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COMPLEX THERMOANALYTICAL METHOD FOR THE SIMULTANEOUS RECORDING OF T, TG, DTG, DTA, TGT, DTGT, TD AND DTD CURVES

PART II. APPLICATION OF THE METHOD TO THE EXAMINATION OF THE THERMAL DECOMPOSITION OF MANGANESE(II) CARBONATE HYDRATE

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ABSTRACT

The thermal decomposition of manganese(II) carbonate hydrate has been studied using a new complex technique for the simultaneous recording of the thermogravimetric, differential thermoanalysis, derivative thermogravimetric, thermodilatation, derivative thermo-dilatation, thermo-gas-titrimetric and derivative thermo-gas-titrimetric curves. The experiments have been carried out in nitrogen, carbon dioxide, air and oxygen.

In a previous paper[1] we reported on a new complex thermoanalytical method. In the present paper the technique described is demonstrated on the thermal decomposition of manganese(II) carbonate hydrate which has been the subject of earlier reports[2-18]. The experiments were carried out in nitrogen, carbon dioxide, air and oxygen.

EXPERIMENTAL

The experimental set-up was described in Part I.

The heating rate applied during the measurements was 10°C/min.

The sample was prepared by precipitation from a cold $2M$ solution of $MnCl_2$ by a $1.5\ M$ solution of Na_2CO_3 used in 50% excess, since dilution, warming and Mn^{2+} ions in excess are known to promote the formation of the basic salt.

The manganese content of the precipipitate was determined gravimetrically according to Winkler[19]. From a knowledge of the manganese content the levels corresponding to the theoretical composition of the intermediate decomposition products could be marked in Figs. 1–4 and thus the inflexion points and the steps on the TG curves could be identified.

In order to control the accuracy of the method, the water and carbon dioxide contents of the sample were determined as for carbon and hydrogen in organic compounds according to Liebig. Thus the sample was heated in a silica tube and the water vapour and carbon dioxide released were absorbed in tubes filled with calcium chloride and sodium asbestos. The amount of the volatile components released was calculated from the increase in weight of the tubes.

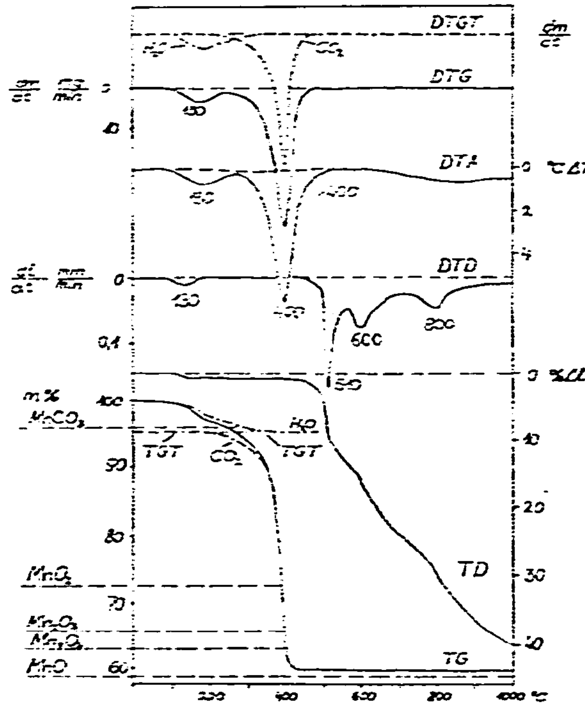

Fig. 1. Thermal decomposition of manganese(II) carbonate hydrate in N_2.

