Thermochimica Acta, 101 (1986) 195–203
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL SOLID–SOLID INTERACTION BETWEEN SODIUM AND MANGANESE OXIDES

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(Received 8 October 1985)

ABSTRACT

The solid–solid interaction between sodium and manganese oxides was studied using DTA, TG, DTG, X-ray diffraction and chemical determination of the amount of sodium ions contributing in solid solutions and in solid–solid interactions.

The results obtained revealed that sodium-doping of $MnCO_3$ enhanced its thermal decomposition and also favoured the thermal decomposition of MnO_2 giving Mn_2O_3 which decomposed less readily at 900°C yielding Mn_3O_4. In other words, sodium treatment decreased the thermal stability of both $MnCO_3$ and MnO_2 but increased that of Mn_2O_3. Such effects were directly proportional to the amount of dopant ions added. The amount of sodium ions dissolved in Mn_2O_3 was not greatly changed by increasing the dissolution temperature from 400 to 500°C and decreased on increasing the temperature to 750°C. A highly crystalline sodium manganate phase, $Na_4Mn_9O_{18}$, was formed by heating the sodium-treated manganese oxides in air at 900°C. Such a newly formed compound was found to decompose readily at 1050°C giving Mn_3O_4 and Na_2O which was effectively dissolved in manganic oxide forming an Na_2O–Mn_3O_4 solid solution.

The observed changes in the thermal stability of manganese oxides due to sodium-treatment were attributed to alterations in the oxidation state of the doped solids.

INTRODUCTION

Manganese carbonate is known to decompose readily on heating in air or under a reduced pressure of 10^{-5} Torr at moderate temperatures (300–400°C) yielding MnO_2 which dissociates simultaneously to form Mn_2O_3 [1–4]. This oxide remained thermally stable to 900°C then decomposed to form Mn_3O_4. The presence of foreign ions has been found to affect the thermal stability of both manganese carbonate and manganese oxides significantly. It has been reported by two of the authors that lithium retarded the thermal decomposition of $MnCO_3$ and enhanced the decomposition of both MnO_2 and Mn_2O_3 [4]. These results have been attributed to an induced increase in the hygroscopic nature of the treated $MnCO_3$ and to a decrease in the oxidation state of the doped oxides. γ-Irradiation has also been shown to affect the thermal decomposition of manganese carbonate and manganese oxides significantly [5].

0040-6031/86/$03.50

The present investigation was devoted to studying the effect of sodium upon the thermal decomposition of manganese carbonate and manganese oxides using DTA, TG, DTG, X-ray and chemical determination of sodium ions dissolved in different manganese oxides.

EXPERIMENTAL

Materials

Pure and treated manganese oxides were prepared by thermal dissociation of pure manganese carbonate and that mixed with different proportions of NaOH (2–30 mol%). The calcination temperature was varied between 400 and 1100°C.

Techniques

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

The amounts of sodium ions effectively retained in manganese oxide specimens, under specified experimental conditions, were determined using a flame photometer (Corning EEL). A known mass of the calcined solid (0.10 g) was dissolved in 50% HCl and the total amount of sodium ions added was thus determined. The fraction of the foreign ions, not dissolved in the oxide lattice, was washed out by boiling water and the difference between the total amount and that extracted by boiling water gave the extent of the alkali metal ions dissolved in manganese oxide specimens.

RESULTS

Thermal behaviour of pure and treated $MnCO_3$

Figures 1 and 2 represent DTA, TG and DTG curves of pure and treated manganese carbonate. Four endotherminc peaks are observed in the case of pure solid specimens, the first two peaks, sharp and strong, are successive with maxima at 420 and 450°C and followed by a total weight loss of 32%. The third peak, not accompanied by any weight loss, has a maximum at

