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EFFECTS OF LITHIUM DOPING ON THE THERMAL DECOMPOSITION OF MANGANESE CARBONATE

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ABSTRACT

The influence of lithium oxide doping on the thermal decomposition of manganese carbonate was studied using DTA, TG, DTG and X-ray diffraction techniques.

Pure $MnCO_3$ was found to undergo thermal decomposition at 450°C losing 31% of its weight to yield Mn_2O_3. The pure solids heated at 900 and 1100°C consisted of well-crystalline Mn_3O_4 with a trace amount of undecomposed Mn_2O_3, the amount of which decreased with increasing calcination temperature from 900 to 1100°C.

The DTA, TG and DTG analyses revealed that lithium doping of $MnCO_3$ effected a slight decrease in the percentage of its decomposition proportional to the amount of doping agent. Manganese carbonate treated with different proportions of Li_2CO_3 underwent thermal decomposition at about 315°C yielding MnO_2 which decomposed readily at about 400°C giving Mn_2O_3. The presence of Li_2CO_3 was found to enhance the decomposition of both MnO_2 and Mn_2O_3 producing Mn_2O_3 and Mn_3O_4, respectively.

X-ray diffraction showed that pure $MnCO_3$ calcined at 500°C consisted entirely of well-crystalline Mn_2O_3, and the lithium-treated solids heated at the same temperature were composed of γ-Mn_2O_3, Mn_2O_3 and Li_2MnO_3. The diffraction lines of Li_2MnO_3 persisted in the case of doped solids heated at 900°C, together with those of Mn_3O_4, and disappeared on heating at 1100°C with the subsequent appearance of Mn_2O_3 which remained stable at such high temperatures due to the formation of a Li_2O–Mn_2O_3 solid solution.

INTRODUCTION

The thermal decomposition of manganese carbonate has been made the object of several investigations [1–5]. However, the results obtained showed some disagreements, probably due to differences in the methods of preparation, calcination conditions and the presence of impurities. It has been reported that the activation energy of the thermal decomposition of pure $MnCO_3$, under reduced pressure of 10^{-5} Torr in the temperature range 300–400°C, is 22.5 kcal mol^{-1}. This value is very close to the heat of dissociation of manganese carbonate [4].

The effect of foreign ions on the thermal decomposition of manganese carbonate, to our knowledge, has not yet been investigated. The presence of foreign ions, of various size and valence, such as Li^+, Na^+, Mg^{2+}, Al^{3+}, Zr^{4+}, Th^{4+}, V^{5+} and Mo^{6+}, has been found to greatly affect the thermal decomposition of basic cobalt carbonate [6–10].

The present investigation reports a study on the effect of lithium upon the thermal decomposition of manganese carbonate using DTA, TG, DTG and X-ray diffraction techniques.

EXPERIMENTAL

Materials

Pure and treated manganese oxides were prepared by thermal decomposition of pure manganese carbonate and that mixed with different proportions of Li_2CO_3 (2–10 mol%). The calcination temperature was varied between 400 and 1100°C.

Techniques

Differential thermal analysis (DTA) of pure and treated $MnCO_3$ was carried out using a Netzsch-Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10° min^{-1}. A 200-mg sample of each solid specimen was employed in each case.

An X-ray investigation of the thermal products of pure and treated manganese carbonate was performed with a Philips diffractometer (type PW 1390). The patterns were run with Mn-filtered iron radiation $\lambda = 1.9373$ Å, at 40 kV and 25 mA with a scanning speed of 2° in 2θ min^{-1}.

RESULTS

Thermal decomposition of pure manganese carbonate

Figure 1 represents DTA, TG and DTG of pure $MnCO_3$ which were simultaneously recorded. Three endothermic peaks were observed: the first weak, broad peak extended between 60 and 220°C with its maximum at 146°C; the second strong, sharp peak extended between 390 and 550°C having its maximum at 450°C; the third extended between 930 and 980°C with its maximum at 950°C. The first peak was accompanied by a 4.5% weight loss and corresponded to the departure of physisorbed water. The second peak was accompanied by a weight loss of 31.25%. The third peak was accompanied by a weight loss of about 1%. The last two peaks were separated by a state of thermal stability between 560 and 930°C.

