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Thermochemistry of manganese oxides in reactive gas atmospheres: Probing catalytic MnO_x compositions in the atmosphere of $CO+O_2$

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Abstract

A series of Mn-oxides in the range MnO_2–MnO were subjected to thermogravimetry on heating up to 1100°C in the reactive gas atmosphere of O_2, CO and $CO+O_2$. Some selected solid residues were analyzed for the MnO_x composition by infrared spectroscopy, and for carbon deposits by CHNS-analyzer. The $CO+O_2$ gas stream was chromatographically analyzed, following heating the gas/solid interface to some selected temperatures. The results indicate that Mn-oxides in the range MnO_2–$Mn_{1.3}$ exhibit catalytic properties towards the CO oxidation in the gas phase. The higher thermal stability (up to $\sim$1000°C) of compositions in the range $MnO_{1.5-1.3}$, i.e. in the Mn_2O_3–Mn_3O_4 system, may render them particularly interesting in the field of applied catalysis. The experimental approach adopted in the present investigation may help accounting for the interfacial chemistry of solid-state reactions involving the surrounding gas atmosphere. © 1998 Elsevier Science B.V.

Keywords: Catalytic behaviour of Mn-oxides in $CO+O_2$ atmosphere; Manganese oxides; Thermal behaviour of Mn-oxides in $CO+O_2$ atmosphere; Thermochemistry of Mn-oxides; Thermogravimetry of Mn-oxides

1. Introduction

The adequate chemical makeup for deep oxidation (combustion) catalysts [1,2], which are increasingly sought after for environmental urgencies [3,4], seem to necessitate the inclusion of metal oxides capable of undergoing reversible oxygenation–deoxygenation cycles [4]. Mn-oxides have been highly rated [1,2,5] amongst the best candidate materials. Thermodynamically stable MnO_x compositions occur in the range $x=2-1$ [6,7], including the differently-structured simple oxides of MnO_2 (Mn^{IV}), Mn_2O_3 (Mn^{III}) and MnO (Mn^{II}), and the mixed oxides of Mn_5O_8 (Mn^{II},Mn^{IV}) and Mn_3O_4 (Mn^{II},Mn^{III}).

Therefore, we have very recently probed the thermal decomposition course of $MnO_2 \rightarrow MnO$ [8], so as to identify the 'redox' MnO_x compositions amongst the products yielding. Cyclic and non-cyclic thermogravimetries (in different reactive gas atmospheres) were amongst the investigation techniques employed. The results have revealed that the mixed-valent Mn_3O_4 ($=Mn^{II}Mn_2{}^{III}O_4$) undergoes perfectly reversible oxygenation–deoxygenation cycles upon heating in air (or oxygen atmosphere) at 500–1050°C. The oxygenation product has been identified to be the univalent Mn_2O_3 [8]. Moreover, Mn^{II}/Mn^{IV} couples in the mixed-valent Mn_5O_8 ($= Mn_2^{II}Mn_3^{IV}O_8$) have been found [8] to undergo a redox reaction during

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deoxygenation at 600–700°C (in air or O_2 atmosphere), giving rise to Mn_2O_3 (Mn^{III}).

The electron-mobile environment thus established in such mixed-valent metal oxides [9] may promise a catalytic potential in redox reactions. In the past, a pronounced catalytic activity of hopcalite ($CuMnO_x$) in the H_2O_2 decomposition reaction had been attributed [10] to electron-exchange interactions between ionic couples in the system $Cu^I/Cu^{II}/Mn^{III}/Mn^{II}$. Recently, Mn_3O_4-like surfaces have been allocated the catalytic responsibility in oxidative coupling reactions of methane [11,12].

The present investigation was basically designed to probe MnO_x compositions occurring in the range MnO_{2-1}, that perform catalytically when heated in a mixed gas atmosphere of CO and O_2. The experimental work was carried out using thermogravimetry of test Mn-oxides (on heating up to 800–1100°C) and gas chromatography of the reaction atmosphere. A comparison with results obtained for the same test oxides, but in separate gas atmospheres of CO and O_2, has been the base on which the catalytic behaviour has been recognized. Similar experimental approaches, whereby interfacial events occurring during solid-state reactions in reactive gas atmospheres are thermogravimetrically resolved, are infrequent in the literature.

