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THERMAL ANALYSIS OF MANGANESE DIOXIDE IN CONTROLLED ATMOSPHERES

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TG and DTA curves of γ-MnO_2 have been obtained in nitrogen, air and oxygen. The reactions $MnO_2 \rightarrow Mn_2O_3$ and $Mn_2O_3 \rightarrow Mn_3O_4$ were observed in the ranges 450° to 600° and 750° to 1100° respectively, and the decomposition temperatures are affected by the partial pressure of oxygen. The endotherm at ~1200° is unaffected by the atmosphere and is not accompanied by weight loss. It is, therefore, due to a polymorphic transformation of Mn_3O_4 rather than formation of MnO. Reaction to form MnO was observed by TG in nitrogen above 1400°, but did not occur on heating in oxygen to 1500°.

When manganese dioxide is heated the reaction sequence, $MnO_2 \rightarrow Mn_2O_3 \rightarrow \rightarrow Mn_3O_4 \rightarrow MnO$, occurs. There is general agreement [1] that the transformation from MnO_2 to Mn_2O_3 occurs at about 550° in air, and that from Mn_2O_3 to Mn_3O_4 at about 950° in air. There is disagreement, however, about the temperature of the transformation from Mn_3O_4 to MnO. Several workers [2–4] have reported an endothermic peak, on DTA, between 1160° and 1230°, which is reversible on cooling and interpret it as due to the polymorphic transformation from tetragonal β-hausmannite (Mn_3O_4) to the cubic γ-form. According to Dollimore [5, 6] this reaction is due to the formation of MnO from Mn_3O_4.

Since the formation of MnO involves weight loss, whereas the polymorphic transformation does not, thermogravimetry (TG) should clearly differentiate between the two possible interpretations for the 1160° endotherm. In spite of this, TG curves have not been reported in the range 1000° to 1500°, nor has DTA been used in controlled atmospheres. Thermodynamic considerations [7] indicate that the various decomposition temperatures depend on the partial pressure of oxygen, whereas the temperature of the polymorphic transformation will not be affected.

This investigation reports TG and DTA curves for MnO_2 when heated in nitrogen, air and oxygen.

Experimental

Thermogravimetry was investigated in a Stanton HT–SF thermobalance using samples of approximately 300 mg and a linear heating rate of 1.1°/min up to 1500°, when the temperature was maintained isothermally until constant weight was reached. Differential thermal analysis was investigated on a Netzsch instrument using approximately 500 mg of sample, and a linear heating rate of 10°/min. The temperature recording thermocouple was located in the sample and the inert reference was approximately 500 mg of fired α-Al_2O_3. In both cases a flow of gas (300 ml/min) was maintained.

X-ray powder diffraction was used to identify the phases present at various stages during the decomposition after quenching to room temperature. Powder photographs were obtained using an 11 cm camera and Cr target with a V filter.

Micro-analytical reagent grade manganese dioxide (Hopkin and Williams) was used. There are various forms of manganese dioxide [1, 8] which probably does not exist as stoichiometric MnO_2 [3]. X-ray powder traces correspond with the form described as γ-MnO_2 (ASTM card 4–0779). No impurities were detectable by means of X-ray diffraction.

Results

DTA curves obtained when manganese dioxide was heated in nitrogen, air and oxygen to 1300° and cooled are shown in Fig. 1, and the peak temperatures are listed in Table 1. The DTA peaks obtained for reactions b, d and e are large and should be resolved with any DTA apparatus. Reactions a and c produced very small peaks which have not been resolved by previous workers, since their magnitude depends on operating and instrumental conditions.