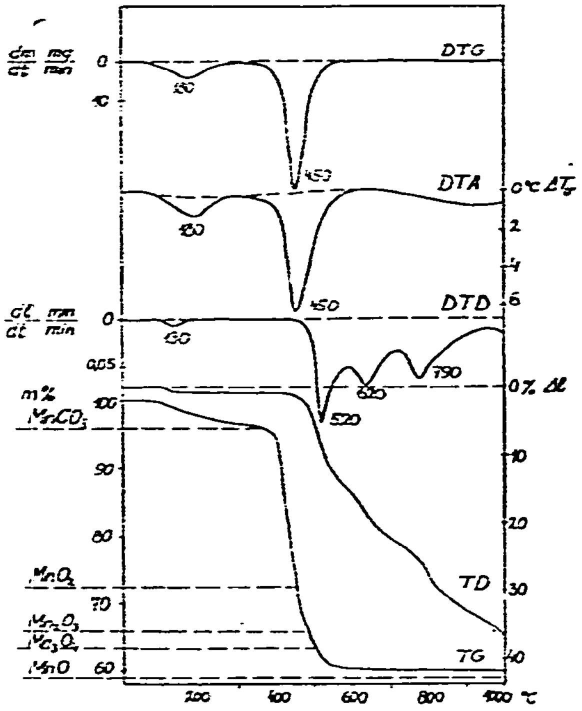

Fig. 2. Thermal decomposition of manganese(II) carbonate hydrate in CO_2.

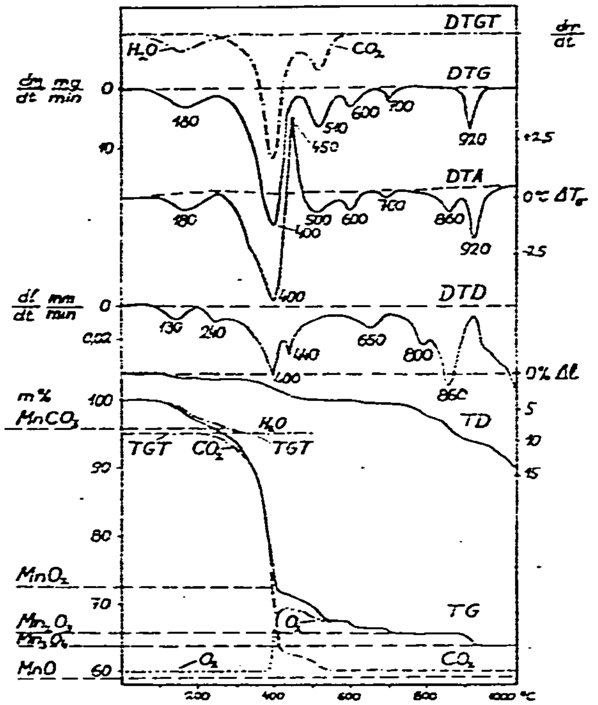

Fig. 3. Thermal decomposition of manganese(II) carbonate hydrate in air.

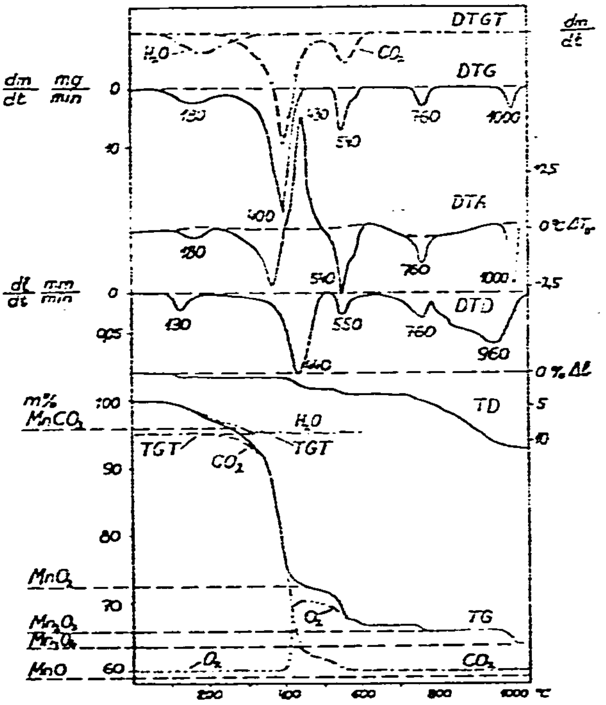

Fig. 4. Thermal decomposition of manganese(II) carbonate in O_2.