2. Experimental

2.1. Test Mn-oxides

MnO_2 was a 99.9% pure product of Fluka (Switzerland), Mn_5O_8 was prepared by calcination of synthetic $MnC_2O_4{\cdot}2H_2O$ at 300°C for 3 h [13], and Mn_2O_3, Mn_3O_4 and MnO were AR-grade products of Aldrich (USA).

For identification purposes, MnO_2 was heated at a rate (ϕ) of 10°C/min in a 30 ml/min stream of CO to 500, 700 and 800°C. A similar heat treatment of MnO_2 was carried out in a mixed stream (30 ml/min) of CO and O_2 (1 : 2) to 600°C. The temperatures applied were chosen on the basis of thermal analysis results (vide infra). The gases were 99.99% pure products of Kuwait Oxygen and Acetylene Company (KOAC), and were used as supplied.

The various oxide samples were kept dry over silica gel (in vacuum) till further use. Those heated in the atmosphere of CO or $CO+O_2$ were analyzed for carbon deposits, using LECO CHNS-932 analyzer (USA), and found to contain hardly any detectable amounts.

2.2. Thermogravimetry (TG)

TG curves were measured while heating (at ϕ=10°C/min) small portions (~20 mg) of test samples in a dynamic atmosphere (30 ml/min) of O_2, CO or $CO+O_2$ (1 : 2) up to 1100°C. The measurements were carried out, using a model TGA-50 Shimadzu automatic analyzer (Japan) equipped with a TA-50WS work station for data acquisition and handling. The O_2 gas was also a 99.99% pure product of KOAC.

2.3. Infrared (IR) absorption spectroscopy

IR spectra were taken from KBr-supported test samples (<1 wt%), over the frequency range 400–4000 cm^{-1} and at a resolution of 4 cm^{-1}, using a model 2000 Perkin–Elmer FT spectrophotometer (UK). An on-line data station facilitated spectra acquisition and handling.

2.4. Gas chromatography (GC)

Gas samples were trapped during the TG measurements of MnO_2 in the mixed stream of $CO+O_2$ (vide supra) at different temperatures, viz. room temperature (RT), 300 and 700°C. The high temperatures were chosen on the basis of TG results (vide infra). The gas samples were then subjected to GC analysis for CO_2 content, using a model CP-9000 Chrompack chromatograph (USA) equipped with a TCD detector (at 260°C) and a packed column of PORAPACK Q (at 60°C). A 99.99% pure He (KOAC) was employed as the carrier gas (20 ml/min).

3. Results and discussion

3.1. TG curves in O_2 atmosphere

Fig. 1 displays TG curves obtained for the various MnO_x materials in the atmosphere of dynamic oxygen (30 ml/min). The results help to characterize the following three temperature ranges, in each of which the