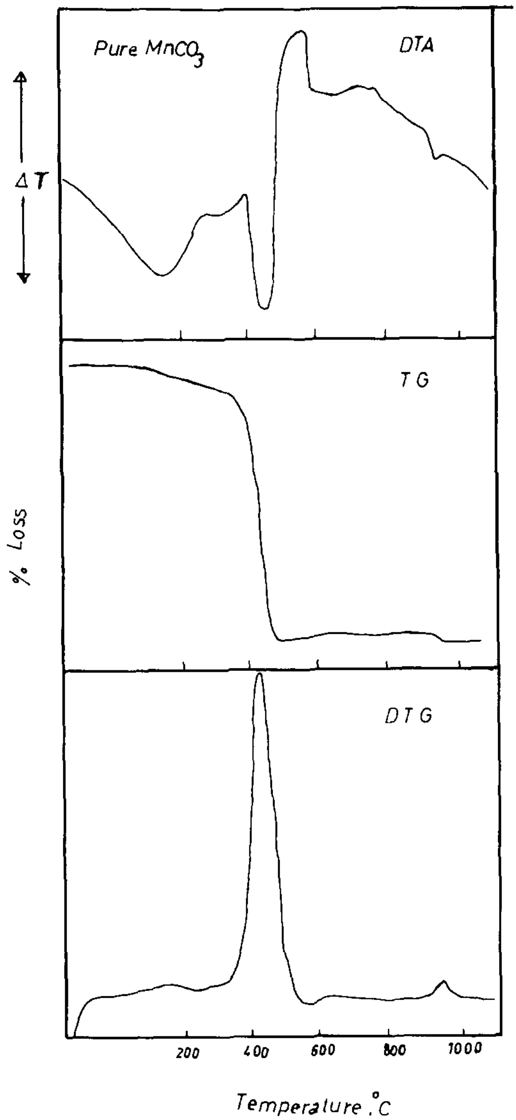


Fig. 1. DTA, TG and DTG curves of pure $MnCO_3$.

Manganese carbonate, upon decomposition to yield MnO_2 or Mn_2O_3, should suffer a weight loss of 24.35 or 31.3%, respectively. The recorded weight loss (31.25%) indicated that $MnCO_3$ decomposed readily to give Mn_2O_3, or gave MnO_2 which underwent a simultaneous decomposition to yield Mn_2O_3 according to

$$2MnCO_3 + \tfrac{1}{2}O_2(g) \xrightarrow{390-550^\circ C} Mn_2O_3 + 2CO_2(g) \tag{1}$$

$$MnCO_3 + \tfrac{1}{2}O_2(g) \xrightarrow{390-550^\circ C} MnO_2 + CO_2(g) \tag{2}$$

$$2MnO_2 \xrightarrow{390-550°C} Mn_2O_3 + \tfrac{1}{2}O_2(g) \quad (3)$$

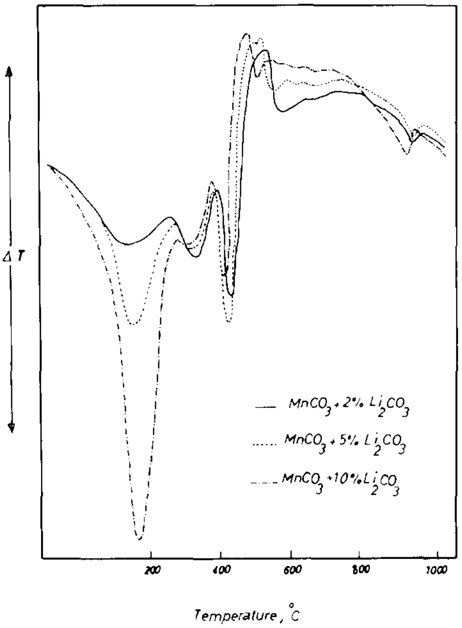
The Mn_2O_3 produced remained thermally stable up to 920°C and decomposed above this temperature to give Mn_3O_4. These results will be confirmed later in this investigation by X-ray diffraction measurements. Mn_2O_3, upon decomposition to produce Mn_3O_4, should suffer a weight loss of 3.37%, according to

$$3Mn_2O_3 \xrightarrow{930°C} 2Mn_3O_4 + \tfrac{1}{2}O_2(g) \quad (4)$$

The recorded loss in weight (1%) indicated that Mn_2O_3 underwent partial decomposition to produce Mn_3O_4, and that the complete decomposition required a thermal treatment at higher temperatures (above 1100°C).

