ATMOSPHERE DEPENDENCE OF THE THERMAL DECOMPOSITION OF MANGANITE, γ-MnO.OH

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ABSTRACT

Thermal analysis using TG and simultaneous DTA-TG-MS has been carried out on a natural manganite in atmospheres of oxygen, air, carbon dioxide, nitrogen and argon. The TG curve shows three distinct weight losses at approximately 300-400°, 500-600° and 800-900°C. The ratio of the first to second weight loss varies dramatically depending on atmosphere and, for oxidizing atmospheres, the heating rate in the range 2-50°C/min. In oxygen at 2°C/min, MnO_2 is the only product of the first (dehydroxylation) reaction but, with increasing heating rate and decreasing $p\,O_2$, Mn_5O_8 becomes a prominent co-product. In inert atmospheres, Mn_5O_8, Mn_2O_3 and Mn_3O_4 may all appear as products of the first reaction. Mn_5O_8 and MnO_2 decompose to Mn_2O_3 between 500° and 600°C and Mn_2O_3 decomposes to Mn_3O_4 at 800-900°C. Mn_3O_4 undergoes a β-γ transition at 1169 C and decomposes to MnO at 1450°C.

MATERIALS AND METHODS

The manganite used was a pure, crystalline variety from Laverock Braes, Aberdeenshire, which gave an X-ray pattern virtually identical with that of JCPDS card 8-99. This was ground to a particle size of <75 μm and thermogravimetric analyses carried out on 10 mg samples in a Stanton Redcroft TG 770 microthermobalance in static air and in flowing oxygen, carbon dioxide and nitrogen. Heating rates were in the range 2° to 50°C/min. Separate TG runs were made to isolate products after significant weight losses for subsequent identification by X-ray powder photography (XPP). Simultaneous TG-DTA-MS at 15°C/min was carried out in argon on 10 mg samples using equipment described by Charsley et al. [1].

