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Note

THERMAL DECOMPOSITION OF BASIC MANGANOUS CHROMATE

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The thermal decomposition of mixed metal complexes, mixed metal carboxylates and oxometallates gives rise to technologically important complex oxides such as spinels and perovskites at moderate temperatures [1]. Thus Hardy [2] has reported the formation of $BaMnO_3$ on thermolysis of $BaMnO_4$ and a mixture of $BaMnO_3$ and MnO_2 is obtained by the decomposition of $Ba(MnO_4)_2$ [3]. It is known [4] that manganese compounds decompose in air to Mn_3O_4 and in reducing atmospheres to MnO. In this context, it was thought interesting to study the thermal behaviour of basic manganous chromate under diverse conditions and to identify the decomposition products. Reported in this communication are the results of thermogravimetry, differential thermogravimetry, differential thermal analysis and evolved gas detection analysis in air, oxygen and in a mixture of 95% argon and 5% hydrogen. The final product of decomposition is characterized by X-ray diffractometry.

EXPERIMENTAL

The basic manganese(II) chromate (BMC), $MnO \cdot MnCrO_4 \cdot 3.5\ H_2O$, used was a commercially available sample obtained from Riedel–de Haen AG and was used without further purification. The X-ray powder diffraction patterns of the sample gave a very diffuse spectrum suggesting it to be almost X-ray amorphous. The thermal decomposition studies were carried out in a Stanton thermobalance and a Netzsch STA 409 thermal analyzer with an attached Netzsch EGD 403 unit. A gas density balance was used as a detector for the evolved gas detection. The simultaneous recording of TG, DTG, DTA and EGD curves were obtained with a continuous heating rate of 5°C min^{-1}. The analyses were carried out both in oxidative and reducing dynamic atmospheres. The X-ray powder diffractograms were recorded using CuK_α radiation.

RESULTS AND DISCUSSION

The thermal plots of BMC in air are given in Fig. 1. The TG curve, obtained by the plot of weight fraction against temperature, suggests that the compound is stable

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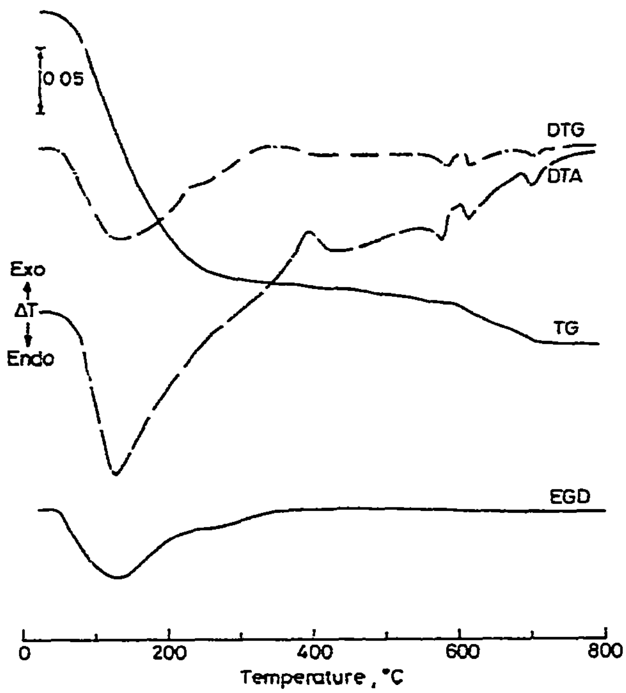

Fig 1 Thermal plots of basic manganous chromate in air.

up to 50°C. There are, apparently, two main stages of decomposition; the first takes place in the temperature range 50–300°C with a loss of 20% and the second occurs between 400 and 700°C, registering a loss of 6%, giving an overall loss of 26% of the initial weight. The rate of weight loss (DTG) curve shows a maximum at 132°C which corresponds to the endothermic peak at 125°C in the DTA curve. This effect is attributed to the dehydration of BMC as the calculated weight loss for the removal of 3.5 molecules of water is 20.6%, which agrees with the observed weight loss. Further confirmation of this dehydration process is obtained by the negative signal observed in the EGD plot, which has a peak maximum at 125°C.

The final product obtained at 800°C was found to be brownish-black in colour and gave characteristic X-ray patterns. The observed 2θ values could easily be indexed on the basis of spinel type lattice. In Table 1 are given the observed and calculated interplanar spacings. The compound belongs to the cubic system with a unit cell length of 8.413 Å.

