

## KINETIC STUDY BY MASS SPECTROMETRY OF THE DECOMPOSITION OF BASIC COBALT CARBONATE

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### ABSTRACT

The thermal decomposition of basic cobalt carbonate was studied by mass spectrometry. Kinetic parameters for the processes leading to H<sub>2</sub>O and CO<sub>2</sub> were determined.

### INTRODUCTION

Mass spectrometry has been applied to the study of the kinetics of solid state decomposition reactions [1–5]. We have recently used this technique [6] to elucidate the processes leading to H<sub>2</sub>O and CO<sub>2</sub> in the thermal decomposition of basic nickel carbonate. The present work reports the kinetic study of the thermal decomposition of pure anhydrous basic cobalt carbonate in a vacuum.

It is possible to determine the values of the decomposed fraction ( $\alpha$ ) from the ion current ( $I$ ) values, which are proportional to the gas evolution rate from the decomposing solid and, hence, to the rate of weight loss during non-isothermal heating [4]. The ion current is measured for a characteristic mass spectral ion and correlated with  $\alpha$  at a given time or temperature,  $x$ , as follows

$$\alpha_x = \frac{\sum_0^{\infty} I_x - \sum_x^{\infty} I_x}{\sum_0^{\infty} I_x} \quad (1)$$

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In order to establish the most probable mechanism in each transformation, the method of kinetic analysis of Jerez et al. [7] was used; this is based on the expression

$$\frac{\Delta[\ln(d\alpha/dt) - \Delta[\ln f(\alpha)]]}{\Delta[\ln(1 - \alpha)]} = -\frac{E}{R} \frac{\Delta(1/T)}{\Delta[\ln(1 - \alpha)]} \quad (2)$$

where  $\alpha$  is the fraction of decomposed sample,  $E$  the activation energy,  $R$  the gas constant,  $T$  the temperature and  $f(\alpha)$  the function which describes different kinetic models.

In addition, Achar's differential method was also used to calculate the kinetic parameters

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = \ln \frac{A}{\beta} - \frac{E}{RT} \quad (3)$$

where  $A$  is the pre-exponential factor and  $\beta$  the heating rate. In both cases, the 24  $f(\alpha)$  functions reviewed in ref. 8 were employed.

## EXPERIMENTAL

Measurements were carried out on a Leybold Quadruvac 200 quadrupole mass spectrometer attached to a vacuum system with a sample container heated by a Chesa furnace controlled by a Rockwell AIM-65 microcomputer. The heating rate was  $3.5 \text{ K min}^{-1}$  and the ion current was monitored for a constant  $m/e$  ratio, first 18 ( $\text{H}_2\text{O}^+$  ions) and later 44 ( $\text{CO}_2^+$  ions).  $\alpha$  Values were calculated from the ion current curves.

The thermal decomposition of basic cobalt carbonate was also studied by conventional thermogravimetric analysis in air.

Anhydrous basic cobalt carbonate of nominal composition  $2\text{CoCO}_3 \cdot 3\text{Co}(\text{OH})_2$  was supplied by Carlo Erba (pure reagent).

## RESULTS AND DISCUSSION

From the mass spectra scanned for  $m/e = 18$  and  $m/e = 44$ , the peak of water loss and of carbon dioxide evolution were found to be situated at around 432 K and 483 K, respectively, which demonstrates that although the evolution of both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  takes place simultaneously in the 364–530 K range, this cannot be considered to be a single process because these are actually two different reactions.

Figure 1 shows the  $I$  versus  $T$  plot for both mass spectrum ions. The  $m/e = 18$  curve has two peaks: one at 397.3 K ( $\alpha = 0.136$ ) and the other with a greater maximum at 432.3 K ( $\alpha = 0.462$ ). Hence, water loss occurs in two stages.

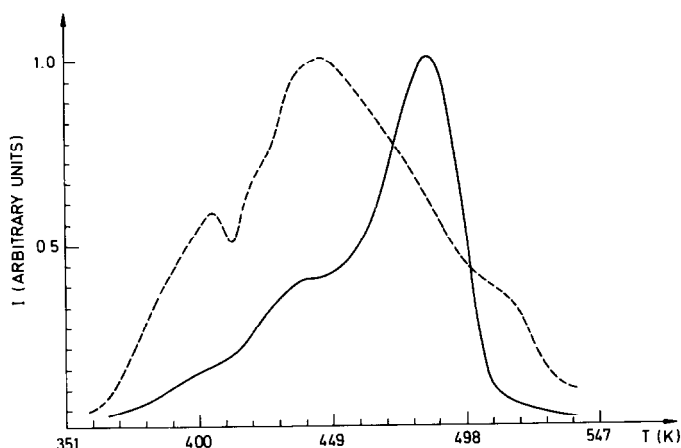


Fig. 1. Ion current curves for  $\text{H}_2\text{O}^+$  (---) and  $\text{CO}_2^+$  (—).

