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INFLUENCE OF THE CO_2 PRESSURE ON THE KINETICS OF THERMAL DECOMPOSITION OF MANGANESE CARBONATE

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Kinetic analysis has been performed on TG and DTG diagrams of the forward reaction $MnCO_3 \rightleftharpoons MnO + CO_2$, recorded at different pressures of CO_2 ranging form $2.6 . 10^{-4}$ Pa to 26.6 kPa. The results obtained show that this reaction follows a first-order kinetic law, independently of the CO_2 pressure used in carrying out the experiments. On the other hand, the activation energy increases on increase of the CO_2 pressure, from 117 kJ/mol up to an asymptotic value of 292 kJ/mol at about 26.6 Pa. This finding cannot be explained by considering the influence of the reverse reaction of formation of $MnCO_3$, for under the described experimental conditions the ratio $P_{CO_2}/P_{\text{equil.}}$ is very close to zero. A mechanism that takes into account the adsorption of CO_2 on the phase boundary has been proposed in order to interpret the results.

A large number of authors [1–10] have studied the thermal decomposition of $MnCO_3$ because of the industrial interest of rhodochrosite as a starting material for the preparation of different manganese oxides. However, papers relating to the decomposition kinetics of this compound are rather scarce [11–13] and there is a lack of agreement among the kinetic parameters obtained by different authors. By way of example, values ranging from 121 kJ/mol [13] to 213 kJ/mol [11] have been reported for the activation energy of the thermal decomposition of $MnCO_3$ under nitrogen atmosphere. This behaviour could perhaps be explained by considering the influence of the CO_2 generated during the salt decomposition. In fact, in a previous paper [14] we have demonstrated that the removal of the gases generated during the thermal decomposition of solids is not attained even by using a very large flow of an inert gas.

The scope of the present paper is to study the influence of the CO_2 pressure on the thermal decomposition of $MnCO_3$, in order to achieve a better understanding of the reaction mechanism.

Experimental

D'Hemio a.r. $MnCO_3$ was used. Rhodochrosite was the only phase observed by powder X-ray diffraction analysis.

A Mettler thermoanalyzer that allows a vacuum better than $2.66 . 10^{-4}$ Pa and the selection of heating rates ranging from 0.5°/min to 25°/min was employed.

A Cahn electrobalance, model RG, equipped with a derivation adapter Mark II, was used as well. This instrument permits the simultaneous recording of both

TG and DTG curves at pressures ranging from $1.33 \cdot 10^{-2}$ Pa to about 26.6 kPa, and heating rates ranging from 0.5°/min to 25°/min.

The kinetic analysis of TG and DTG data was performed by means of the Coats and Redfern [15] and Sharp *et al.* [16] methods, respectively.

Results and discussion

The thermogravimetric analysis of $MnCO_3$ and the X-ray diffraction analysis of the final product of the thermal decomposition of the above salt showed that this reaction takes place according to the equation:

$$MnCO_3 \rightleftharpoons MnO + CO_2 \tag{1}$$

both in vacuum and under a CO_2 atmosphere. This finding agrees with previous papers [4, 13], which report that the oxidation of MnO under CO_2 atmosphere takes place at temperatures higher than 660°.

Figure 1 shows the TG diagrams of $MnCO_3$ obtained by means of the Mettler equipment under a vacuum of $2.6 \cdot 10^{-4}$ Pa and a heating rate of 6°/min, for different sample weights.

The DTG and TG curves yielded from a Cahn electrobalance under a vacuum of $1.33 \cdot 10^{-2}$ Pa at a heating rate of 6°/min and a starting sample weight of 23 mg are included in Fig. 2.

The TG and DTG traces in Figs 1 and 2 fit quite well a first-order kinetic law:

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot \exp(-E/RT)(1-\alpha) \tag{2}$$

In other words, in agreement with the Coats and Redfern integral method and the Sharp *et al.* differential method, DTG and TG data, respectively, obey the following equations:

$$\ln \frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)} = \ln A - E/RT \tag{3}$$

and

$$\ln \frac{1}{(1-\alpha)} - 2\ln T = \ln \frac{AR}{E\beta} - E/RT \tag{4}$$

where α is the reacted fraction at time t, E is the activation energy and A is the pre-exponential factor of Arrhenius.

The parameters calculated from the plot of the data taken from Figs 1 and 2, according to Eqs (2) and (3), are included in Table 1.

It is clear that there is good agreement between the kinetic parameters obtained from the analysis of a TG or a DTG trace, independently of the sample weight and the experimental equipment used.