TABLE I

CHANGE IN THE COMPOSITION OF MANGANESE(II) CARBONATE DURING THERMAL DECOMPOSITION

			$MnCO_3$ 1	MnO_2 2	$Mn_x O_y$ 3	Mn_vO_z 4	Mn_2O_3 5	Mn_3O_4 6	MnO 7	Mn 8	H_2O 9	CO_2 10
Determined as $Mn_2P_2O_7$ gravimetrically according to Winkler		a	[95.8]*	[72.4]*			[65.7]*	[63.6]*	[59.1]*	45.8		[36.7]*
Absorbed in calcium chloride and sodium asbestos according to Liebig		b									5.1	35.4
Determined with the Derivatograph	in N_2 atm.	c							60.1	[46.5]**	5.4	35.0
	in CO_2 atm.	d							59.8	[46.3]**		
	in air	e	[96.0]†	70.8	67.2	66.2	65.6	63.7	[59.0]†† [59.2]†	[45.7]†† [45.9]†	4.9	35.2
	in O_2 atm.	f	[96.1]†	72.0	67.5	66.8	66.1	63.8	[59.4]†† [59.3]†	[46.0]†† [46.0]†	4.7	34.8

Values calculated on the basis of quantities: * Mn, ** MnO, † Mn_3O_4, †† Mn_2O_3 ; given in percentages.

The calculated and measured percentage contents of the decomposition products are summarized in Table I. The values represent in each case the mean of six experiments.

The release of water during the thermal decomposition of the sample and the rate of this release are shown in Figs. 1, 3 and 4 (curves marked with H_2O). These curves were plotted by the thermo-gas-titrimetric method described, using isopropylalcohol as absorption liquid, Karl–Fischer solution as titrant and the dead-stop method for end-point indication[20].

Rates of release of carbon dioxide are shown by curves marked CO_2 in Figs. 1, 3 and 4. In a separate experiment the amount of carbon dioxide released was titrated acidimetrically to sodium hydrogen carbonate. The pH of the absorption solution was maintained at 9.3 (theoretical value of the equivalent point lies at pH 8.4). Some few percent of the CO_2 was not absorbed by the absorption solution and a second absorber containing a known amount of NaOH solution was therefore used. After the measurement the quantity of NaOH was back-titrated and the value obtained was taken into account in the CO_2 curve.

The oxygen content of the sample changed in a broad temperature interval during the experiment. Curves marked with O_2 in Figs. 1, 3 and 4 show the amount of oxygen, both released and taken up. These curves were constructed using the H_2O and CO_2 curves by difference calculation.

RESULTS AND DISCUSSION

The experiments prove that the thermal decomposition of manganese(II) carbonate hydrate is relatively simple in an inert gas atmosphere but becomes more complex in the presence of oxygen. The explanation of this apparently complex process is simple and convincing using the information furnished by the eight thermoanalytical curves.

The TG, DTG and DTA curves, plotted in nitrogen gas in the usual way, show only that the sample has decomposed in two steps, i.e. in two endothermic reactions between 100 and 450 °C with formation of manganese(II) oxide. However, the amount of this was 1.0% greater than the calculated value (see columns 7a and 7c in Table I). This is probably due to slight oxidation of the preparate during precipitation.

According to the TG curve the manganese(II) oxide, which combines violently with even traces of oxygen[21], was completely stable in weight between 450 and 1000 °C. Therefore in spite of the fact that the silica bell surrounding the sample is open at the bottom, the inert gas flowing in the opposite direction completely excludes air. Consequently, it seems to be impossible that an amount of oxygen of about 1.0% has been bound during the thermal decomposition of the sample below 450 °C.

According to earlier opinions it could be supposed that the carbon dioxide released has oxidized the manganese(II) oxide. However, this supposition is not supported by a deficiency in the amount of the carbon dioxide (see columns 10b and 10c in Table I) which would correspond to this oxidation reaction. Furthermore manganese(II) oxide has been found to be completely stable in weight in a carbon dioxide atmosphere between 500 and 1000°C (see Fig. 2).

