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THE THERMAL DECOMPOSITION OF CHROMIUM CARBONATE

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ABSTRACT

The kinetics of the thermal decomposition of chromium carbonates prepared by precipitation at different temperatures was studied. The kinetic parameters, especially the values of the activation energy and the pre-exponential function for rising temperature experiments, have been established.

In addition the textural characteristics of the thermally decomposed chromium carbonate are investigated by measurement of surface area and density of samples in varying stages of decomposition.

INTRODUCTION

Carbonate decompositions

The kinetics of carbonate decompositions have been studied by many workers for their practical and theoretical importance [1,2]. Carbonate decompositions generally proceed to completion in one or more stages which are usually endothermic and reversible. It has been noted that the presence of CO_2 alters the kinetics of carbonate reactions considerably [3].

The vast majority of work has centred around Group I and II metal carbonates and relatively little work has been done on transition metal carbonates.

However, recent work on transition metal carbonates [4] suggests that the kinetic parameters obtained from decompositions of transition metal carbonates all lie on a common compensation plot (log A vs. E).

Many transition metal carbonates are non-stoichiometric, hence, varied methods of preparation will lead to slightly different carbonates.

The thermal decomposition of chromium carbonate prepared by precipitation at different temperatures was studied, as a forerunner to a study of the decomposition of chromium carbonate which had been adsorbed as a thin layer on silica.

EXPERIMENTAL

Sample preparation

All samples of chromium carbonate were prepared by precipitation from copper nitrate with excess sodium carbonate. Initially, five samples were prepared using stock solutions of the reagents at 12, 25, 40, 72 and 86 °C. A larger scale preparation was also made at room temperature.

The precipitates were filtered through a vacuum pump, washed with distilled water, and dried in an oven at 100–110 °C for 24 h.

Thermal analysis

Rising temperature and isothermal TG

The instrument used for rising temperature and isothermal TG experiments was the Stanton-Redcroft TG 750 microbalance. This is a very low furnace-mass instrument allowing heating rates of 1–100 °C min^{-1} with a cut-out switch at 1000 °C.

The thermobalance was run at a constant rate of 1.2 °C min^{-1} for the rising temperature experiments. All the experiments (isothermal and rising temperature) were performed under an atmosphere of nitrogen.

Differential thermal analysis

The instrument used for the DTA experiments was the DuPont 900 system fitted with the 1000 °C cell.

This instrument allowed a variety of atmospheres to be used including a vacuum, although the swept volume of the furnace was very small.

RESULTS

Rising temperature TG

The results were obtained as plots of percentage weight loss vs. temperature. α-Temperature data was derived from these plots at suitable intervals (typically every 5 K) and is shown graphically in Fig. 1.

The plots show an initial loss of free water followed by a loss of water of hydration. The main decomposition then occurs followed by a change in the oxide formed by the main reaction. This is thought to be $CrO_2 \rightarrow Cr_2O_3$.

There is an overlap to some extent between the stages of the reaction, particularly the loss of water of hydration and the main carbonate decomposition. Before kinetic parameters can be calculated for the main reaction it is necessary to eliminate the contribution due to the loss of water from α.

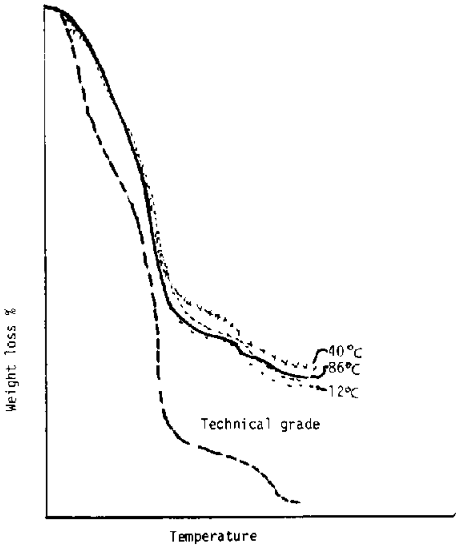


Fig. 1. The percentage weight loss for the preparations of chromium carbonate and technical grade carbonate.