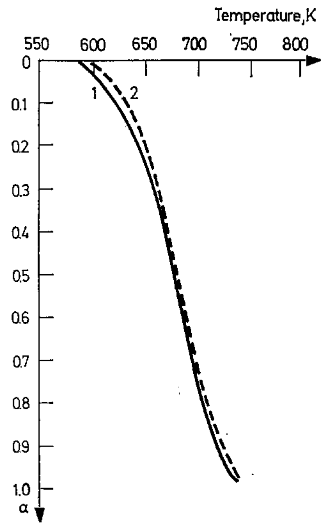

Fig. 1. TG curves of thermal decomposition of MnCO$_3$ obtained with a Mettler thermobalance under a vacuum of 1.33 . 10^{-4} Pa, a heating range of 6°/min and different sample weights. 1. 2.45 mg, 2. 24.82 mg

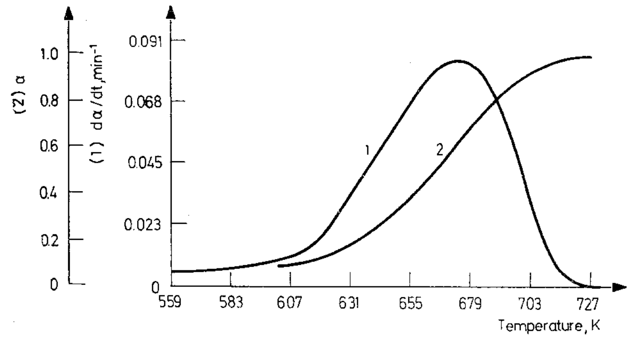

Fig. 2. DTG curve of thermal decomposition of MnCO$_3$ obtained with a Cahn electrobalance under a vacuum of 1.33 . 10^{-2} Pa, a heating rate of 6°/min and a sample weight of 23 mg

The DTG curves of the thermal decomposition of MnCO$_3$ obtained with a Cahn electrobalance at different pressures of CO$_2$ are included in Fig. 3. It can be seen that the higher the CO$_2$ pressure, the higher the decomposition temperature.

For the kinetic analysis of the data in Fig. 1, the basic Eq. (2) must be modified in order to consider the presence of CO$_2$ [17]. Therefore, bearing in mind the microreversibility principle, one obtains the following new equation:

$$d\alpha/dt = A \cdot \exp(-E/RT)(1-\alpha)[1-(P/P_d)] \tag{5}$$

Table 1

Kinetic parameters of thermal decomposition of $MnCO_3$ calculated from TG and DTG data obtained in vacuum, using different sample weights and/or experimental equipment and assuming a first-order kinetic law. Heating rate, 6°/min

Equipment	Sample weight, mg	Integral method			Differential method		
		E, kJ/mol	A, min^{-1}	regression coefficient	E, kJ/mol	A, min^{-1}	regression coefficient
Mettler thermo-balance	2.45	112.0	5.10^7	−0.9942	—	—	—
Mettler thermo-balance	24.82	117.0	1.10^8	−0.9941	—	—	—
Cahn electro-balance	23.0	121.0	4.10^8	−0.9985	121.0	$4.7 . 10^8$	−0.9989

where P is the pressure of CO_2 and P_d is the dissociation pressure of $MnCO_3$. From the P_d data calculated from ref. [18] we obtained the $(1 - P/P_d)$ values that are plotted against $1/T$ in Fig. 4.

These plots show fairly clearly that, at the CO_2 pressures and temperatures at which the DTG curves in Fig. 3 were obtained, $(1 - P/P_d) \approx 1$. Therefore, the

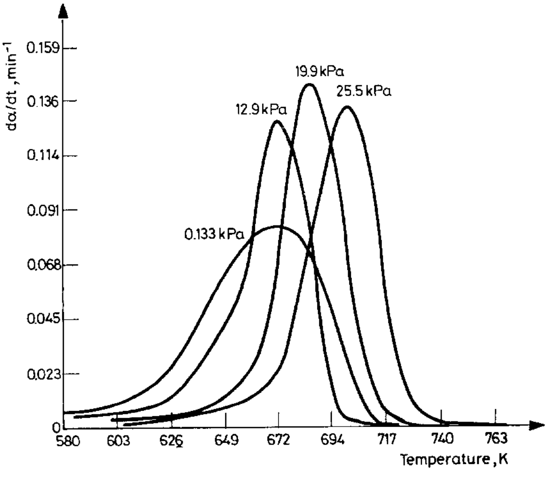

Fig. 3. DTG curves of $MnCO_3$ recorded with a Cahn electrobalance under different pressures of CO_2, using a starting sample weight of 23 mg and a heating rate of 6°/min

Table 2

Influence of CO_2 pressure on kinetic parameters of thermal decomposition of $MnCO_3$

CO_2 pressure, Pa	E, kJ/mol	A, min^{-1}
vacuum	121	4.10^{8}
12.9	271	6.10^{20}
19.9	250	1.10^{18}
25.5	288	4.10^{21}

same values of the kinetic parameters of the thermal decomposition of $MnCO_3$ would be calculated from Eqs (2) or (5). This means that Eq. (2) can be used for the kinetic analysis of the data in Fig. 3. The results obtained from the analysis of these data by means of Eq. (3) are included in Table 2, together with the one taken from Table 1 for the thermal decomposition in vacuum.

The plot of the values of the activation energy of the forward reaction (1) against the pressure of CO_2, included in Fig. 5, shows that E increases on increase of the pressure of CO_2, until an asymptotic value is attained at about 26.6 kPa.

It is noteworthy that these results cannot be explained by considering the influence of the reverse reaction of formation of $MnCO_3$, as we have mentioned before, $P/P_d \approx 0$.