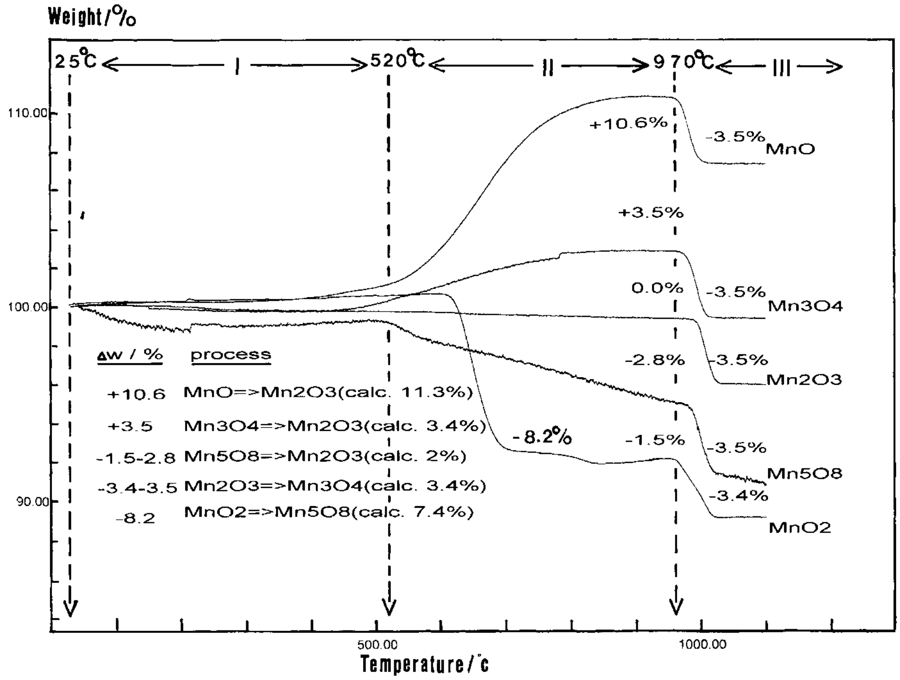

Fig. 1. TG curves recorded on heating of small portions (20±2 mg) of the Mn-oxides indicated at ϕ=10°C/min in a dynamic atmosphere (30 ml/min) of pure O_2 gas.

TG behaviours of the test materials are either analogous or similar. Range-I, RT-520°C, in which MnO and Mn_3O_4 suffer nothing but insignificant weight changes (ΔW). Range-II, 520–970°C, in which all the test materials concede major weight changes due either to weight gain (WG) processes (viz. MnO & Mn_3O_4) or weight loss (WL) processes (viz. Mn_5O_8 & MnO_2), except for Mn_2O_3 which remains weight invariant. Range-III, >970°C, in which all the test materials, without exception, undergo WL process.

The weight change values conceded by test materials in the temperature ranges (II) and (III), together with the processes assigned are indicated in Fig. 1. Earlier reports [7,8] can lend strong support for the assigned processes. It is obvious that the atmosphere of oxygen could not sustain the compositions of MnO_2, Mn_5O_8 and Mn_2O_3 against thermal decomposition (deoxygenation) which is seen to start near 600, 500 and 1000°C, respectively. The sequence of decomposition (Fig. 1) is as follows: $MnO_2 \rightarrow Mn_5O_8$ (T_{max}=680°C), $Mn_5O_8 \rightarrow Mn_2O_3$ (T_{max}=800°C) and, then, $Mn_2O_3 \rightarrow Mn_3O_4$ (T_{max}=990–1000°C).

It is also obvious from Fig. 1 that the atmosphere of oxygen could not sustain the compositions of Mn_3O_4 and MnO against heating at 400–970°C. These materials are shown to suffer a major WG process, whereby they are oxygenated (oxidized) to yield Mn_2O_3. The product is then decomposed in the temperature range-III (>970°C) to give Mn_3O_4, which is a high-temperature thermodynamically stable composition of Mn-oxide in O_2-rich atmosphere [6,7].

Thus, Fig. 1 helps to confirm that the test Mn-oxides (MnO_{2-1}) are thermally quite stable to heating in O_2 in the temperature range-I (RT-520°C). However in the higher temperature ranges (II) and (III), the thermal stability is maintained only for Mn_2O_3 (up to 970°C) and Mn_3O_4 (at >970°C), respectively. These findings are in line with our previous results [8], in confirming the critical temperature dependence of the equilibrium position of the reversible transformation $3Mn_2O_3 \leftrightarrow 2Mn_3O_4 + 1/2O_2$. The equilibrium is considerably displaced to the right side at >970°C, and vice versa. It is interesting to realize that the presence of Mn^{II} in both Mn_3O_4 and MnO triggers their sus-