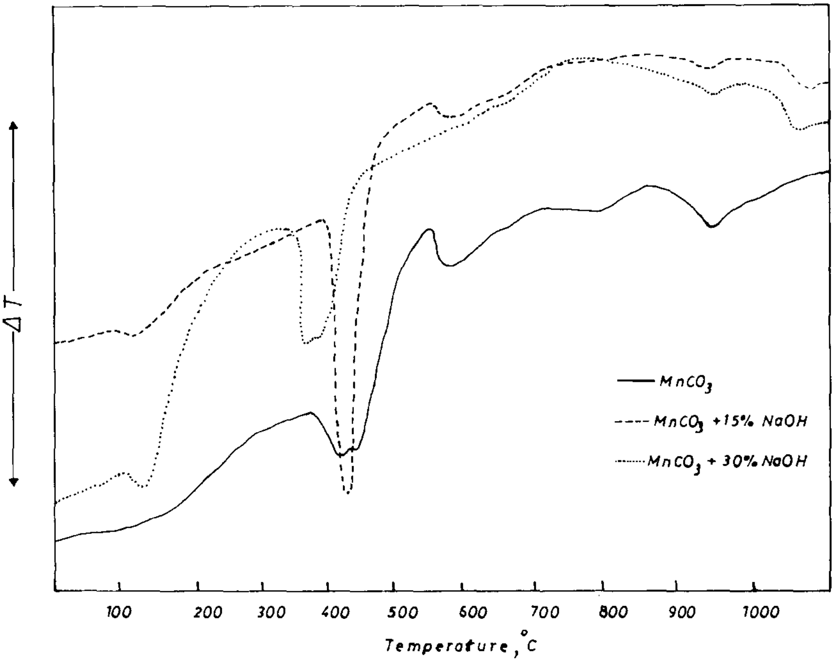

Fig. 1. DTA curves of pure and sodium-doped $MnCO_3$.

580°C and indicates a phase transformation. The last peak, which is relatively broad extending between 900 and 1000°C with its maximum at 950°C, was followed by a 0.75% weight loss. The two successive peaks at 420 and 450°C indicated the decomposition of $MnCO_3$ to MnO_2 which underwent a simultaneous thermal decomposition giving Mn_2O_3. The Mn_2O_3 produced remained thermally stable to 900°C then decomposed at temperatures above 900°C yielding Mn_3O_4 [4]. The endothermic peak at 950°C characterizes the last chemical change: $Mn_2O_3 \rightarrow Mn_3O_4$.

In the case of the specimen treated with 15 mol% NaOH, the first two endothermic peaks were unified forming a very strong and sharp peak having its maximum at 425°C. This peak was followed by a 31.2% weight loss. Three other endothermic peaks were observed, the first is broad with a maximum at 590°C and was not followed by any change in weight indicating a phase transformation process. The next peak is very weak and broad extending between 900 and 1000°C. The last peak is weak but not broad with a maximum at 1050°C. The last two peaks were accompanied by a very small weight loss (0.5%).

Five endothermic peaks were detected in the DTA curve of the manganese carbonate specimen treated with 30 mol% NaOH. The first three peaks were strong and sharp with maxima at 130, 370 and 390°C, respectively. The last two peaks were relatively weak and broad with their maxima located at 960 and 1050°C, respectively. The first peak at 130°C, not observed in the case