This was done by extrapolating both parts of the curve where it becomes "disjointed" and taking the midpoint as $\alpha = 0$ for the main carbonate reaction. The process is shown in Fig. 2. Thus, all subsequent use of α refers to the main carbonate reaction only. The corrected α–T plots are shown in Fig. 3.

The majority of methods proposed for obtaining kinetic parameters from rising temperature TG curve are based on the combination of the following

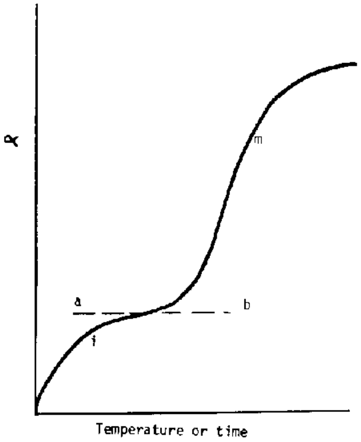


Fig. 2. Method of separating the main reaction, the line *ab* representing $\alpha = 0$ for the main reaction.

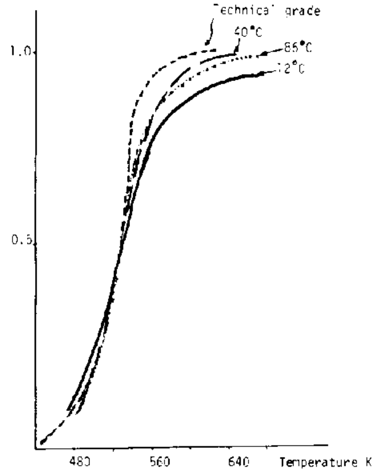


Fig. 3. The variation of fraction decomposed with temperature for the main carbonate reaction for the decomposition of chromium carbonate.

equations.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K\,\mathrm{f}(\alpha) \tag{1}$$

$$K = A\,\mathrm{e}^{-E/RT} \tag{2}$$

$$T = T_0 + \beta T \tag{3}$$

Where α is the fraction decomposed at time t; K is the specific reaction rate; A is the pre-exponential factor; E is the activation energy; T is the temperature (K); T_0 is the initial temperature (usually ambient); and β is the heating rate, i.e., $\mathrm{d}T/\mathrm{d}t$.

Flynn and Wall [5] have classified the different methods for obtaining kinetic data: (1) integral methods; (2) differential methods; (3) difference differential method, involving difference in rate of change; (4) methods applicable to initial rates; and (5) non-linear or cyclic heating rate methods. The method chosen for this work was a differential type. This is less complex than the other methods and with limited computer access making fewer assumptions. Since

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\,\frac{\mathrm{d}t}{\mathrm{d}T}$$

then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\,\frac{1}{\beta}$$

and

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\beta$$

If $\mathrm{d}\alpha/\mathrm{d}t$ is substituted into eqn. (1), we get

$$(\mathrm{d}\alpha/\mathrm{d}T) = K\,\mathrm{f}(\alpha)$$

$$K = \beta\frac{\mathrm{d}\alpha/\mathrm{d}T}{\mathrm{f}(\alpha)} \tag{4}$$

Two ways are open for the analysis of the expression:
(1) combination of eqn. (4) with eqn. (2) for the Arrhenius equation gives

$$\frac{\mathrm{d}\alpha/\mathrm{d}t}{\mathrm{f}(\alpha)} = \frac{A}{\beta}\exp\frac{-E}{RT}$$

(2) an approach used by a variety of authors [6–8] is to take the natural log of the above expression

$$\ln\frac{\mathrm{d}\alpha/\mathrm{d}t}{\mathrm{f}(\alpha)} = \ln\frac{A}{\beta} - \frac{E}{RT}$$

If the left-hand side of the above expression is plotted against $1/T$ a straight line should be observed. The activation energy, E, can be derived from the slope and A from the intercept.