Thermal decomposition of Li_2CO_3-treated $MnCO_3$

Figures 2 and 3 represent the DTA, TG and DTG curves of manganese carbonate treated with different proportions of lithium carbonate (2–10



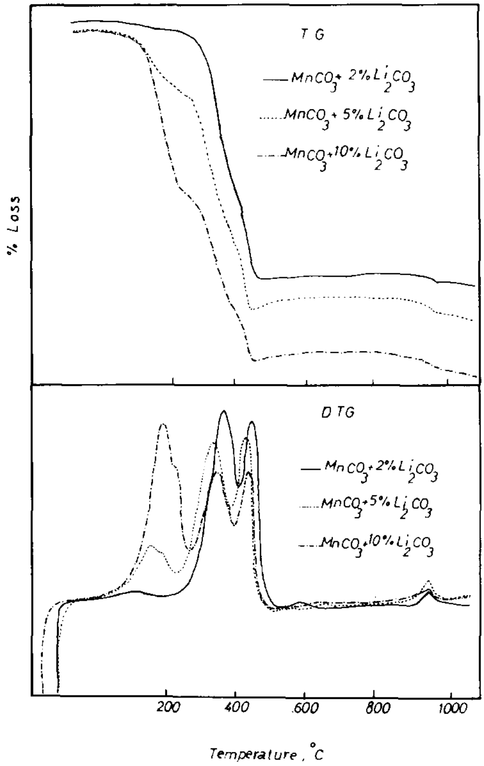


Fig. 2. DTA curves of Li-doped $MnCO_3$.

Fig. 3. TG and DTG curves of Li-doped $MnCO_3$.

mol%). Five endothermic peaks were recorded. The area of the first peak (60–220°C) greatly increased with increasing lithium carbonate added; its maximum was located at 120, 140 and 160°C for the manganese carbonate samples treated with 2, 5 and 10 mol% Li_2CO_3, respectively. This peak was accompanied by a weight loss of 2.5, 6.25 and 21%, respectively. It can be concluded that the addition of lithium carbonate to $MnCO_3$ greatly increased the amount of physisorbed water. The second endothermic peak (265–370°C) had a maximum at 325, 310 and 300°C for the manganese carbonate specimens treated with 2, 5 and 10 mol% Li_2CO_3, respectively. This peak was accompanied by a weight loss of 21.25, 18.5 and 14%, respectively. The area of the second peak decreases with increasing lithium carbonate added. It can thus be concluded that the doping agent produces a decrease in the percentage decomposition of manganese carbonate in proportion to the amount of foreign ions employed. The third sharp, strong peak (380–450°C) had a maximum located at 430, 415 and 390°C for the solids treated with 2, 5 and 10 mol% Li_2CO_3, respectively. This peak was followed by almost the same weight loss of 9% for all doped specimens. This percentage corresponds to the decomposition of MnO_2 to Mn_2O_3 according to

$$2MnO_2 \xrightarrow[Li_2CO_3]{380\text{–}450°C} Mn_2O_3 + \tfrac{1}{2}O_2(g)$$

The weight loss of 9% indicated a complete decomposition of MnO_2 to Mn_2O_3. The fact that the maximum of the third peak, corresponding to the decomposition of MnO_2, shifted to lower temperatures to an extent proportional to the amount of lithium carbonate added, revealed that the doping agent enhanced the thermal decomposition of manganese dioxide. In other words, lithium doping decreased the thermal stability of MnO_2. The fourth peak (490–580°C), not observed in the case of pure solid, had a maximum at 560, 530 and 500°C for the solids treated with 2, 5 and 10 mol% Li_2CO_3, respectively. Preliminary experiments showed that lithium carbonate decomposed at 700°C to give Li_2O. This peak might correspond to a solid–solid interaction between Li_2CO_3 and Mn_2O_3. (The identity of the phase produced will be defined later in this investigation by X-ray diffraction measurements.) The last peak (885–945°C) had a maximum at about 930°C. This peak was accompanied by a weight loss of about 2%, instead of 1% in the case of the pure solid. The last two peaks are separated by a stage of thermal stability of Mn_2O_3 between 580 and 885°C. These results clearly indicate that the doping agent also enhanced the decomposition of Mn_2O_3 to yield Mn_3O_4, i.e., Li doping greatly decreased the thermal stability of Mn_2O_3.

