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DEVELOPMENT OF A NEW EQUIPMENT FOR USING THE CONSTANT RATE THERMAL ANALYSIS (CRTA) UNDER FLOW OF INERT OR REACTIVE GASES.

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ABSTRACT

New equipment has been designed for applying the Constant Rate Thermal Analysis (CRTA) technique to a flow reactor in order to study solid state reactions during which a gas is generated as a product.

The flow rate of the inert or reactive gas through the sample, located in a quartz reactor is controlled by means of a needle valve of high accuracy. The gases flow through a catharometer detector after leaving the reactor in order to monitor the gases produced in the reaction. The control of the temperature of the sample is carried out by interfacing both the furnace surrounding the quartz reactor and the output signal of the catharometer to a P.I.D. controller that allows to monitor the sample temperature in such a way that the output of the catharometer (and, therefore, the partial pressure of the gases generated in the reaction) is mantained constant during the process at a value previously selected by the user.

INTRODUCTION

The Constant Rate Thermal Analysis (CRTA) or "quasi-isothermal" heating technique was first developed by Rouquerol (1) and Paulik (2). This method implies to program the reaction temperature in such a way that the reaction rate is kept constant at a particular value arbitrarily selected. It has been pointed out that this technique allows to separate overlapping solid state reactions better than the conventional procedures (3). On the other hand, it has been reported that CRTA allows to yield solid with homogeneous structure and low particle size. It has been shown (4) as well that this method discriminated the kinetic model of solid state reactions better than conventional non isothermal methods.

It is noteworthy that the experimental system developed by Paulik brothers implies the use of the derivative unit of an electrobalance for controlling the reaction rate. This fact strongly limits the maximum sample weight to be used in order to employ this tool for preparative purposes. On the other hand,

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Rouquerol's equipment requires to work at very low pressures.

The scope of the present paper is to develop a Constant Rate Thermal Analysis (CRTA) reactor for synthetising solids under a flow of inert or reactive gases.

EXPERIMENTAL

The experimental tool developed in this work is outlined in Fig. 1. It basically constitutes of a double cell catharometer whose millivolts output is interfaced to the furnace through a proper temperature controller. The carrier or reactive gas sweeps the gases selfgenerated in the reaction towards the gas sample cell after flowing through both the reference cell and the reactor. The output of the catharometer is proportional to the partial pressure of these products into the carrier gas. The temperature controller has been designed in order to monitor the temperature of the sample in such a way that the output of the catharometer remains constant all over the process. Therefore, the reaction rate will be constant provided that both the partial pressure of the gas product and the flow of the carrier gas are constant.

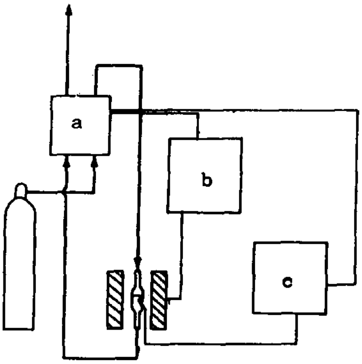

Fig. 1. A plot of the experimental system. a) Catharometer. b) Temperature controller. c) Recorder. The arrows shows the gas flow way.

RESULTS AND DISCUSSION

Fig. 2 shows the diagrams obtained for the thermal decomposition of $CaCO_3$ using the method described above under different flow rates of helium. A sample weigh of 422.4 mg has been used. The output of the conductivity cell has been kept constant at 11.2 mv.

These results point out that the time required for completing the reaction is proportional to the reverse of the flow rate. It has been calculated that the partial pressure of CO_2 has been kept constant at a value of 5.03×10^{-3} atm in all the experiments described in Fig. 2.

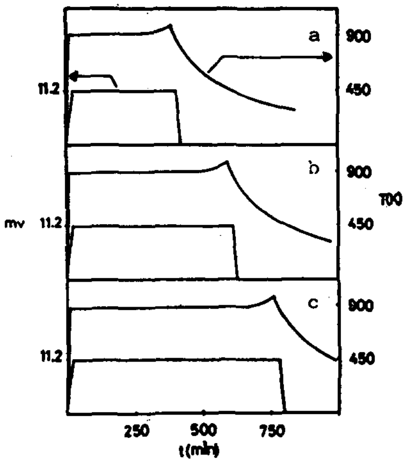

Fig. 2. CRTA plots obtained for the thermal decomposition of $CaCO_3$ at following flow rates of helium: a) 95 cc/min; b) 70 cc/min; c) 50 cc/min

Similar procedures have been obtained selecting other constant values for the output of the catharometer. It is evident that the reacted fraction α at time t is given by the ratio between the area enclosed by the catharometer output trace and the total area when the reaction is over. Fig. 3 shows a plot of the values calculated from Fig. 1 as a function of the temperature. It can be seen that the CRTA curves move at higher temperatures by increasing the constant decomposition rate.

