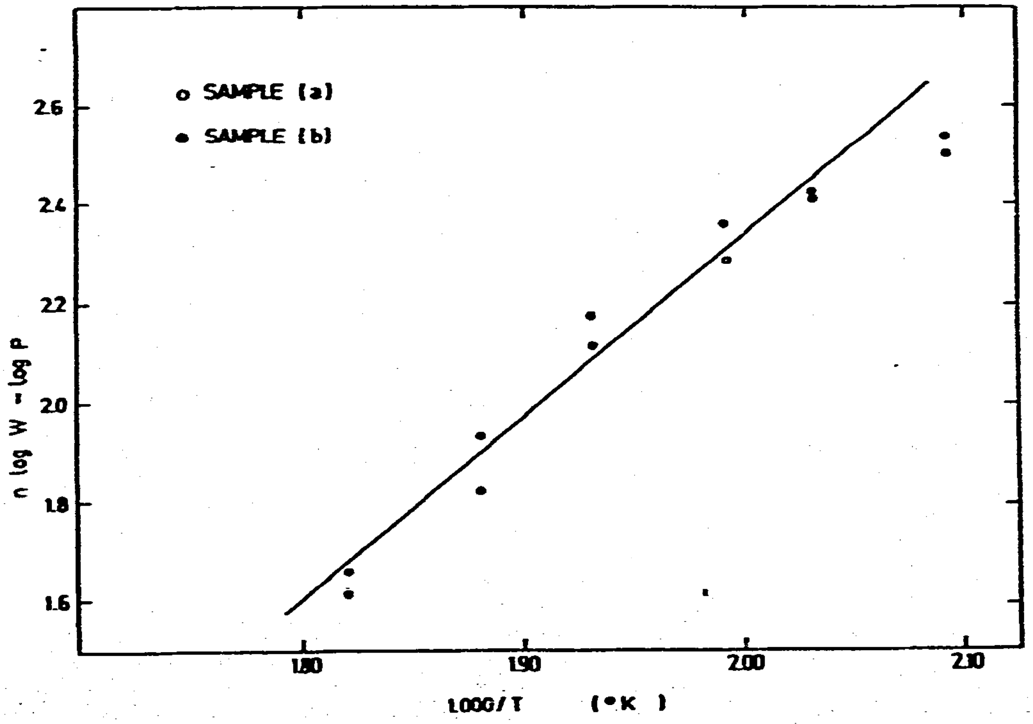

Fig. 3. Temperature dependence of $n \log w - \log P$ for the thermal decomposition of $CuCO_3Cu(OH)_2$ in air.

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