The ion current curve  $m/e = 44$  shows a marked change in the acceleration period at around 432 K and later reaches a maximum at 483 K ( $\alpha_{\text{max}} = 0.695$ ). The first of these temperatures coincides with the second maximum in the water loss process. Thus, the shape of the two ion curves demonstrates the considerable influence that each process exerts on the other.

Tables 1 and 2 give the kinetic results, obtained by dividing each ion current curve into two sections depending on the temperatures.

From the calculations, it can be concluded that the water loss and the  $\text{CO}_2$  evolution occur by diffusion with decreasing reactant activity, according to a D5 kinetic model [9] described by the following functions

$$f(\alpha) = (1 - \alpha)^{4/3} [(1 - \alpha)^{-1/3} - 1] \quad (4)$$

$$g(\alpha) = 2/3 [(1 - \alpha)^{-1/3} - 1] \quad (5)$$

Figure 2 shows the corresponding  $\alpha$  versus  $T$  curves in the complete temperature range for the thermal decomposition in vacuo. In both cases the

TABLE 1

Kinetic results for the water loss

Section	$T$ (K)	$E$ ( $\text{kJ mol}^{-1}$ )	$A$ ( $\text{s}^{-1}$ )	Mechanism
First				
$\Delta\alpha = 0.0036-0.183$	365.8-404.3	$188 \pm 11$	$1.4 \times 10^{20}$	D5
Second				
$\Delta\alpha = 0.236-0.997$	414.8-512.8	$138 \pm 2$	$1.1 \times 10^{13}$	D5
Total				
$\Delta\alpha = 4 \times 10^{-4}-0.997$	358.8-512.8	$144 \pm 1$	$7.3 \times 10^{13}$	D5

TABLE 2  
Kinetic results for the CO<sub>2</sub> evolution

Section	$T$ (K)	$E$ (kJ mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	Mechanism
First $\Delta\alpha = 0.0002-0.254$	367.5-444.5	$170 \pm 5$	$1.5 \times 10^{16}$	D5
Second $\Delta\alpha = 0.334-0.999$	455.0-539.0	$242 \pm 2$	$4.3 \times 10^{23}$	D5
Total $\Delta\alpha = 2 \times 10^{-4}-0.999$	367.5-539.0	$174 \pm 1$	$2.9 \times 10^{16}$	D5

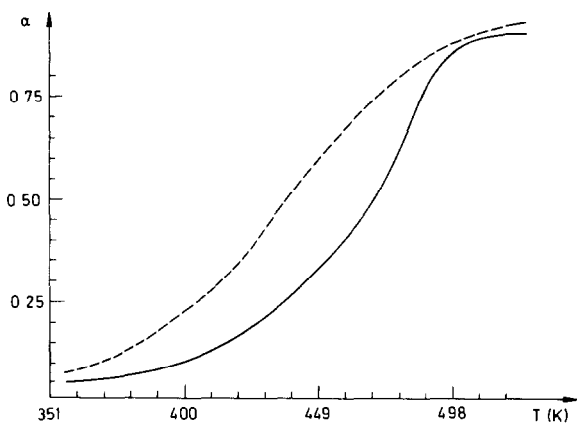


Fig. 2.  $\alpha$  vs.  $T$  curves obtained from  $I$  vs.  $T$  curves,  $m/e = 18$  (---) and  $m/e = 44$  (—).

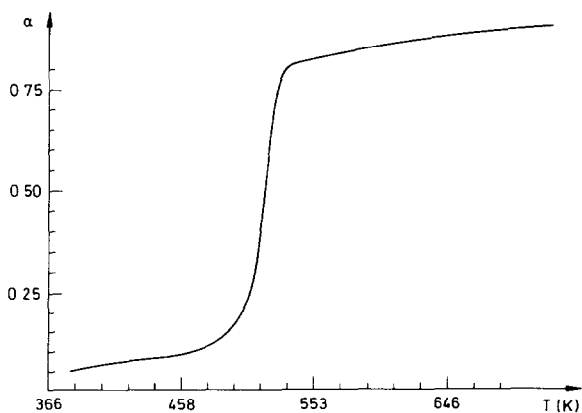


Fig. 3.  $\alpha$  vs.  $T$  curve obtained from thermogravimetry of basic cobalt carbonate.

induction and acceleration periods overlap, but in the CO<sub>2</sub> evolution curve the induction period is larger.

Figure 3 shows the  $\alpha$  versus  $T$  curve obtained from the single weight loss step observed by conventional thermogravimetry, which cannot discriminate these overlapping processes. Kinetic analysis of this curve gave  $E = 103 \pm 10$  kJ mol<sup>-1</sup> and  $A = 2.4 \times 10^6$  s<sup>-1</sup>. These are very different values from those obtained for the separate reactions, although the most probable kinetic mechanism is the same (D5).

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