The assumption of this method is that when a particular function $\mathrm{f}(\alpha)$ is selected it assumes that this is correct, and that the Arrhenius equation holds for the part of decomposition curve under investigation.

As previously described [1] the specific rate constant can be calculated from eqn. (4). Knowledge of $\mathrm{d}\alpha/\mathrm{d}T$ is required and can best be obtained using a computer program to calculate the polynomial equation over a range of about nine points. However, previous reports [5] have shown that computer program results are inaccurate over the sections of the curve representing maximum rates of change in the system. Thus, $\mathrm{d}\alpha/\mathrm{d}T$ was calculated using tangents drawn to the curve. A plot of $\ln K$ vs. $1/T$ is presented in Fig. 4. The values of A and E obtained from these plots are summarised in Table 1.

Compensation plot

The values of $\ln A$ vs. E obtained were plotted in Fig. 5. The resultant plot shows a linear relationship between $\ln A$ and E and thus obeys the equation

$$\ln A = mE + C$$

It has been shown that the gradient, m, is given by [2]

$$m = (RT_{\mathrm{S}})^{-1}$$

where T_{S} is the isokinetic temperature at which all the rates of reaction are

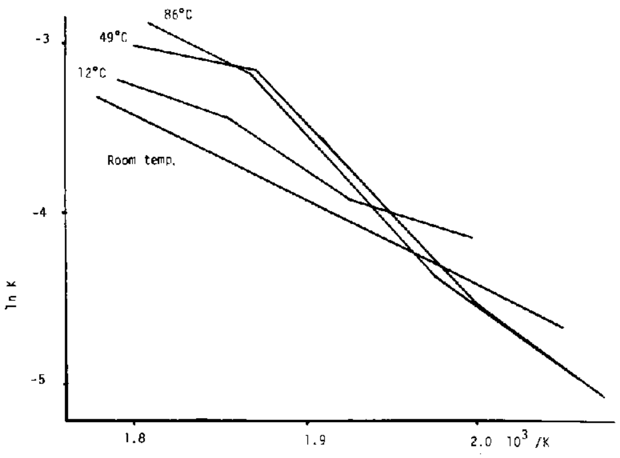


Fig. 4. The plot of ln K vs. $1/T$ for chromium carbonate prepared at the temperatures shown.

identical (assuming the reaction mechanism is the same) and is the test for a compensation plot.

The gradient of the compensation plot obtained here was calculated as 0.225 mol kJ^{-1}. The value for T_S was thus found to be 534.6 K.

Differential thermal analysis

No discernable endotherms were observed for the differential thermal analysis of the prepared chromium carbonate or the technical grade chromium carbonate, except around 120°C (393 K) which was assumed to be due to the loss of water.

TABLE 1

Kinetic parameters obtained from rising-temperature experiments on the prepared chromium carbonates

T(K)	E	Ln A	Temp. of preparation (K)
485–510	62.4	10.4	
512–538	103.5	20.1	359
539–555	32.2	4.1	
480–500	62.4	10.5	
505–532	89.8	17.5	313
535–551	15.8	0.4	
480–560	57.7	9.5	298
503–518	24.9	1.9	
523–543	52.7	8.0	285
543–558	23.8	1.9	