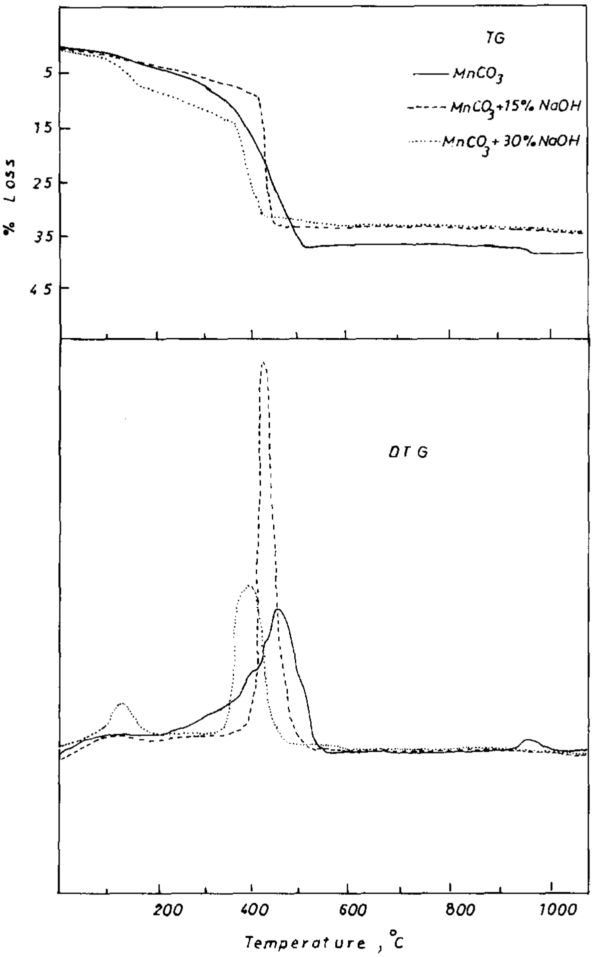

Fig. 2. TG and DTG curves of pure and sodium-doped $MnCO_3$.

of the other solid specimens, was followed by a 7% weight loss. This peak indicated the departure of physisorbed water showing that sodium hydroxide-treatment of manganese carbonate increased its hygroscopic nature. Similar results have been reported by two of the authors in the case of $MnCO_3$ treated with Li_2CO_3 [4]. The effect of lithium was, however, more pronounced. The total weight loss corresponding to the peaks at 370 and 390°C attained 28%. The area of the endothermic peak at 1050°C was found to increase on increasing the amount of sodium hydroxide added to the manganese carbonate samples.

It can be concluded from the previously presented results that the treatment of $MnCO_3$ with NaOH lowered its decomposition temperature yielding MnO_2 and Mn_2O_3 to an extent proportional to the amount of sodium hydroxide added. In other words, NaOH-treatment of manganese carbonate decreased the thermal stability of both $MnCO_3$ and MnO_2. The weight loss accompanying the decomposition of Mn_2O_3 to Mn_3O_4 (endothermic peak at 950°C) was greatly decreased by treatment with NaOH and the area of such a peak was found to decrease by this treatment. These results indicated that sodium-treatment of manganese oxides retarded the thermal decomposition of Mn_2O_3 or increased its thermal stability. Sodium hydroxide-treatment of $MnCO_3$ led to the appearance of an additional endothermic peak at 1050°C in its DTA curve. Such a peak might characterize a solid–solid interaction between sodium and manganese oxides or thermal decomposition of a sodium–manganese compound. The nature of such a process and the identity of the solids involved made the object of the next part of the present work through an X-ray investigation of pure and treated solids calcined at different temperatures.

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

Figure 3 represents the X-ray diffraction patterns of manganese carbonate treated with 15 mol% sodium hydroxide and heated in air for 6 h at different temperatures, namely 400, 750, 900 and 1100°C. The solid calcined at 400°C, whose diffraction lines were not included in Fig. 3, was poorly crystalline γ-Mn_2O_3. By contrast, the solid heated at 750°C was entirely