X-ray investigation of the thermal products of pure $MnCO_3$

X-ray diffraction patterns were recorded for pure manganese carbonate heated in air at 500, 900 and 1100°C for 6 h. Figure 4 represents the diffraction lines of the pure solids calcined at different temperatures. It can be seen from Fig. 4 that all the characteristic lines of Mn_2O_3 were detected in the diffraction patterns of the solid calcined at 500°C, together with an additional line with a small intensity at $d = 3.12$ Å. This line might indicate the presence of trace amounts of un-decomposed MnO_2. Figure 4 also shows that the pure solids heated at 1000 and 1100°C consisted mainly of a well-crystalline Mn_3O_4 phase together with a diffraction line at $d = 2.71$ Å. The intensity of this line, which is relatively small, suffered a further decrease on increasing the calcination temperature from 900 to 1100°C. This line might correspond to the presence of a minute amount of un-decomposed Mn_2O_3. In fact, it has been shown from the TG and DTG curves of Fig. 1, that the observed weight loss in the case of the pure solid heated at 900°C (1%) is smaller than that (3.37%) corresponding to the complete thermal decomposition of Mn_2O_3 to Mn_3O_4.

X-ray investigation of the thermal products of $MnCO_3$ treated with different proportions of Li_2CO_3

Figure 5 represents the X-ray diffraction patterns of manganese carbonate treated with 5 mol% Li_2CO_3 and heated in air for 6 h at 500, 900 and 1100°C. It can be observed from Fig. 5 that in the case of the doped solid heated at 500°C all the characteristic lines of both Mn_2O_3 and γ-Mn_2O_3 are detected. However, the intensity of the γ-Mn_2O_3 lines is slightly lower than that of the other phase. A comparison between the diffraction lines of pure and doped solids heated at 500°C showed that the degree of crystallinity of Mn_2O_3 in the doped solid is much greater than that in the case of the pure solid. Additional new diffraction lines of relatively high intensity were also

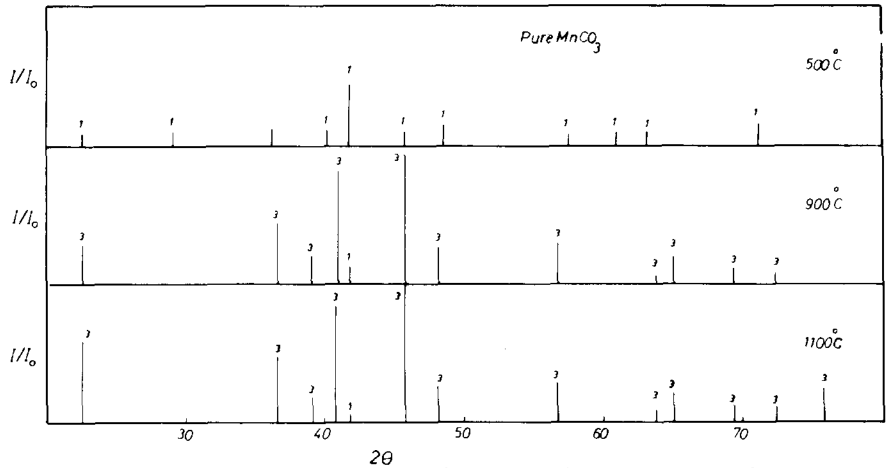


Fig. 4. X-ray diffraction patterns of the thermal products of pure $MnCO_3$. (1) Mn_2O_3; (3) Mn_3O_4.

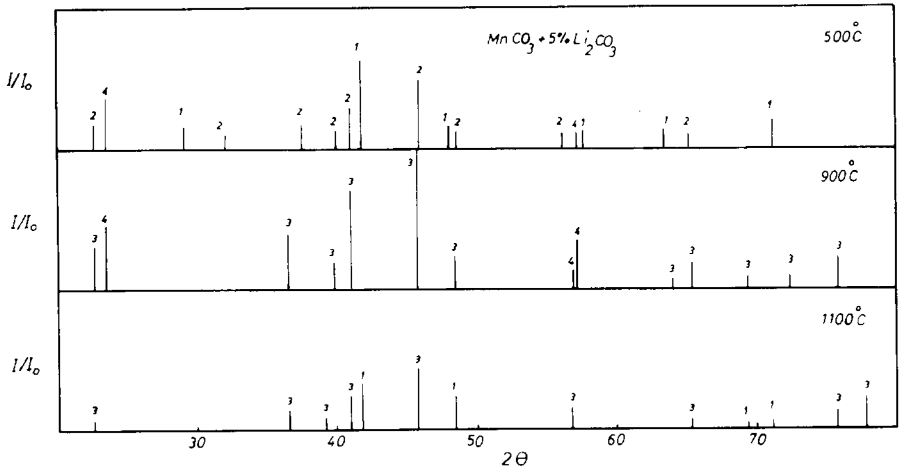


Fig. 5. X-ray diffraction patterns of the thermal products of Li-doped $MnCO_3$: (1) Mn_2O_3; (2) Mn_2O_3; (3) Mn_3O_4; (4) Li_2MnO_3.

detected in the case of doped oxide calcined at 500°C. The 2θ values and d-spacings of these lines were calculated and found to be: $2\theta = 23.50$, 57.00, 57.30; $d = 4.75$, 2.03, 2.02, respectively. These lines correspond to the lithium manganate phase [11].