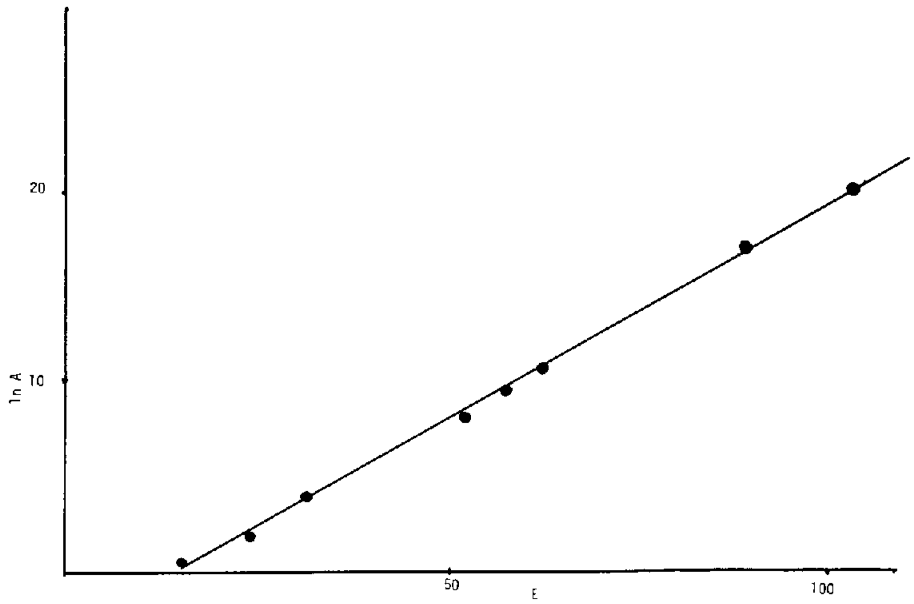


Fig. 5. Compensation plot for the rising temperature decomposition of chromium carbonate.

Isothermal TG

Chromium carbonate samples that had been prepared by precipitation at room temperature were used for this study. Temperatures were selected from rising temperature data in which the main reaction occurred and samples were decomposed isothermally at 424 and 561 K. From the TG traces α vs. t plots were constructed. Using the data obtained from the TG traces a reduced time plot to the experimental data was the Jander equation

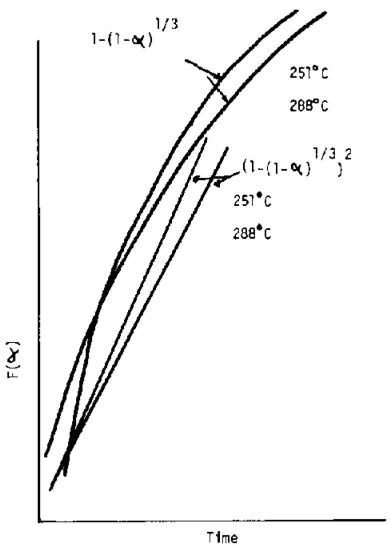
$$\left[1-(1-\alpha)^{1/3}\right]^2=\frac{K}{r^2}t$$

The plots of $[1-(1-\alpha)^{1/3}]^2$ vs. t are shown in Fig. 6. Although a very slight curvature of the graph was noticed, they approximated very well to a straight line up to $\alpha = 0.9$. Other laws were plotted for comparison: first order, $\ln(1-\alpha)$ vs. t (Fig. 7); Erofeev equation with $n = 2$, $\ln(1-\alpha)$ vs. t^2 (Fig. 7); contracting sphere equation, $1-(1-\alpha)^{1/3}$ vs. t (Fig. 6). None of these showed as close an approximation to a straight line as $[1-(1-\alpha)^{1/3}]^2$ vs. t.

The gradients from these plots will be K/r^2 and without knowledge of r, which related to the difference in product and reactant volume, it is not possible to work out values of K and, hence, A and E (K/r^2 for the 561 K decomposition = 0.0173; K/r^2 for the 524 K decomposition = 0.0042).

Surface area measurements

Surface area of the samples were determined using the single point adsorption methods [9,10].



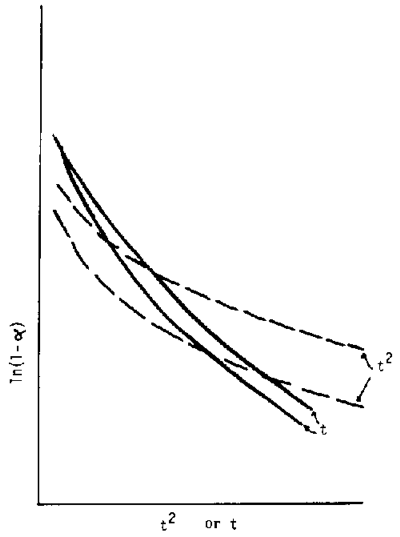


Fig. 6. Graph of $1-(1-\alpha)^{1/3}$ and $[1-(1-\alpha)^{1/3}]^2$ vs. time for the isothermal decomposition of chromium carbonate.