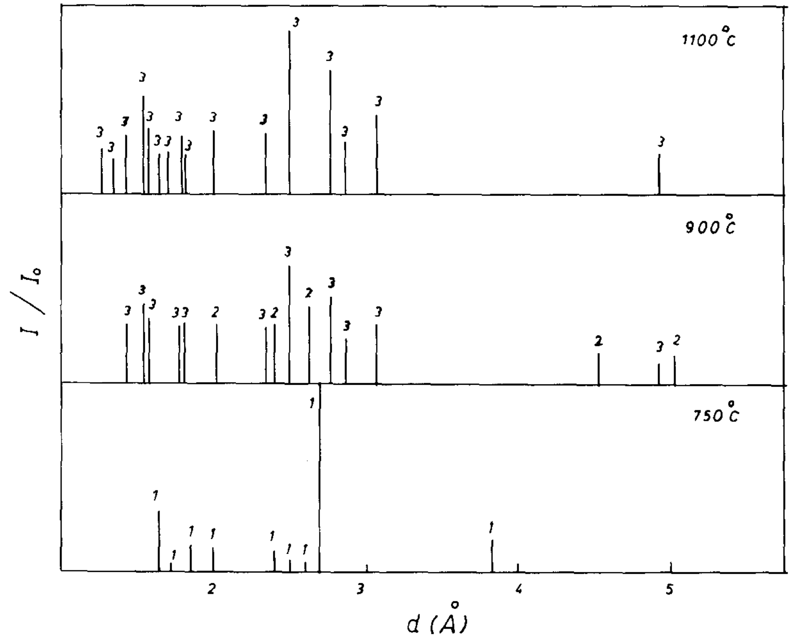

Fig. 3. X-ray diffraction patterns of the thermal products of Na-doped $MnCO_3$; (1) partridgeite Mn_2O_3; (2) $Na_4Mn_9O_{18}$; (3) Mn_3O_4.

composed of highly crystalline partridgeite (Mn_2O_3) phase indicating the absence of any free NaOH, Na_2O, or sodium–manganese compound(s). It could be argued that a temperature of 750°C was not high enough to conduct a solid–solid interaction between manganese and sodium oxides. Indeed, the absence of any free sodium species might indicate a possible dissolution of Na^+ ions into the Mn_2O_3 lattice. Such a speculation finds experimental evidence in the next part of this investigation. The rise in calcination temperature of the doped solid from 400 to 750°C led to a complete conversion of the poorly crystalline γ-Mn_2O_3 to highly crystalline partridgeite (Mn_2O_3) phase. Therefore, the endothermic peak at 590°C observed in the DTA curve of the treated solid (cf. Fig. 1) accounted for such a phase transformation. Increasing the calcination temperature of the treated solid to 900°C led to the appearance of a highly crystalline Mn_3O_4 phase together with a new sodium–manganese compound with a high degree of crystallinity. The *d*-spacings of the newly formed compound were calculated and found to be: 2.63_x, $4.54_{0.8}$, $2.03_{0.6}$, $2.39_{0.5}$, $5.27_{0.3}$. These lines corresponded to the sodium manganate phase, $Na_4Mn_9O_{18}$ [6]. The reaction leading to the formation of the new compound might proceed according to:

$$9\,Mn_2O_3 + 4\,Na_2O + 2.5\,O_2(g) \xrightarrow{900°C} 2\,Na_4Mn_9O_{16} \qquad (1)$$

and/or

$$3\,Mn_3O_4 + 2\,Na_2O + 2\,O_2(g) \xrightarrow{900°C} Na_4Mn_9O_{16} \qquad (2)$$

The fact that the formation of sodium manganate has not been detected in the DTA curves of the treated solids (Figs. 1 and 2) indicated that such a process occurred very slowly at 900°C. By contrast, the formation of lithium manganate via the interaction between Li_2O and Mn_2O_3 has been found to take place rapidly at 500°C [4]. The stoichiometry of reactions (1) and (2) indicates that the amount of sodium oxide in the mixed oxide sample (15 mol%) is, thus, very small to convert the manganese oxides, entirely, into sodium manganate. In fact, Mn_3O_4 and sodium manganate phases coexisted in the case of the mixed oxide solid heated at 900°C (Fig. 3). The augmentation of the roasting temperature of the treated solid up to 1100°C effected a complete decomposition of the sodium manganate produced into the Mn_3O_4 phase. The diffraction lines of such a phase were only detected in the diffraction patterns of the mixed oxide solid heated at 1100°C (Fig. 3). The absence of any line relative to free sodium oxide indicated the formation of Na_2O–Mn_3O_4 solid solution. On this basis, the endothermic peak observed at 1050°C in the DTA curves of the mixed oxide solid (Figs. 1 and 2) indicated decomposition of the sodium manganate produced which occurred rapidly at 1050°C according to:

$$Na_4Mn_9O_{18} \xrightarrow{1050°C} 3\,Mn_3O_4 + 2\,Na_2O + 2\,O_2(g) \qquad (3)$$

The thermal decomposition of lithium manganate has been shown, in a previous investigation [4] to take place very slowly at 1100°C leading to the formation of both Mn_2O_3 and Mn_3O_4. These oxides dissolved the Li_2O produced to form solid solutions.