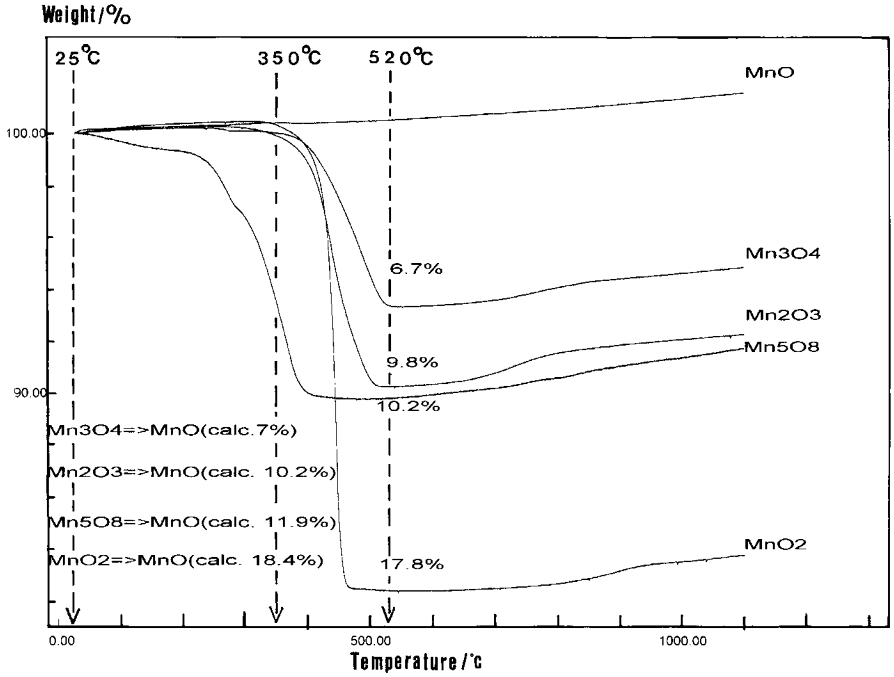

Fig. 2. TG curves recorded on heating the Mn-oxides indicated in a dynamic atmosphere of pure CO gas.

ceptibility to oxygenation reactions, while its presence in Mn_5O_8 does not do likewise. Mn_5O_8 has been shown [8] to deoxygenate into Mn_2O_3, but has not been found to oxygenate into MnO_2.

3.2. TG curves in CO atmosphere

TG curves obtained for the various MnO_x materials in a dynamic atmosphere of CO (30 ml/min) are compared in Fig. 2. It is evident that heating to 520°C in the CO atmosphere forces the test materials to suffer a significant WL, except for MnO. The WL is shown (Fig. 2) to commence at $\geq$350°C for MnO_2, Mn_2O_3 and Mn_3O_4, but at a considerably lower temperature for Mn_5O_8. The WL values determined correspond very well to the formation of MnO as the eventual product in all the cases (Fig. 2). It is shown to suffer no further weight changes on heating up to 1100° in CO, except for minute (<2%) WGs.

In the temperature range (<520°C) of the WL process observed in the CO atmosphere (Fig. 2), the test materials are shown to be weight-invariant in O_2 (Fig. 1). A similar weight-invariant behaviour has been observed earlier [8] for the test materials on heating up to 500°C in N_2 atmosphere. Accordingly, the WL effected at <520°C (Fig. 2) is CO-induced, i.e. chemically, rather than thermally, assisted. In other words, the effected WL marks the CO-reduction of MnO_2, Mn_5O_8, Mn_2O_3 and Mn_3O_4, eventually giving MnO as the reduction product of each of them. Consistently, MnO is shown (Fig. 2) to exhibit a pronounced stability to heating in the CO atmosphere up to 1100°C. The minute WGs, observed at >520°C, are most likely due to surface interactions with the CO atmosphere, rather than to bulk interactions.