Fig. 7. Graph of $\ln(1-\alpha)$ vs. time and time^2 for the isothermal decomposition of chromium carbonate.

The results summarised in Table 2 are shown as surface area against α as opposed to time of heating. It can be seen that an initial increase in surface area from 12.817 to 37.122 $m^2\ g^{-1}$ occurs during the initial weight loss of $\alpha = 0.484$. This can largely be attributed to the loss of water during the main carbonate reaction. The main reaction caused an increase in surface area to 48.99 $m^2\ g^{-1}$. It must be remembered that the value of α at the start of the main increase in surface area cannot be compared with TG experiments as different sample weights and atmospheres were used.

Density measurements

The density measurements on the heat-treated carbonate are shown against α in Table 2; up to $\alpha = 0.484$ the density showed a decrease from 2.3 to 1.3 g cm^{-3} and then increased up to 2.236. This could be indicative of the initial water loss followed by the main reaction.

Dollimore et al. [11] have suggested that it is essential in the recording of density data that the solid should be well outgassed, however, in the measurement of these densities, no attempt was made to outgas and the densities were measured by means of an ordinary density bottle. Furthermore, to obtain reasonably accurate results by this method for salts with a density of about 2 g cm^{-3} about 1.5 g of sample should be used. In the preparation of the heat-treated samples only 0.5 g of starting material was used to ensure maximum homogeneity of product decomposition, hence,

TABLE 2

The variation of surface area, density and the number of particles formed against the fraction decomposed of chromium carbonate

α	Surface area ($m^2\ g^{-1}$)	Density ($g\ cm^{-3}$)	Number of particles, n
0	12.817	2.308	
0.484	37.122	1.307	7.78
0.766	40.766	1.772	18.92
0.783	45.034	1.844	27.67
0.968	46.266	1.826	29.38
0.973	48.349	1.917	37.69
0.982	48.215	1.944	37.82
0.986	44.742	1.637	21.44
0.992	42.979	2.201	34.34
0.996	44.965	2.555	44.89
0.997	48.986	2.100	46.24
0.999	44.323	2.236	38.83

much smaller samples than normal were available for measurement. Too much reliance on, and inference from, the density measurements should not thus be made.

Number of particles present

As described by Dollimore et al. [11] the number of particles present in a sample can be followed provided the surface areas and densities are known.

The equation

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{1.5} n^{0.5}$$

where n is the number of product particles formed from a single particle of the original carbonate, V_1 is the molar volume of the carbonate, V_2 is the volume of the equivalent amount of product, S_1 is the surface area of the carbonate, and S_2 is the surface area of the product (both the surface areas being quoted per gram of product).

Table 2 shows the values obtained.

DISCUSSION

Rising temperature TG

The values of K (the rate constant) covered a larger range for each different preparation decomposition than those obtained in previous rising-temperature studies using nitrogen atmospheres [4] or carbon dioxide atmospheres [12]. Ln K varied with a typical range of -2.8 to -5.5. The large range obtained emphasises the considerable differences between rising-temperature and isothermal data.

The presence of two or three linear regions on the plots of ln K vs. $1/T$ for rising-temperature experiments has been reported widely in the literature. Zmijewski et al. [13] in a communication on the compensation effect, showed several plots exhibiting multiple Arrhenius values for the carbonate/CO_2 system. Dollimore et al. [14] postulated that this may be due to an alteration in reaction-site energy distribution going from one linear Arrhenius region to another. This has been established for carbon oxidation and some oxides [15,16].

In the alteration of the energy distribution, sintering is the main effect as temperature and time of heating influence the particle size and distribution of defects in the lattice.

Sintering can be shown to occur by the use of density and surface area measurements. The results of textural measurement in this report on chromium carbonate at 250 °C indicate that sintering does not occur. The number of particles formed increased during the isothermal decomposition.

