Thermochimica Acta, 195 (1992) 163–167
Elsevier Science Publishers B.V., Amsterdam

A study of the influence of particle size on the thermal decomposition of $CaCO_3$ by means of constant rate thermal analysis

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(Received 10 May 1991)

Abstract

The influence of particle size on the kinetic parameters of the thermal decomposition of calcite is investigated. The new constant rate thermal analysis (CRTA) technique which allows considerably better control of the heat and mass transfer phenomena has been used. It is found that the activation energy of the thermal decomposition of calcite smoothly increases by increasing the particle size.

INTRODUCTION

A number of authors [1,2] have paid attention to the influence of both sample size and particle size on the thermal decomposition of $CaCO_3$. In general, it has been reported that a diminution of the activation energy takes place when the sample size increases. This behaviour would be attributed to the influence of heat and mass transfer effects [3] because of the poor control that is usually exerted on both decomposition rate (i.e. rate of heat evolution) and pressure of the environment. This is true even when working under a vacuum.

The influence of the particle size on the kinetic parameters of the thermal decomposition of $CaCO_3$ is investigated in the present paper by mean of constant rate thermal analysis (CRTA). This technique developped by Rouquerol [4] and widely described elsewhere [5], allows, firstly, a constant and selected value of the residual pressure in the close vicinity of the sample to be maintained and secondly, the sample temperature to be monitored in such a way that the decomposition rate remains constant over the whole reaction range. Therefore, one can decrease the residual pressure and the decomposition rate until kinetic data independent of both parameters can be obtained. In this way it is possible to eliminate the influence of heat and mass transfer effects much more effectively than when using classical TG procedures [6].

EXPERIMENTAL

Materials

Ground and sieved calcite from Madagascar has been used. CRTA diagrams of samples of particle size, d, in the ranges 25 μm $< d <$ 50 μm, 50 μm $< d <$ 100 μm and 100 μm $< d <$ 160 μm are included in Fig. 1.

A Mettler thermoanalyzer with a platinum crucible of 16 mm diameter was employed. The apparatus has been modified in order to monitor the furnace temperature in such a way that the total decomposition rate remains constant over the decomposition range. This has been attained by controlling both the residual pressure in the close vicinity of the sample and by maintaining a constant pumping rate which can be selected by means of a butterfly valve. It is worth pointing out that the thermoanalyzer was modified without losing its original performance from the suppliers. Therefore, it is also possible to record TG diagrams at linear heating rates ranging from 0.5 to 25 K min^{-1}.

The selected residual pressure was 4×10^{-5} Torr in all the experiments. We had previously stated that the thermal decomposition of $CaCO_3$ is not

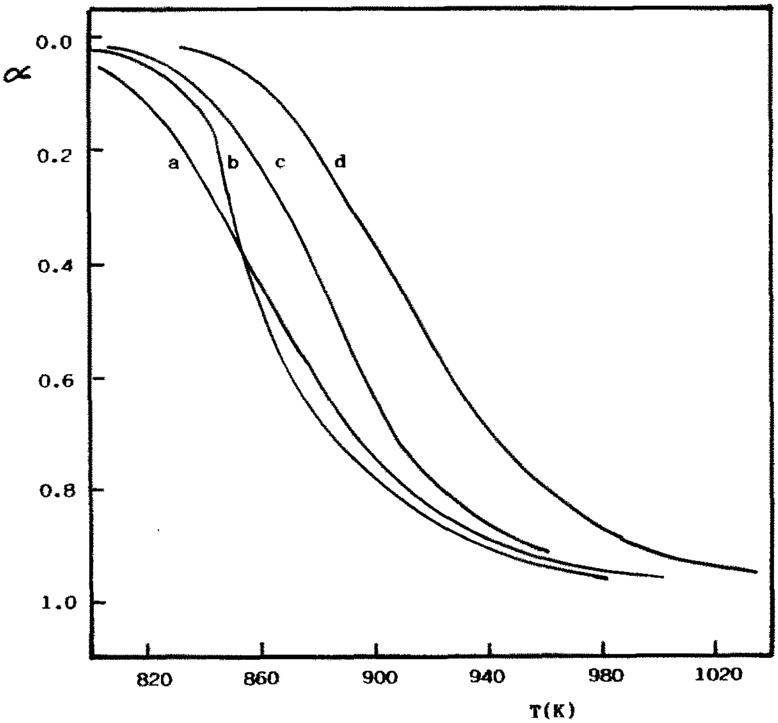

Fig. 1. CRTA curves of calcite from Madagascar recorded at a residual pressure of 5×10^{-5} Torr and different particle size and reaction rate.

TABLE 1

Kinetic function of the most common mechanism operating in solid state reactions

Mechanism	Symbol	$f(\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Unimolecular decay law	F1	$(1-\alpha)$
Avrami–Erofeev equation	Am	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$
Two-dimensional diffusion	D2	$1/-\ln(1-\alpha)$
Three-dimensional diffusion (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$
Three-dimensional diffusion (Ginstlein–Brounshtein equation)	D4	$\dfrac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$

influenced by the pressure in the range from 4×10^{-5} to 10^{-3} Torr that was investigated. Sample sizes of about 20 mg and a reaction rate in the range 1×10^{-3} to 2×10^{-3} min^{-1} were used. The analysis of CRTA curves in Fig. 1 has been performed assuming a first order kinetic model, in agreement with the results reported in a previous paper [6]. Therefore, values of α were taken from the diagrams in Fig. 1 and the corresponding values of $\ln C/(1-\alpha)$ (Table 1) were calculated and are represented in Fig. 2 against the reciprocal of temperature, according to

$$\ln\frac{C}{(1-\alpha)} = \ln A - \frac{E}{RT} \qquad (1)$$

where C is the decomposition rate, α the reacted fraction and the other parameters have their usual meanings.