RESULTS AND REACTIONS

TG curves of manganite at 15°C/min in different atmospheres are given in Fig. 1. Three weight losses are shown in all cases, termed A (300-400°C), B (500-600°C) and C (800-900°C), but the ratio of A to B increases in the order oxygen < air < nitrogen < carbon dioxide. Table 1 summarizes results from TG runs carried out under atmospheres ranging from "maximum oxidation" (slow heating under flowing oxygen) to neutral (flowing argon). The Table demonstrates well the systematic increase of weight loss A at the expense of B with decreasing $p\,O_2$. Weight loss C increases to a maximum of 3.2% in static air at 15°C/min and then decreases to 2.3% in argon, while the total
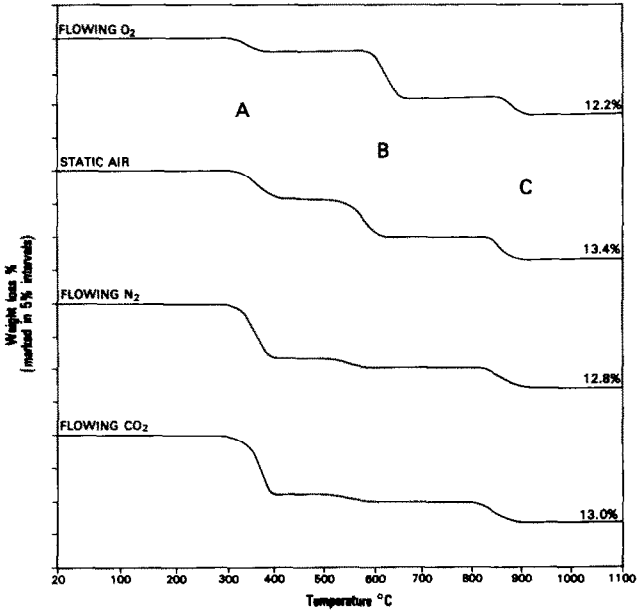
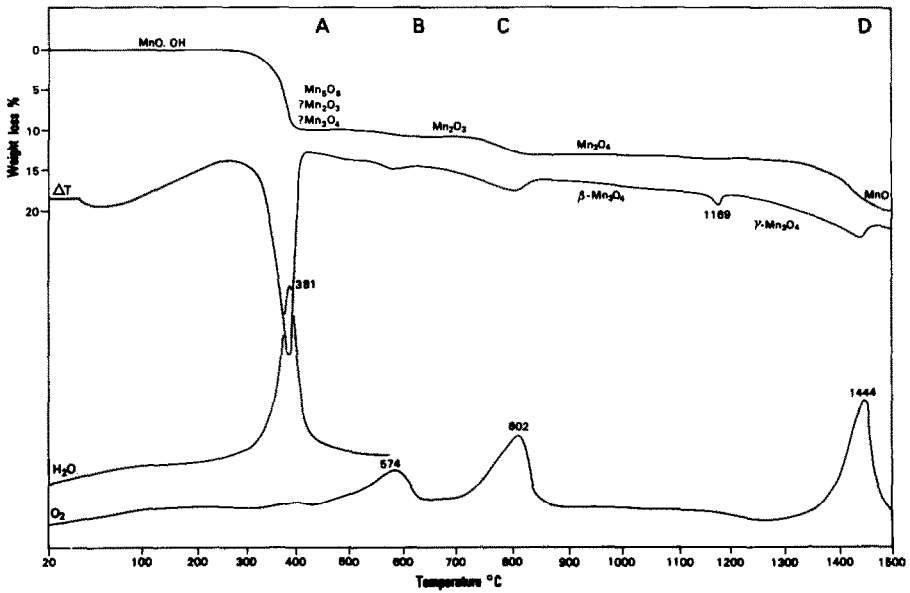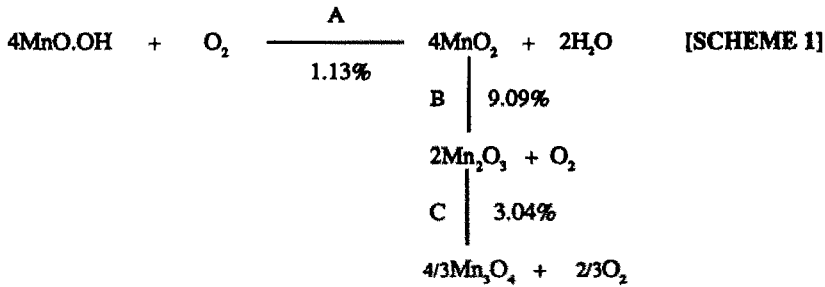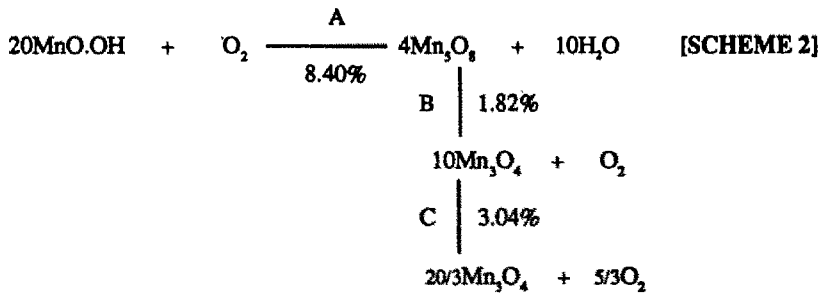Fig. 1. TG curves of manganite under different flowing gas atmospheres at 15°C/min.