Hence, when O_2 is replaced by CO in the surrounding gas atmosphere, the Mn-oxides (except for MnO) are chemically destabilized on heating in the temperature range (RT–520°C) over which they are otherwise thermally stable (Fig. 1). The solid residues of heating MnO_2 in CO up to 500, 700 and 800°C were subjected to IR analysis. The spectra obtained (not shown) showed four detectable absorption bands (at 415(s,sh), 509(s,sp), 614(s,sp) and 694(w,sh) cm^{-1}) for the residue at 500°C, and two bands only (at 469(vs) and 704(w,sh) cm^{-1}) for the residues at 700 and 800°C. The former four bands are assignable to a mixture of Mn_2O_3 and Mn_3O_4 [14], whereas the latter two bands are most likely due to highly distorted MnO [15]. These results may imply that the TG-displayed single WL step for the CO-reduction of test samples is somewhat composite in nature and conceals a multistep course to the eventual reduction product (MnO).

3.3. TG curves in CO+O_2 atmosphere

TG curves obtained on heating the test Mn-oxides in a mixed atmosphere of CO+O_2 (1 : 2) are displayed in Fig. 3, which also insets, for comparison purposes, the TG curves obtained for the given oxide in the separate gas atmospheres of CO (Fig. 2) and O_2 (Fig. 1). The results help to characterize either of the following two behaviours: (i) a behaviour to which both CO and O_2 have comparably contributed, and (ii) a behaviour to which O_2 is the dominant contributor. The former behaviour is the one reflected by the TG curves of MnO_2 (Fig. 3(A)), Mn_5O_8 (Fig. 3(B)) and Mn_2O_3 (Fig. 3(C)), whereas the latter is the one monitored by the TG curves of Mn_3O_4 (Fig. 3(D)) and MnO (Fig. 3(E)).

For MnO_2, Fig. 3(A) reveals that the coexistence of CO in the surrounding gas atmosphere accelerates the thermal decomposition to Mn_5O_8 (possibly plus Mn_2O_3) to commence near 500°C instead of 630°C in pure O_2. On the other hand, the coexistence of O_2 may be seen to completely suppress, or compensate for, the reductive influence of CO; the reductive WL step commencing near 350°C in the CO atmosphere is not visible in the mixed atmosphere of CO+O_2 (Fig. 3(A)). A similar behaviour can be seen in Fig. 3(B) and (C) for Mn_5O_8 and Mn_2O_3, respectively. The results reveal, for both materials, a complete suppression of the CO-reduction, due to the coexistence of O_2, and show alternatively a steady WG till the decomposition temperature (near 1000°C) of Mn_2O_3 to Mn_3O_4 is reached.

For Mn_3O_4, the TG obtained in CO+O_2 (Fig. 3(D)) is largely similar to that obtained in pure O_2. Thus, the CO-reduction to MnO is completely prevented, whereas the oxidation to Mn_2O_3 is maintained. The same is shown (Fig. 3(E)) to apply to MnO. The sole difference here lies in the fact that CO originally has no reductive influence on MnO over the temperature range scanned.

The fact that the CO-reduction of the test MnO_x materials to MnO is completely suppressed, or compensated for, in the mixed atmosphere of CO+O_2 may imply either complete unavailability of CO, or simultaneous re-oxidation by the coexisting O_2. The behaviour communicated for MnO_2 and Mn_5O_8, in particular, may rather sustain the CO unavailability option. The corresponding TG curves (Fig. 3) do not display the tendency of both the test materials towards the required dissociative uptake of O_2. Consequently, the CO molecules have most likely been catalytically oxidized in the oxygen-rich atmosphere over the operational temperature range of the CO-reduction of the test oxides, i.e. at 200–500°C (Fig. 2). The subsequent WG observed detectably at 500–1000°C for Mn_5O_8 (Fig. 3(B)) and Mn_2O_3 (Fig. 3(C)), may be ascribed tentatively to CO_2 absorption by the test materials.