The TG curve suggests that there is a gradual sluggish rate of weight loss from 400 to 600°C and thereafter the decomposition rate is fairly fast. There is no significant shift in the EGD base line, indicating that the weight loss is due to the removal of oxygen as the molecular weights of oxygen (32) and air (29) are not much different. Thus, $MnO \cdot MnCrO_4$ loses an atom of oxygen to give Mn_2CrO_4, which may be better formulated as $[Mn(II)Mn(III)Cr(III)O_4]$, spinel. The exothermic effect at 398°C is probably attributed to the breakage of the basic chromate network as there is no change in weight at this temperature. However, the DTA curve shows more than one endothermic effect in the deoxygenation stage as does the DTG

TABLE I

X-Ray data for Mn(II)Mn(III)Cr(III)O_4

hkl	d_{obs} (Å)	d_{cald} (Å)	Relative intensity [a]
111	4 929	4.857	s
220	2 981	2 974	s
311	2 522	2 537	s
222	2 429	2 429	m
400	2 073	2 103	m
422	1 682	1 717	w
333	1 612	1 619	m
440	1 509	1.487	m
533	1 280	1 283	w
444	1 221	1 214	w

[a] s = strong, m = medium, w = weak

curve, which clearly suggests the complexity of the process.

The decomposition of BMC in a pure oxygen atmosphere is found to be basically similar to that in air in the sense that it completely dehydrates between 40 and 300°C and deoxygenates in the temperature range 400–750°C with an overall weight loss of 26%. The end product is verified to be identical with that obtained in air. The thermal plots in the range 350–800°C are illustrated in Fig. 2. It is clear from the TG curve that deoxygenation is a two-step process, one occurring between 400 and 610°C, losing 2% weight, and the other taking place in the range 620–720°C with a loss of 4%. It has been reported [5] that Mn_5O_8 is an intermediate phase during the decomposition of γ-MnOOH. The weight loss process, in the present case, suggests

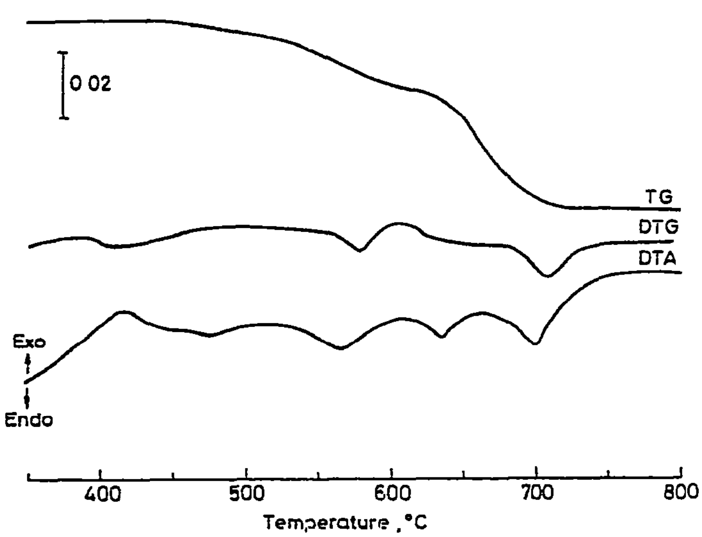

Fig. 2 Thermal plots of basic manganous chromate in oxygen

that $MnO \cdot MnCrO_4$ probably decomposes to give a mixture of Mn_5O_8 and Cr_2O_3 according to the equation

$$20\,[MnO \cdot MnCrO_4] \rightarrow 8\,Mn_5O_8 + 10\,Cr_2O_3 + 3\,O_2$$

Mn_5O_8 further loses oxygen and interacts with Cr_2O_3 to form Mn_2CrO_4. This supposition is supported by the endothermic peak maxima at 569, 638 and 698°C in the DTA curve and the DTG peaks at 577 and 705°C. However, the X-ray patterns of the decomposition residue at 610°C gave very weak lines which reasonably correspond to those of Cr_2O_3 only. This may be due to the poor crystallinity of the phase.

The thermal behaviour was repeated in an atmosphere consisting of a mixture of argon and hydrogen. The decomposition seems, in this case, to be a single-step process, occurring between 40 and 550°C with the overlapping of both the dehydration and deoxygenation steps. The total weight loss was found to be 25.6% and the final residue at 550°C confirmed to be Mn_2CrO_4 as in the previous case. Thus, it is clear that, whatever the atmosphere, BMC decomposes to give the spinel Mn(II)Mn(III)Cr(III)O_4.

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