This behaviour can be explained by taking into account that the reaction rate is given by the following equation:

$$\frac{d\alpha}{dt} = C = A\, e^{-E/RT} f(\alpha) \qquad (1)$$

where C is the constant reaction rate; A, the preexponential factor of Arrhenius; E, the activation energy; T, the absolute temperature and f(α) a function depending on the kinetic model obeyed by the reaction.

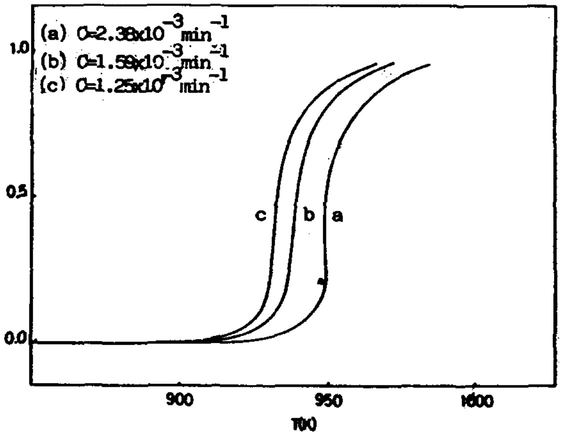

Fig. 3. α-T plots calculated from fig. 1. The following helium flow rates have been used: a) 95 cc/min; b) 70 cc/min; c) 50 cc/min

Eqn. (1) points out that the temperature at which any particular value of α is reached increases by increasing the value of C.

Diagrams similar to the ones included in Fig. 2 have been obtained for the thermal decomposition of $Ca(OH)_2$ using helium as carrier gas. The α-T plots calculated from these diagrams are shown in Fig. 4.

On the other hand, it has been studied the reaction of reduction of NiO using pure hydrogen as both reactive and carrier gas for sweeping the water vapor yield in the reaction. Fig. 5 shows the CRTA curve obtained.

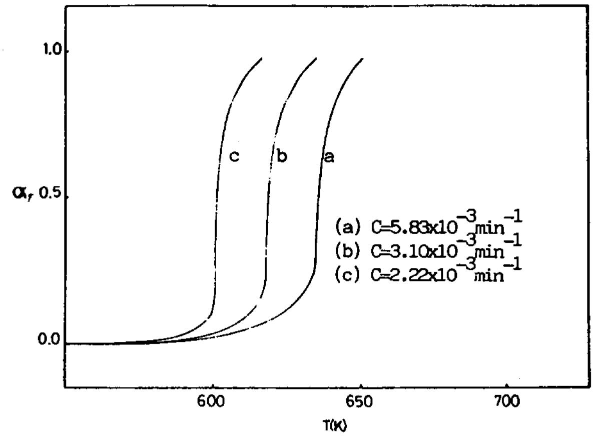

Fig. 4. CRTA plots obtained for the thermal decomposition of $Ca(OH)_2$ using the following flow rates of helium: a) 95 cc/min; b) 70 cc/min c) 50 cc/min.

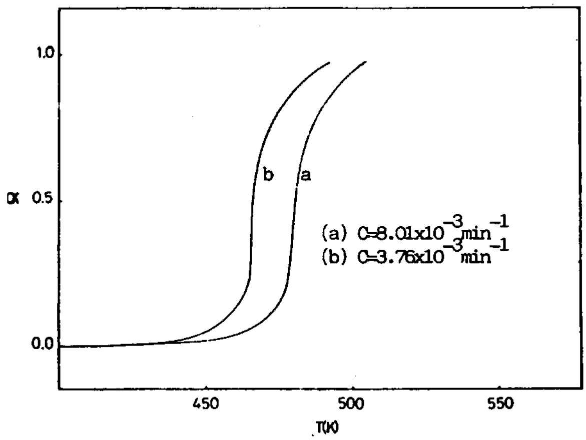

Fig. 5. CRTA plots obtained for the reduction of NiO under the following flow rates of pure hydrogen: a) 95 cc/min; b) 50 cc/min.

In summary, it can be suggested that the experimental method here outlined could be a general procedure to study solid state reactions yielding a gas product at a controlled reaction rate.

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