GC analysis results of the CO+O_2 stream at RT, and following heating over MnO_2 to 300 and 700°C are shown in Fig. 4. These results show the formation of CO_2 at 300 and 700°C. IR analysis of the solid residues of MnO_2 characterizes Mn_5O_8 (bands at 424(w,sh), 493(s,sp) and 608(s,sp) cm^{-1} [7]) and Mn_2O_3 (bands at 429(w,sh), 494(s,sp), 604(s,sh) and 694(w,sh) cm^{-1} [14]) following heating in CO+O_2 to 400 and 600°C, respectively. Consequently, it is not until the temperature reaches 400°C that MnO_2 commences to reduce in CO+O_2, and the reduction product, even at 600°C, is not MnO. Thus, the catalytic CO+O_2 reaction (at 300°C in particular) is the only source left for CO_2 production in the gas phase [16].

The above results indicate that all of the MnO_x compositions tested, except for MnO, exhibit catalytic activity towards CO oxidation in O_2-rich atmosphere. However, the higher thermal stabilities of compositions in the range $MnO_{1.5-1.3}$, i.e. in the Mn_2O_3—Mn_3O_4 system, might render them particularly interesting in the field of applied catalysis. The failure in detecting carbon deposits on the solid residues of the heating of MnO_2 in CO+O_2 atmosphere at 600°C may exclude the Boudouart mechanism ($2CO_{(g)} \rightarrow CO_{2(g)} + C_{(s)}$ [17]) from the likely surface reaction pathways of CO oxidation [16]. It may, alternatively, suggest Mn-oxides as promising ingredients for the catalyst being sought [4] for soot combustion in automobile exhaust emissions.