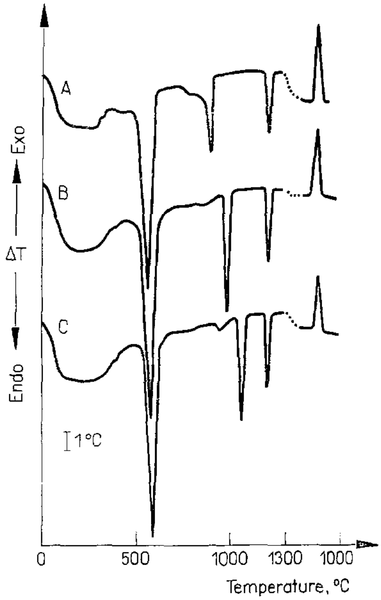

Fig. 1. DTA curves of γ-manganese dioxide. (A) nitrogen; (B) air; (C) oxygen

TG curves on heating in nitrogen and oxygen to 1500° are shown in Fig. 2. From these curves, DTG curves were drawn and the peak temperatures are compared with the DTA peaks in Table 1. A separate sample was heated in nitrogen at 260°, 560°, 850° and 1500° until constant weight was obtained. The average weight losses associated with the three stages of decomposition of the manganese dioxide (i.e. ignoring weight loss below 260°) were 8.71 %, 3.20 % and 6.73 %.

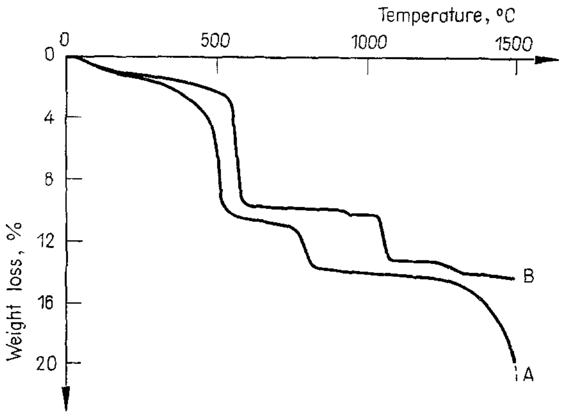

Fig. 2. TG curves of γ-manganese dioxide. (A) nitrogen; (B) oxygen

X-ray powder photographs showed that MnO was not formed in any of the DTA runs, but was formed after heating to 1500° in nitrogen. The end product of all other runs was Mn_3O_4 (ASTM card 8–17).

Discussion

When manganese dioxide was heated in all atmospheres, a broad endotherm accompanied by weight loss was observed between room temperature and 400°. This is due principally to the loss of water and other adsorbed species, although loss of oxygen probably occurs, since manganese dioxide is non-stoichiometric [3, 8, 9] and its composition varies with oxygen partial pressure and temperature. Either superimposed on this endotherm or almost immediately after it is a very small exotherm, whose peak temperature varies slightly with the oxygen partial pressure (Table 1, reaction a). This is similar to the small exothermic peak reported at 360° to 510° in air for the transition from ramsdellite to pyrolusite [1, 4, 10]. It is almost certainly due to a "polymorphic" transformation of manganese

Table 1

Thermal analysis data for manganese dioxide

Method	Atmosphere	Peak temperature					
		Reaction					
		a	b	c	d	e	f
DTA	N_2	345	555	765	890	1200	—
DTA	Air	360	575	860	980	1200	—
DTA	O_2	400	590	955	1060	1190	—
TG	N_2	—	520	—	800	—	1460
TG	O_2 x	—	560	940	1060	—	—

dioxide, perhaps from γ to β (pyrolusite). Since the peak temperature increases as the partial pressure of oxygen increases, it may be associated with a slight loss of oxygen and consequent change in composition. A true polymorphic transition should not vary in temperature with oxygen pressure.

The endotherms described as reactions b and d (Fig. 1, Table 1) are due to the decompositions of MnO_2 into Mn_2O_3, and Mn_2O_3 into Mn_3O_4. The decompositions occur at a higher temperature in oxygen than in nitrogen and are observed at lower temperatures in DTG than in DTA because of the difference in heating rate (1.1° and 10°/min, respectively). The temperatures for these decompositions are in the same range quoted by other workers [1–7, 10–12].

The temperature of the small endotherm (reaction c, Table 1) depends on the oxygen partial pressure and is probably due to a change in stoichiometry similar to that reported by Malinin and Tolmacher [12]. The TG in oxygen shows a small weight loss (940°) which corresponds to the DTA peak, which was found to be reversible in oxygen but not in nitrogen. It is not possible to distinguish the weight loss for this reaction in nitrogen since weight loss was slight but continuous between 550° and 750°, in spite of the very slow heating rate used.