Fig. 2. Simultaneous DTA-TG-MS curves of manganite in flowing argon at 15°C/min.

weight loss to 1000°C generally increases with decrease in $p\,O_2$. Weight losses from slow heating rates in oxygen are in general agreement with the reaction scheme:

$$4MnO.OH \; + \; O_2 \quad \xrightarrow[\substack{A \\ 1.13\%}]{} \quad 4MnO_2 \; + \; 2H_2O \qquad [SCHEME\ 1]$$

$$B \;\Big|\; 9.09\%$$

$$2Mn_2O_3 \; + \; O_2$$

$$C \;\Big|\; 3.04\%$$

$$4/3Mn_3O_4 \; + \; 2/3O_2$$

With decreasing $p\,O_2$, Mn_5O_8 was identified by XPP as an increasingly important co-product of weight loss A. A possible scheme to account for the formation of this phase, and subsequent reactions, is:
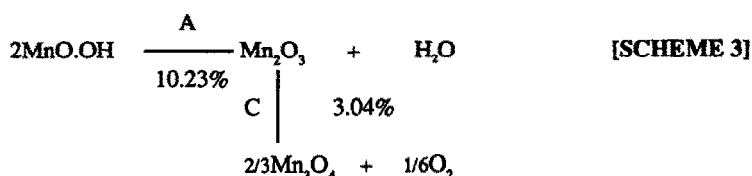
$$20MnO.OH \; + \; O_2 \quad \xrightarrow[\substack{A \\ 8.40\%}]{} \quad 4Mn_5O_8 \; + \; 10H_2O \qquad [SCHEME\ 2]$$

$$B \;\Big|\; 1.82\%$$

$$10Mn_3O_4 \; + \; O_2$$

$$C \;\Big|\; 3.04\%$$

$$20/3Mn_3O_4 \; + \; 5/3O_2$$

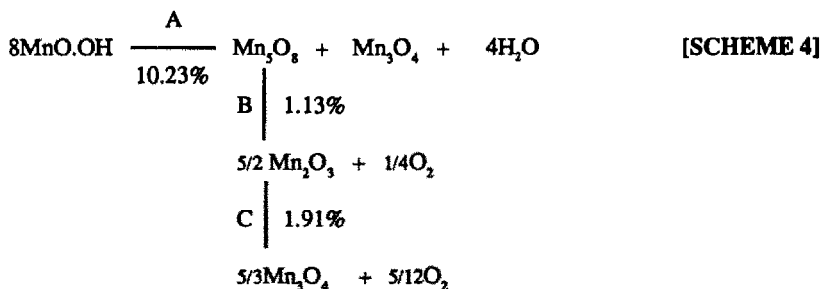| Atmosphere	Heating rate (°C/min)	Weight loss (%)			
		A 300-400°C	B 500-600°C	C 800-900°C	Total
Oxygen	2	1.2	8.2		
	5	1.5	7.9	2.1	11.5
	15 *	2.3	7.3	2.6	12.2
	50	2.95	6.15		
Static air	5	3.0	7.0		
	15 *	4.4	5.8	3.2	13.4
	50	5.5	3.8	3.1	13.4
Nitrogen	15 *	8.5	1.45	2.85	12.8
Carbon dioxide	15 *	9.0	1.3	2.7	13.0
Argon	15†	10.0	0.9	2.3	13.2

Table 1. Weight losses shown by manganite under different flowing gas atmospheres.
*TG curves shown in Fig. 1; †TG curve shown in Fig. 2.

Schemes 1 and 2 probably occur simultaneously in the presence of oxygen, with scheme 2 predominating with decreasing $p\ O_2$. As both MnO_2 and Mn_5O_8 decompose to Mn_2O_3 between 500° and 600°C [2,3], it is possible to estimate the proportions of the two phases formed during weight loss A from its actual value - for instance, the amount of Mn_5O_8 formed in static air varied from 25% at 5°C/min to 60% at 50°C/min.