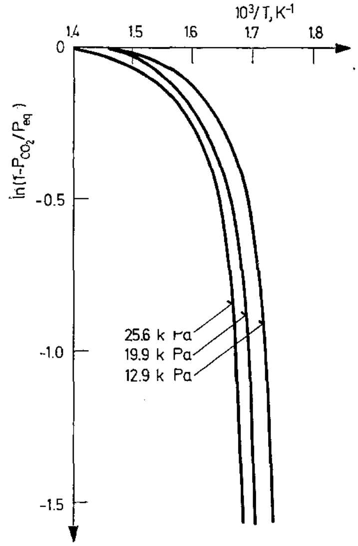

Fig. 4. Plots of the ln $(1 - P_{CO_2}/P_{eq})$ values calculated for $MnCO_3$ at different pressures as a function of the inverse temperature

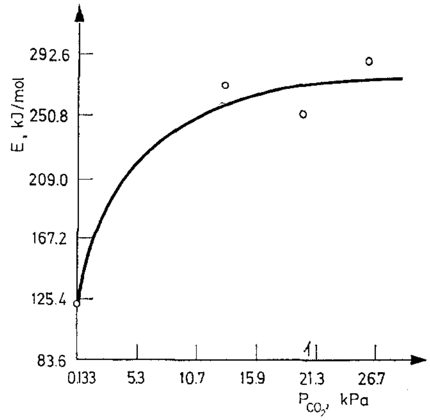

Fig. 5. Apparent activation energy of thermal decomposition of $MnCO_3$ as a function of the CO_2 pressure

The above data could be interpreted if we consider that CO_2 is chemisorbed on the MnO surface. Therefore, if we assume that the active phase boundary is the surface not covered by CO_2, Eq. (2) becomes:

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot \exp(-E/RT)(1-\alpha)(1-\theta) \tag{6}$$

where θ represents the surface coverage.

If the adsorption follows the Langmuir – Hinshelwood law:

$$\theta = aP/(1+aP) \tag{7}$$

one obtains from Eqs (6) and (7):

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot \exp(-E/RT)(1-\alpha)[1/(1+aP)] \tag{8}$$

where the adsorption coefficient a depends on the adsorption heat λ through the expression:

$$a = a_0 \cdot \exp(\lambda/RT) \tag{9}$$

where a_0 is a constant.

One can deduce from Eq. (8) that the reaction rate decreases on increase of the pressure of CO_2 and, therefore, the DTG curves move to higher temperatures, in agreement with our results in Table 2. Moreover, from Eqs (8) and (9) it would be expected that the apparent activation energy, E_a, varies from $E_a + E$ if $aP \ll 1$, to $E_a = E + \lambda$ when $aP \ll 1$. The trend followed by the activation energy in Fig. 5 would agree with this interpretation, which is similar to the one given in ref. [19], in order to explain the mechanism of thermal decomposition of $MnCO_3$.

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ZUSAMMENFASSUNG — Die kinetische Analyse der Reaktion $MnCO_3 \rightleftharpoons MnO + CO_2$ in Richtung des oberen Pfeiles wurde an Hand von TG und DTG Diagrammen durchgeführt, welche bei verschiedenen CO_2-Drucken im Bereich von $2.6 \cdot 10^{-4}$ bis 26.6 kPa aufgenommen wurden. Die erhaltenen Ergebnisse zeigen, daß diese Reaktion einem kinetischen Gesetz erster Ordnung folgt, unabhängig von dem zur Durchführung der Experimente angewandten CO_2-Druck. Andererseits nimmt die Aktivierungsenergie mit steigendem CO_2-Druck von 117 kJ/mol bis zu einem asymptotischen Wert von 292 kJ/mol bei etwa 26 660 Pa zu. Dieses Ergebnis kann unter Berücksichtigung der Umkehrreaktion der $MnCO_3$-Bildung nicht erklärt werden, da unter den beschriebenen Versuchsbedingungen das Verhältnis $P_{CO_2}/P_{equil.}$ sehr nahe zu Null ist. Um die Ergebnisse zu deuten wurde ein Mechanismus vorgeschlagen, welcher die Adsorption des CO_2 an der Phasengrenzfläche berücksichtigt.

Резюме — На основе ТГ и ДТГ проведен кинетический анализ реакции $MnCO_3 \rightleftharpoons MnO + CO_2$, протекающей при давлениях CO_2 от $2.6 \cdot 10^{-4}$ Па до 26.6 кПа. Полученные результаты показали, что реакция протекает согласно кинетического закона первого порядка, независимо от давления CO_2 в данной системе. С другой стороны, значения энергии активации, с увеличением давления CO_2, увеличиваются от 117 кдж/моль до 292 кдж/моль при давлении 26.6 кПа. Этот результат не может быть объяснен на основе протекания обратной реакции образования углекислого марганца, поскольку в описанных экспериментальных условиях отношение $P_{CO_2}/P_{равн.}$ очень близко к нулю. Для объяснения этого явления был предложен механизм адсорбции CO_2 на границе фаз.