The endotherm described as reaction e (Table 1) has been interpreted differently by Dollimore [6, 7] and Rode [4]. There can be no doubt that Rode is correct in concluding that this peak is due to a polymorphic transformation of Mn_3O_4 for the following reasons:

i) it is not accompanied by weight loss (Fig. 2),

ii) X-ray analysis of samples heated to 1300° showed the presence of Mn_3O_4 only, whereas those heated to 1500° in nitrogen and cooled in nitrogen showed the presence of MnO only,

iii) on cooling from 1300° in all atmospheres the DTA peak was reversible (Fig. 1),

iv) the temperature of the DTA peak does not vary with the partial pressure of oxygen,

v) on heating to 1500° in nitrogen, further weight loss occurred above 1200°, giving a DTG peak at 1460°, due to the formation of MnO (reaction f, Table 1).

The endotherm associated with this reaction might be observed in nitrogen between 1500° and 1600°.

The final weight loss was not observed in oxygen, although a small weight loss does occur at 1300°, but this is probably due to a small change in stoichiometry. X-ray analysis shows the presence of Mn_3O_4 only. The weight losses in nitrogen between 260° and 560°, 560° and 850°, and 850° and 1500° are in the ratio 2.59 : 0.95 : 2.00 rather than the ideal 3 : 1 : 2 for the reactions, $Mn_6O_{12} \rightarrow$ $\rightarrow Mn_6O_9 \rightarrow Mn_6O_8 \rightarrow Mn_6O_6$. The first ratio is low since the starting material is non-stoichiometric; calculation suggests the formula $MnO_{1.94}$ which is within the range quoted for γ-manganese dioxide [9].

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Résumé — Etude de γ-MnO_2 par TG et par ATD, dans l'azote, dans l'air et dans l'oxygène. Entre 450 et 600° on observe la réaction $MnO_2 \rightarrow Mn_2O_3$ et entre 750 et 1100° $Mn_2O_3 \rightarrow$ $\rightarrow Mn_3O_4$. La pression partielle de l'oxygène influence la température de la décomposition. A ~1200°, il apparaît un phénomène endothermique undépendant de la nature de l'atmosphère et qui ne s'accompagne d'aucune variation de poids. C'est pourquoi il est attribué à une transformation polymorphique de Mn_3O_4 plutôt qu'à la formation de MnO. Celle-ci s'observe en TG au-dessus de 1400°, dans l'azote, mais ne se produit pas par chauffage dans l'oxygène jusqu'à 1500°.

Zusammenfassung — Die TG und DTA Kurven von γ-MnO_2 wurden in Stickstoff, Luft und Sauerstoff ermittelt. Die Umwandlungen $MnO_2 \rightarrow Mn_2O_3$ und $Mn_2O_3 \rightarrow Mn_3O_4$ wurden im Temperaturbereich von 450° bis 600° bzw. 750° bis 1100° beobachtet. Die Zersetzungstemperaturen werden durch den partiellen Sauerstoffdruck beeinflußt. Der end-

endothermische Vorgang von ~1200° bleibt von der Atmosphäre unbeeinflußt, ist mit keinem Gewichtsverlust verbunden. Er ist eher einer polymorphen Umwandlung von Mn_3O_4 als der Bildung von MnO zuzuschreiben. Die Bildung von MnO wurde thermogravimetrisch in Stickstoff oberhalb 1400° beobachtet, nicht jedoch in Sauerstoff bis zu 1500°.

Резюме — В атмосфере азота, воздуха и кислорода получены кривые ТГ и ДТА γ-MnO_2. Установлено, что реакции $MnO_2 \rightarrow Mn_2O_3$ и $Mn_2O_3 \rightarrow Mn_3O_4$ происходят в пределах температур 450°—600° и 750°—1100°, соответственно, и что на температуру разложения влияет парциальное давление кислорода. Эндотермика при 1200° не зависит от атмосферы и не сопровождается потерей веса. Следовательно, она обусловлена скорее полиморфным превращением Mn_3O_4, чем образованием MnO. Реакция образования MnO наблюдалась по ТГ в атмосфере азота выше 1400°, однако, при нагревании в кислороде до 1500° она не имела места.