Sintering processes occur as an accelerated process above the Tammon temperature where $T/T_m = 0.5$ (T_m = melting point). This temperature could have some significance in that it is the temperature above which vacancies in the lattice are no longer frozen in so that ions can migrate.

Huttig and Torkar [17] referred to sintering change by the use of the ratio $S = L^1/L$ where L^1 is the density of the powdered material and L is the density of the bulk material. However, due to the way in which densities were measured in this report and the believed low accuracy few conclusions can be drawn on the sintering characteristics of chromium carbonate.

Different methods of sample preparation have been shown by Razouk et al. [18] to give a large spread of values for A and E for a particular reaction. The work done for this project confirmed this. As the chromium carbonates formed are non-stoichiometric there are different $Cr/CO_3/H_2O$ ratios for each preparation and these factors will influence the decomposition characteristics as shown in the ln K vs. $1/T$ plots in Fig. 4.

Compensation plot

The compensation plot obtained in this work (Fig. 5) shows very good agreement with those obtained by Taylor and Rodgers [4] for a large selection of other carbonates and doped carbonates. Rodgers obtained a compensation plot of 0.2119 mol kJ^{-1}, Taylor obtained one of 0.2196 mol kJ^{-1}, whilst the value obtained here was 0.225 mol kJ^{-1}. As the isokinetic temperature is characteristic of any system it appears that with the evidence to date all carbonates have decompositions which proceed by a similar mechanism. All the ln K vs. $1/T$ plots should intersect at 534 K from the compensation plot, this being the isokinetic temperature. In fact, the data indicate that the isokinetic point is around 515–520 K which could be considered as reasonable within experimental accuracy limits.

In explaining the compensation effect some theories are only applicable to specific examples. In the decompositions of a complex Zmijewski et al. [13] considered protons tunnelling through a three-dimensional potential wall. However, it seems likely that consideration of the surface activity is likely to lead to a more generally meaningful explanation of the compensation effect.

To allow for a Boltzmann energy distribution amongst reaction sites

$$n_i = a\ \mathrm{e}^{E_i/b}$$

where n_i = number of sites, E_i = energy of sites, a and b are constants. Then

$$\text{total rate} = Ka\ \mathrm{e}^{gE}$$

where

$$g = (1/b) - (1/RT)$$

This can be integrated between the two energy limits E_1 and E_2 and an approximation made to give

$$\text{rate} = \frac{Ka\ \mathrm{e}^{-E_1/b}}{g\ \mathrm{e}^{-E_1/RT}}$$

Cremer [19] showed that for a model involving only two types of reaction sites each of different activation energy with reactions occurring at both, then

$$K = A_1\ \mathrm{e}^{-E_1/RT} + A_2\ \mathrm{e}^{-E_2/RT}$$

If in a sample undergoing decomposition A_2 changes with each sample, while A_1, E_1 and E_2 remain constant then a compensation effect will result. The use of two sites is a simplification and in real systems there is probably a graduation of sites also producing compensation effects.

Chromium carbonate

In any study it is important to use several techniques and establish relationships between the results obtained from each. The study of textural characteristics can be seen as an important aspect of the investigation of the compensation effect. Previous work on other systems indicated that sintering causes an alteration in the energy distribution during decomposition. The results obtained here suggest that this may not be the case for chromium carbonate. If, however, sintering did not occur it is difficult to understand how particle formation has caused definite and sudden changes in energy distribution. As has been previously mentioned the density measurement accuracy was not great and sintering may have occurred but not been detected by textural measurements.

The isothermal TG experiments showed that the decomposition of chromium carbonate follows the law

$$\left[1-(1-\alpha)^{1/3}\right]^2=\frac{Kt}{r^2} \qquad \text{(three dimensional bulk diffusion)}$$

This was not the law used to obtain the rising temperature results where $f(\alpha)=(1-\alpha)$ was used. Arrhenius parameters are not very susceptible to the form of the kinetic law, therefore, provided a single expression is used in the rising temperature calculations, both E and A may be regarded as satisfactory.

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