In carbon dioxide, nitrogen and argon, however, weight loss A exceeds 8.40% so a different reaction scheme must operate. Oswald et al. [3] found that manganite transformed topotactically to Mn_5O_8 in nitrogen, but this is not possible stoichiometrically unless another Mn-oxide of lower valency accompanies the Mn_5O_8. XPP examination of the product from weight loss A in nitrogen identified both Mn_5O_8 and Mn_2O_3. The formation of Mn_2O_3 alone as the product of weight loss A could be explained by reaction scheme 3:

$$2MnO.OH \quad \overset{A}{\underset{10.23\%}{\text{———}}} \quad Mn_2O_3 \quad + \quad H_2O \qquad \text{[SCHEME 3]}$$

$$\overset{C}{\underset{3.04\%}{\Big|}}$$

$$2/3Mn_3O_4 \quad + \quad 1/6O_2$$

Although this would account for the larger weight loss A shown in inert atmospheres, there would be no weight loss B as the Mn_2O_3 formed decomposes to Mn_3O_4 between 800° and 900°C. Table 1 shows that there is a weight loss B in inert atmospheres, this decreasing from nitrogen to argon. Lee et al. [4] demonstrated that, under vacuum, MnO.OH decomposed to equimolar amounts of Mn_5O_8 and Mn_3O_4, which forms the basis for reaction scheme 4 below:

$$8MnO.OH \quad \overset{A}{\underset{10.23\%}{\text{———}}} \quad Mn_5O_8 \quad + \quad Mn_3O_4 \quad + \quad 4H_2O \qquad \text{[SCHEME 4]}$$

$$\overset{B}{\underset{1.13\%}{\Big|}}$$

$$5/2\ Mn_2O_3 \quad + \quad 1/4O_2$$

$$\overset{C}{\underset{1.91\%}{\Big|}}$$

$$5/3Mn_3O_4 \quad + \quad 5/12O_2$$

Weight losses A, B and C are close to those shown under argon in Table 1, as is the overall loss to 1000°C of 13.27%. Simultaneous DTA-TG-MS curves in argon (Fig. 2) show water evolution during weight loss A and oxygen evolution during weight losses B and C, in accordance with scheme 4. There also appears to be a slight oxygen evolution during weight loss A, which could be accounted for by an accompanying reaction of the type:

$$12MnO.OH \quad \overset{A}{\underset{13.27\%}{\text{———}}} \quad 4Mn_3O_4 \quad + \quad 6H_2O \quad + \quad O_2 \qquad \text{[SCHEME 5]}$$
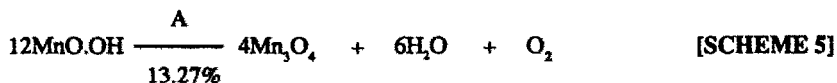
The generation of oxygen from such reactions would explain the discrepancies between weight losses in the diffent "inert" atmospheres in Table 1.

Fig. 2 also shows two further high-temperature reactions of manganite - the β–γ transition of the Mn_3O_4 reaction product at 1169°C [2] and decomposition of this to MnO above 1400°C.

CONCLUSIONS

Reaction schemes have been proposed that explain most of the variations shown by the TG curve of manganite in different atmospheres. Topotactic decomposition to Mn_5O_8 occurs at low p O2 between 300-400°C [3], but other Mn-oxides appear as products of the initial decomposition at high p O_2 and in inert atmospheres and these influence subsequent reactions. Variations in TG curves found at different heating rates in the same atmosphere are due to differences in rate of expulsion of the product gases (O_2 and H_2O) vs. rate of inward diffusion of atmosphere gas. Discrepancies in Table 1 between weight losses given in different "inert" atmospheres may be due, at least in part, to differences in diffusivity of the gases used, and thus variations in the self-generated sample atmosphere. This demonstrated dependence of decomposition mechanism on atmosphere and heating rate has important implications to the quantitative determination of manganite or similar artificial analogues by thermal methods, particularly TG.

REFERENCES

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4. J A Lee, C E Newnham, F S Stone & F L Tye. J. Sol. St. Chem. 31 (1980) 81-93.