From the H_2O and CO_2 curves in Fig. 1, which can be brought into line with the TG curve, it can be seen that the dehydration and the release of carbon dioxide occur in the main successively, but overlap one another to a small extent. From the TG, H_2O and CO_2 curves and the theoretical decomposition levels, as well as the measured and theoretical values of carbon dioxide (see columns 9 and 10 in Table 1) it is clear that the compound was not the basic salt but that its composition was $MnCO_3 \cdot 0.3H_2O$.

The picture of the decomposition process can be completed using the information obtained from the TG and DTG curves. According to these curves change of crystal form starts in manganese(II) oxide at about 500°C, i.e. at a temperature about 100°C above that at which it has been formed. This process led to a 40% contraction in the test piece. This is in good agreement with an earlier observation[22] according to which the oxygen binding capacity of manganese(II) oxide (more accurately the speed of its oxidation) decreases at higher temperatures, presumably because of the decrease in active surface area.

When the precipitate was examined in a carbon dioxide atmosphere instead of nitrogen (see Fig. 2), its thermal decomposition did not essentially change, except that the dissociation of manganese(II) carbonate was shifted in the direction of higher temperatures.

The TG and DTG curves recorded in the presence of air (Fig. 3) show the thermal decomposition of the precipitate as a process consisting of six steps. The TD and DTD curves indicate here only a 10% contraction of the precipitate. On the basis of the exothermic maximum of the DTA curve at 450°C the cause of this change can be predicted but can only be proved by the difference in the TGT and TG curves. Although the amount of both water and carbon dioxide released did not change when the nitrogen atmosphere was replaced by air (columns 9 and 10 in Table 1) the loss in weight of the sample itself was less in air than in a nitrogen atmosphere (see TG curve in Fig. 1). The only possible explanation of this is that the manganese(II) oxide has taken oxygen from the air, which it is known to do. The curve marked with O_2, indicating the change in the amount of the oxygen both released and taken up, shows that the manganese(II) oxide was oxidized immediately after its formation at about 400°C. The composition of the primary oxide phase has seemingly been manganese(IV) oxide. However, the decomposition of manganese(II) carbonate is, in the presence of air, a process which takes place in two steps, the escape of ca. 10% of the carbon dioxide extending until 550°C. This can probably be explained by the formation of a compact oxide layer which hinders diffusion of carbon dioxide from the inside of the grains.

According to the 400°C endothermic and 450°C exothermic peaks of the DTA curve the oxidation has been delayed to some extent compared with the thermal decomposition of the sample, as opposed to the decomposition taking place in an oxygen atmosphere (Fig. 4).

The double process of decomposition and oxidation was followed, according to the TG curve, by a slow decomposition of the oxide phase, occurring in five steps. The first three decomposition levels cannot be interpreted in spite of the fact that they are reproducible. The last but one level of the TG curve between 700 and 900°C corresponds to the composition manganese(III) oxide, while the level above 900°C corresponds accurately to manganese(II, IV) (see columns 5a, 5e, 6a, and 6e in Table I).

The literature suggests that an intermediate unstable tetragonal modification of manganese(III) oxide may be formed under certain circumstances from manganese(II) oxide; this then changes through monotropic transformations into a stable cubic modification at higher temperatures. The peak at 860°C of the DTA curve as well as the peaks at 800 and 860°C of the DTG curve are probably an indication of this change. It is however of interest, that in experiments carried out in oxygen (Fig. 4) this transformation did not take place.

If instead of air the experiments were carried out in oxygen (Fig. 4), the thermal decomposition of the precipitate did not change essentially; the decomposition of manganese(IV) and manganese(III) oxides, as well as of the intermediate product corresponding to the second (not interpretable) decomposition level (section 600–730°C of the TG curve) was merely shifted in the direction of higher temperatures.

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