The kinetic parameters calculated from Fig. 2 are included in Table 2. We can see that the activation energy of the thermal decomposition of $CaCO_3$ smoothly increases as the particle size increases. This behaviour may be explained by taking into account that the lower the particle size, the

TABLE 2

Relationship between particle size of $CaCO_3$ and activation energy of its thermal decomposition

Particle size (μm)	E (kJ mol^{-1})
$25 < d < 50$	142
$50 < d < 100$	150
$100 < d < 160$	163

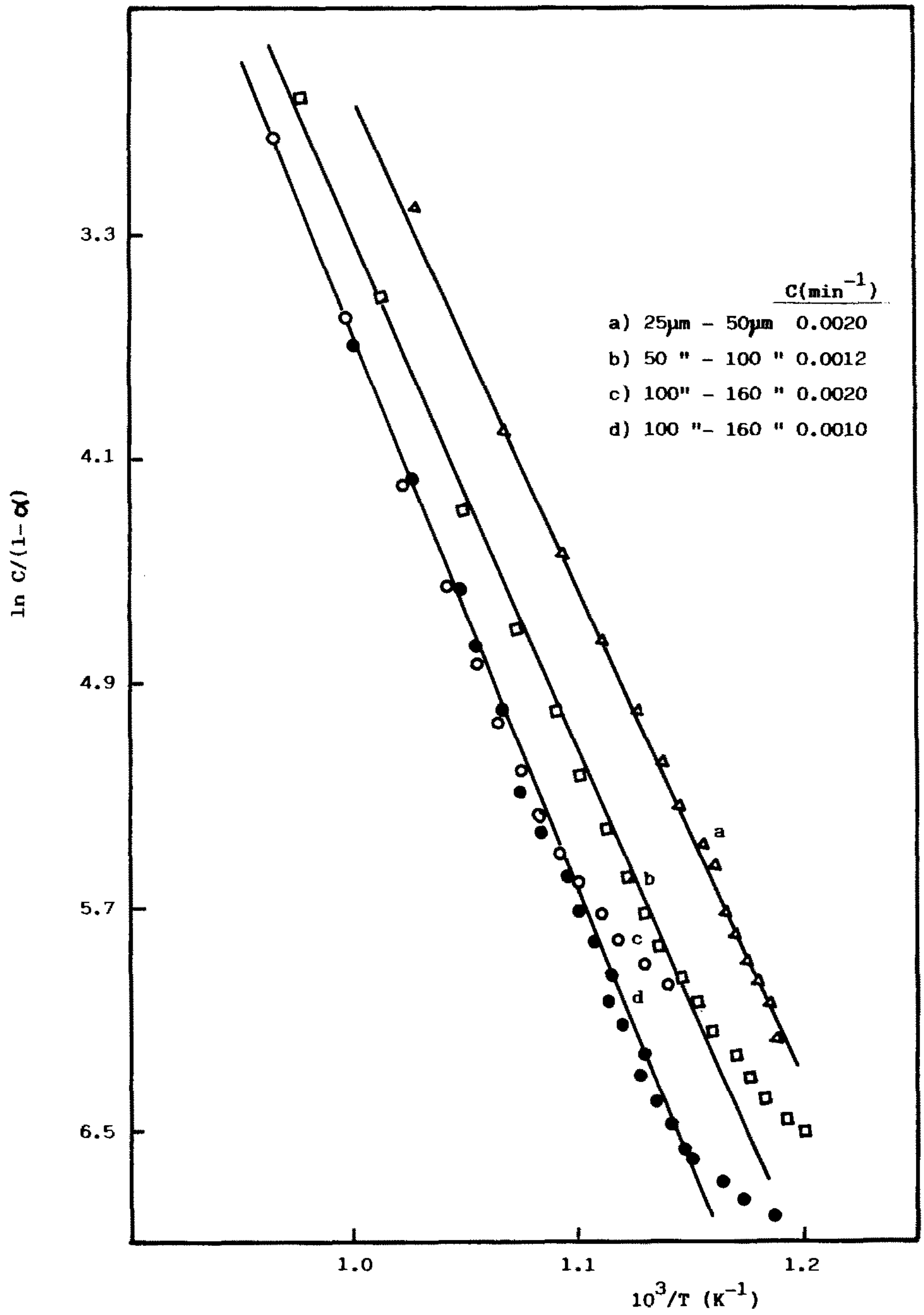

Fig. 2. Kinetic analysis of CRTA curves of Fig. 1 using eqn. (1).

greater the fraction of "$CaCO_3$ molecules" located on the surface with regard to the bulk. Therefore, the activation energy decreases because of the "extra" energy stored on the surface of the smaller particles.

It is necessary to point out that as the particle size of $CaCO_3$ increases, the values of $\ln C/(1-\alpha)$ corresponding to small values of α deviate towards lower temperatures than those that would be expected from the plots of Fig. 2. In contrast, this figure also shows that the α range that fulfils eqn. (1) increases as the selected decomposition rate C decreases. We have not yet found any explanation for this behaviour.

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