Thermal dissolution of sodium ions in Mn_2O_3 and Mn_3O_4 solids

The solubility of sodium ions in both Mn_2O_3 and Mn_3O_4 was studied by flame photometry. This method depended on the fact that the portion of sodium ions dissolved in the oxide lattice could not be extracted by boiling water which dissolved only the portion of the foreign ions, not retained in the oxides, remaining in a separate phase. Various specimens of Mn_2O_3 treated with different proportions of sodium ions (2–30 ion%) were heated in air for 6 h at 400, 500 and 750°C. The amounts of sodium ions dissolved in Mn_2O_3 samples were determined in each case; the data obtained are given in Table 1. It can be seen that the extent of sodium ions dissolved in Mn_2O_3 increases on increasing the total amount of the foreign ions added and decreases on increasing the calcination temperature from 500 to 750°C. This decrease is, however, more pronounced in the case of the solids treated with the smallest extent of sodium ions (2 ion% per mole of Mn_2O_3). The solubility of sodium ions in the Mn_2O_3 lattice was not greatly influenced by

TABLE 1

Effects of calcination temperature and concentration of sodium ions added to Mn_2O_3 upon their dissolution in the oxide lattice

Calcination temp. (°C)	Total sodium (ion% per mole of Mn_2O_3)	Sodium dissolved in Mn_2O_3 (ion% per mole)
400	2.0	2.0
400	5.0	3.2
400	10.0	3.8
400	15.0	4.4
400	30.0	8.0
500	2.0	1.9
500	5.0	3.0
500	10.0	3.5
500	15.0	4.4
500	30.0	7.3
750	2.0	0.7
750	5.0	1.7
750	10.0	2.5
750	15.0	4.0
750	30.0	6.4

increasing the calcination temperature from 400 to 500°C. The solubility of sodium ions in Mn_3O_4 was determined for one specimen treated with 15 mol% NaOH and calcined at 1100°C. Such a specimen was found to dissolve 3.3 ion% per mole of Mn_3O_4. It can be concluded that the treatment of manganese carbonate with different proportions of sodium hydroxide followed by calcination in air at temperatures ranging between 400 and 750°C led to the dissolution of some foreign ions in the lattice of the solids produced, greatly affecting their thermal stability. On heating the mixed oxide solids at 900°C, most of the added doping oxide underwent a solid–solid interaction with manganese oxides yielding sodium manganate which decomposed, readily, at 1050°C yielding Mn_3O_4 and Na_2O which dissolved in manganic oxide forming an Na_2O–Mn_3O_4 solid solution.

DISCUSSION AND CONCLUSIONS

The observed decrease in the thermal stability of MnO_2 due to sodium treatment could be attributed to a decrease in the concentration of charge carriers in MnO_2 which behaves as an n-type semiconductor [7–9]. In fact, the dissolution of monovalent ions in p-type semiconductors is known to increase the concentration of their charge carriers and to decrease the concentration of the charge carriers in n-type semiconductors [9–12]. The decrease in the concentration of charge carriers is followed by a decrease in the n-type semiconducting character and a subsequent decrease in the oxidation state of the treated oxide. These effects are to be expected when dissolution of the foreign ions takes place via substitution of some of the host cations of the doped oxides. However, the dissolution process might occur via location of the doping ions in interstitial positions and in cationic vacancies of the treated oxide lattice [10–12]. In such a case the incorporation of monovalent ions in the lattice of an n-type semiconductor might be accompanied by an increase and not a decrease in the oxidation state of the treated solid. The chemical determination of the amounts of sodium ions dissolved in Mn_2O_3 (Table 1) did not account for the mechanism of the dissolution process but gave a quantitative measure for the total amounts of sodium ions dissolved in the Mn_2O_3 lattice irrespective of how the dissolution process took place. Mn_2O_3, to our knowledge, also behaves as an n-type semiconductor and the observed increase in its thermal stability due to sodium-treatment might indicate an increase in its oxidation state. It is plausible to argue that the dissolution of most of the sodium ions in the Mn_2O_3 lattice occurred via location in interstitial positions and in cationic vacancies. By contrast, the dissolution of sodium ions in MnO_2 solid, not experimentally determined, might take place via normal substitution of some of the host manganese ions in the MnO_2 lattice.

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