The observed endothermic peak (the fourth one) with a maximum at 530°C (cf. Fig. 2) thus indicated the solid–solid interaction between Mn_2O_3 and Li_2CO_3 giving the Li_2MnO_3 phase, according to

$$Mn_2O_3 + Li_2CO_3 \xrightarrow{500^\circ C} Li_2MnO_3 + MnCO_3 \tag{5}$$

This reaction is not, in fact, accompanied by any change in the weight of the reacting species and the $MnCO_3$ produced, which decomposed readily to give Mn_2O_3, interacted with Mn_2O_3 to give lithium manganate.

It can be observed from Fig. 5 that the thermal treatment of the 5% lithium-doped solid at 900°C resulted in a complete disappearance of all the diffraction lines of the Mn_2O_3 phase with subsequent appearance of the characteristic lines of the Mn_3O_4 phase. The degree of crystallinity of the Li_2MnO_3 produced was found to increase on increasing the calcination temperature of the doped solid from 500 to 900°C. Increasing the calcination temperature to 1100°C led to the complete disappearance of all the characteristic diffraction lines of lithium manganate with the appearance of the diffraction lines of Mn_2O_3 together with those corresponding to Mn_3O_4. However, the crystallinity of Mn_3O_4 heated at such temperatures was much smaller than that for the solid heated at 900°C (cf. Fig. 5). It can be concluded that the Li_2MnO_3 produced decomposed readily on heating at 1100°C to give Mn_2O_3 and Li_2O dissolved in its lattice.

$$Li_2MnO_3 \xrightarrow{1100^\circ C} Li_2O\text{–}Mn_2O_3 + \tfrac{1}{2}O_2(g) \tag{6}$$

The lithium oxide-doped Mn_2O_3 strongly resisted thermal decomposition to give Mn_3O_4, even on heating at such high temperatures.

DISCUSSION AND CONCLUSIONS

The results of DTA, TG, DTG and X-ray diffraction clearly indicate that the addition of small proportions of lithium carbonate (2–10 mol%) to manganese carbonate greatly affect its thermal decomposition and the decomposition of the manganese oxides produced. Lithium doping was also found to greatly increase the hygroscopic nature of $MnCO_3$ which might lead to the creation of an energy barrier opposing the complete decomposition of manganese carbonate.

The presence of monovalent lithium ions was found to decrease the thermal stability of MnO_2. Manganese dioxide is known to behave as an intrinsic n-type semiconductor of very high charge carrier concentration and very low mobility [12,13]. It has been shown by one of the authors [6,9] that lithium doping of Co_3O_4, a p-type semiconductor, totally prevents its decomposition even on heating at very high temperatures (1100°C). The dissolution of Li^+ ions in the lattice of n-type semiconductors, via substitution of some of their host cations, is known to reduce the concentration of the charge carriers [13,14] effecting a decrease in their n-type semiconducting character. By contrast, Li doping greatly increases the concentration of the charge carriers in the case of p-type semiconductors [14]. It is plausible to argue that the monovalent lithium ions being added to MnO_2 effected a noticeable decrease in the concentration of its charge carriers and a subsequent decrease in the oxidation state of the doped manganese dioxide. The diminution in the oxidation character of MnO_2 due to doping with lithium might contribute to the observed decrease in its thermal stability.

It has also been shown, in the present investigation, that lithium doping decreases the thermal stability of Mn_2O_3. This oxide, to our knowledge, also behaves as an n-type semiconductor. The observed decrease in the thermal stability of Mn_2O_3 due to lithium doping might also be attributed to a possible diminution of its oxidation state resulting from a diminution of the concentration of its charge carriers. However, Mn_2O_3 left from the thermal decomposition of lithium manganate, Li_2MnO_3, at 1100°C exhibited a remarkably high thermal stability. This might indicate that such Mn_2O_3 is different from that produced from the thermal decomposition of pure manganese dioxide. It seems that a homogeneous Li_2O–Mn_2O_3 solid solution was produced by heating the doped solid at 1100°C. Such a solid solution has a high thermal stability. The departure of lithium ions from the lattice of Mn_2O_3 required heating at temperatures much higher than 1100°C.

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