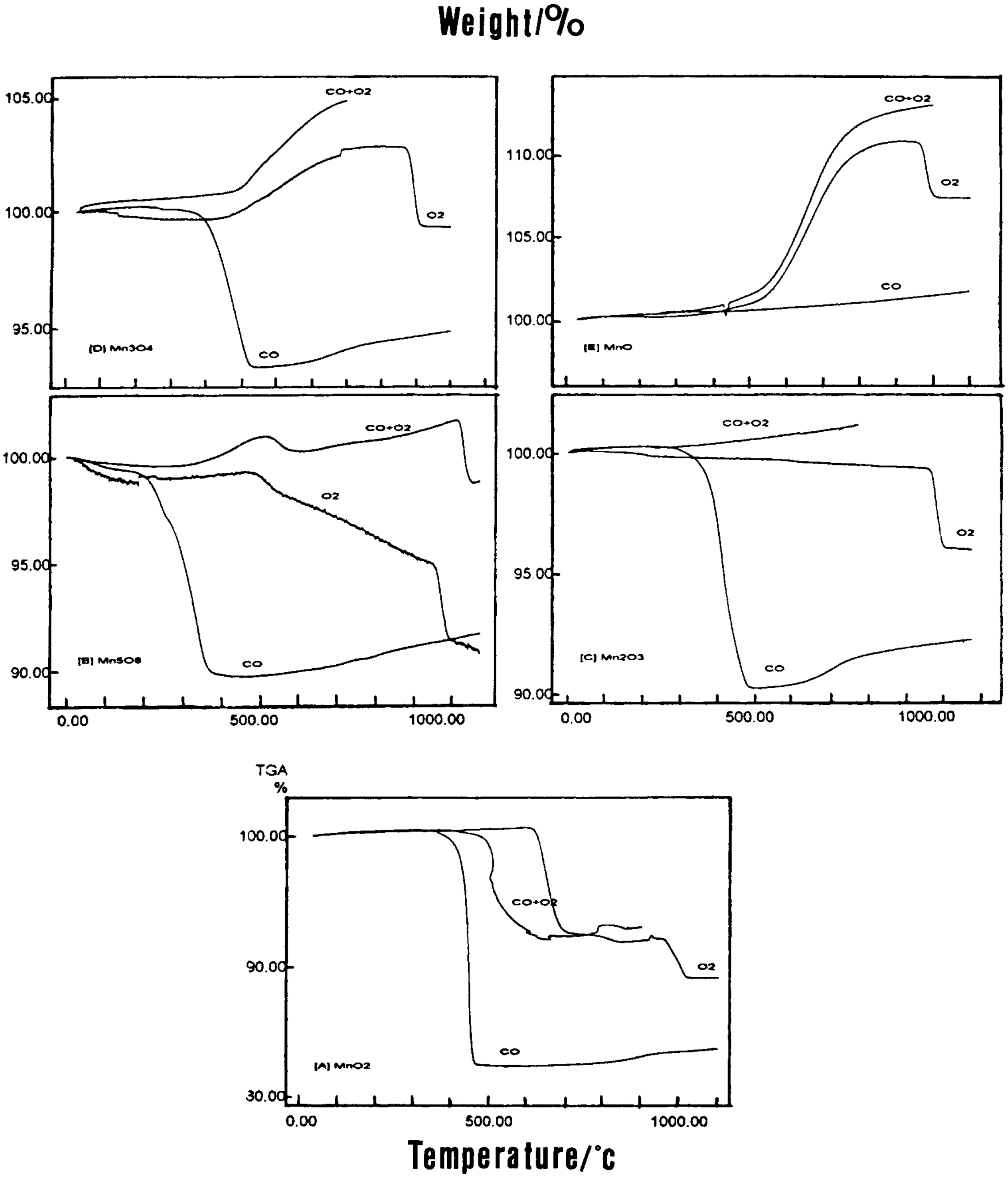

Fig. 3. TG curves recorded on heating MnO_2 (A), Mn_5O_8 (B), Mn_2O_3 (C), Mn_3O_4 (D) and MnO (E) in a dynamic atmosphere of $CO+O_2$ (1 : 2). Corresponding curves obtained in separate atmospheres of pure O_2 (Fig. 1) and CO (Fig. 2) are inset for comparison.

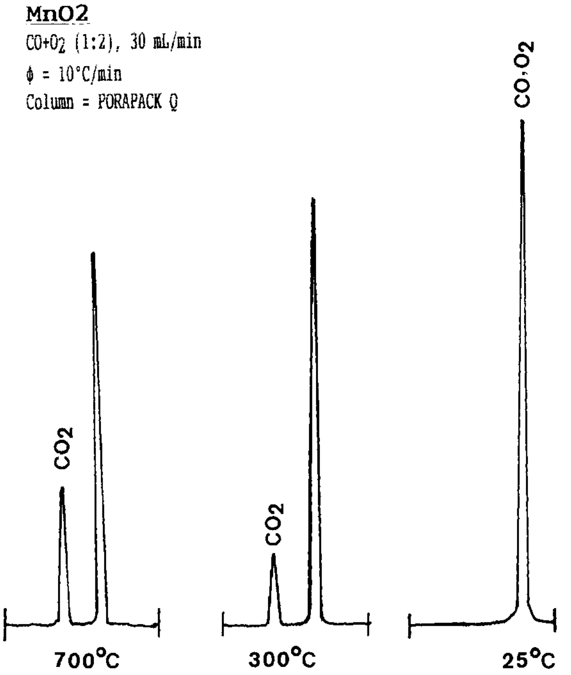

Fig. 4. Gas chromatograms for samples taken from the gas phase of $CO+O_2$ at room temperature and following heating over MnO_2 to 300 and 700°C.

4. Conclusion

Mn-oxide compositions in the range $MnO_{2-1.3}$, i.e. in the MnO_2–Mn_3O_4 system, do exhibit catalytic activity towards CO oxidation in O_2-rich atmosphere. The higher thermal stabilities (up to near 1000°C) of compositions in the range $MnO_{1.5-1.3}$, i.e. in the Mn_2O_3–Mn_3O_4 system, may render them particularly interesting in the field of applied catalysis.

The experimental approach adopted in the present investigation can help examining solid catalysts under working conditions by thermogravimetry in the reactive gas atmosphere. Resolution of the interfacial events is quite likely, provided that systematic thermogravimetry of the solid/gas system, including analogous series of the test solids and gases, is carried out.

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