Thermochimica Acta, 99 (1986) 181–186
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF γ-IRRADIATED MANGANESE CARBONATE

A.M. DESSOUKI

National Center for Radiation Research and Technology, Cairo (Egypt)

G.A. EL-SHOBAKY and K.A. EL-BARAWY

National Research Centre and CMRDI, Dokki, Cairo (Egypt)

(Received 6 September 1985)

ABSTRACT

Pure manganese carbonate was subjected to different doses of γ-irradiation, namely 250, 500 and 800 K Grey. The effects of this treatment upon the characteristic X-ray diffraction and thermal decomposition of $MnCO_3$ were investigated.

The results obtained revealed that the employed doses of γ-irradiation brought about a two-fold increase in the relative intensity of the main diffraction line of $MnCO_3$ ($d = 2.85$ Å), indicating an enhanced increase in the crystallinity of the $MnCO_3$ phase. The DTA investigation showed that γ-irradiation greatly enhanced the thermal decomposition of manganese carbonate yielding MnO_2 which was more readily decomposed at about 430°C producing Mn_2O_3. γ-Irradiation was also found to increase greatly the amount of Mn_2O_3 decomposing at 930°C to give Mn_3O_4. In other words, γ-irradiation greatly decreased the thermal stability of both $MnCO_3$ and Mn_2O_3. The maximum decrease in thermal stability of Mn_2O_3 (76%) was attained by exposing the parent manganese carbonate to 800 K Grey.

INTRODUCTION

The effects of γ-rays and ionizing radiation on the physicochemical, surface and catalytic properties, lattice defects, structure and thermal stability of various solids have been investigated by several authors [1–10]. γ-Rays induce important changes in the amounts of chemisorbed oxygen of various mixed-oxide catalysts [5]. γ-Rays and neutron irradiation effect an appreciable shift in the equilibrium of lattice defects and formed new centres in some binary metal oxide systems [6]. Positive and negative effects of γ and neutron radiations on the catalytic activities of various solids have been reported [1–10]. The sign of the induced effect depends mainly on the prehistory of irradiated solids and the doses employed [6–10]. It has been shown by two of the authors that γ-irradiation effects a considerable decrease in the thermal stability of cobaltic oxide [10].

0040-6031/86/$03.50

The present investigation was devoted to studying the effect of different doses of γ-irradiation on the thermal decomposition of manganese carbonate and the manganese oxides produced. The techniques employed were DTA and X-ray diffraction.

EXPERIMENTAL

Materials

Pure manganese carbonate, dried at 110°C for 24 h, was subjected to γ-irradiation using a ^{60}Co source. The doses were 250, 500 and 800 K Grey and the solid samples were left for 2 weeks before the X-ray and DTA measurements were carried out.

Techniques

An X-ray investigation of unirradiated and γ-irradiated $MnCO_3$ samples was carried out 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}.

Differential thermal analysis (DTA) of unirradiated and γ-irradiated manganese carbonate specimens was carried out using a DuPont thermal analyser with a differential scanning calorimeter. The rate of heating was kept at 20°C min^{-1}, and the sensitivity was 0.4 mV cm^{-1}. A 20-mg sample of each solid specimen was employed in each case.

RESULTS AND DISCUSSION

X-ray investigation of unirradiated and irradiated $MnCO_3$

X-ray diffractograms were recorded for unirradiated specimens of manganese carbonate. The results obtained are given in Fig. 1. All the characteristic diffraction lines of the $MnCO_3$ phase were detected in all cases. The relative intensity of the main diffraction line of $MnCO_3$ ($d = 2.85$ Å) was found to suffer about a two-fold increase after γ-irradiation (250–800 K Grey). Indeed no broadening in the diffraction lines of $MnCO_3$ was observed in the case of irradiated solids indicating the absence of any change in the lattice parameter of γ-irradiated manganese carbonate specimens. It seems that the energy of γ-rays absorbed by $MnCO_3$ solids greatly enhanced the crystallization process of the irradiated solids. It has been reported that γ-irradiation of NiO–MgO, reduced by hydrogen, induces an important shift in the equilibrium of the lattice defects then formed and stabilizes new

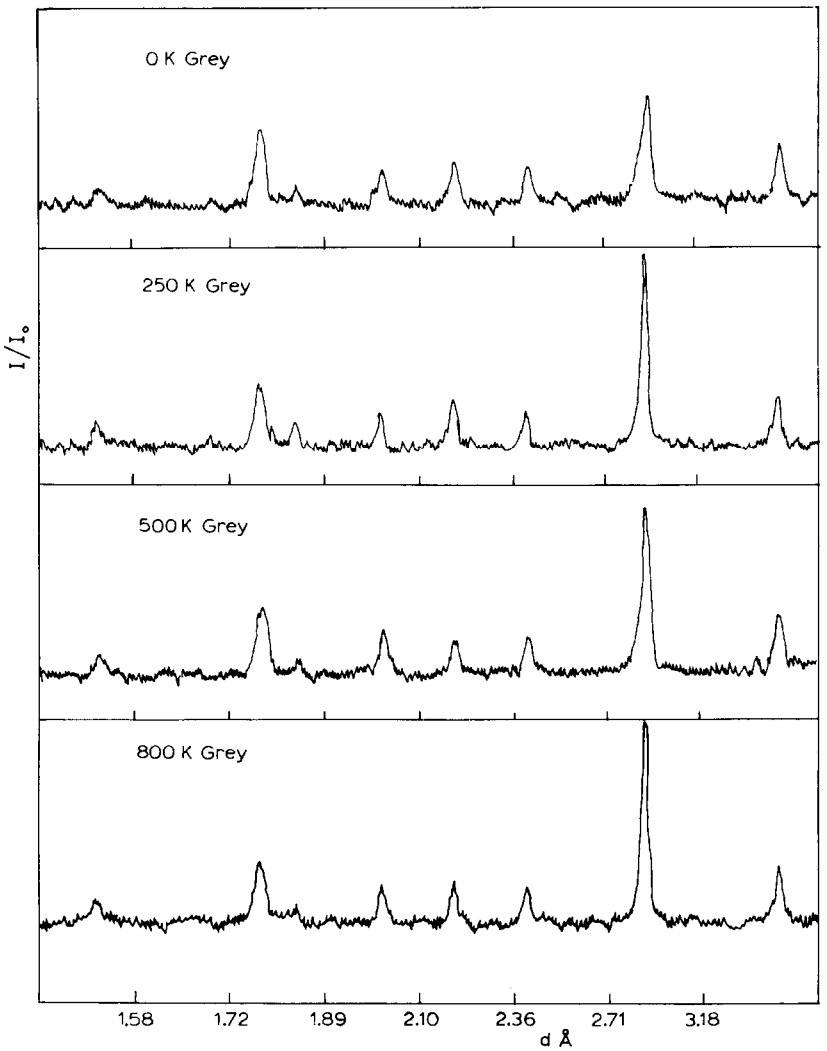

Fig. 1. X-ray diffractograms of unirradiated and γ-irradiated specimens of manganese carbonate.

centres, which increase the rate of nucleation of the metal phase [7]. On this basis, it might be argued that the observed enhancement in the crystallization of $MnCO_3$ due to γ-irradiation results in an increase in the degree of ordering and nucleation of $MnCO_3$ crystallites. The absence of any change in the lattice parameter of manganese carbonate due to γ-irradiation has been reported for sodium chloride crystals [2].

Thermal behaviour of unirradiated and irradiated $MnCO_3$

Figure 2 represents the DTA of unirradiated and γ-irradiated manganese carbonate. Three endothermic peaks were observed, the first two successive

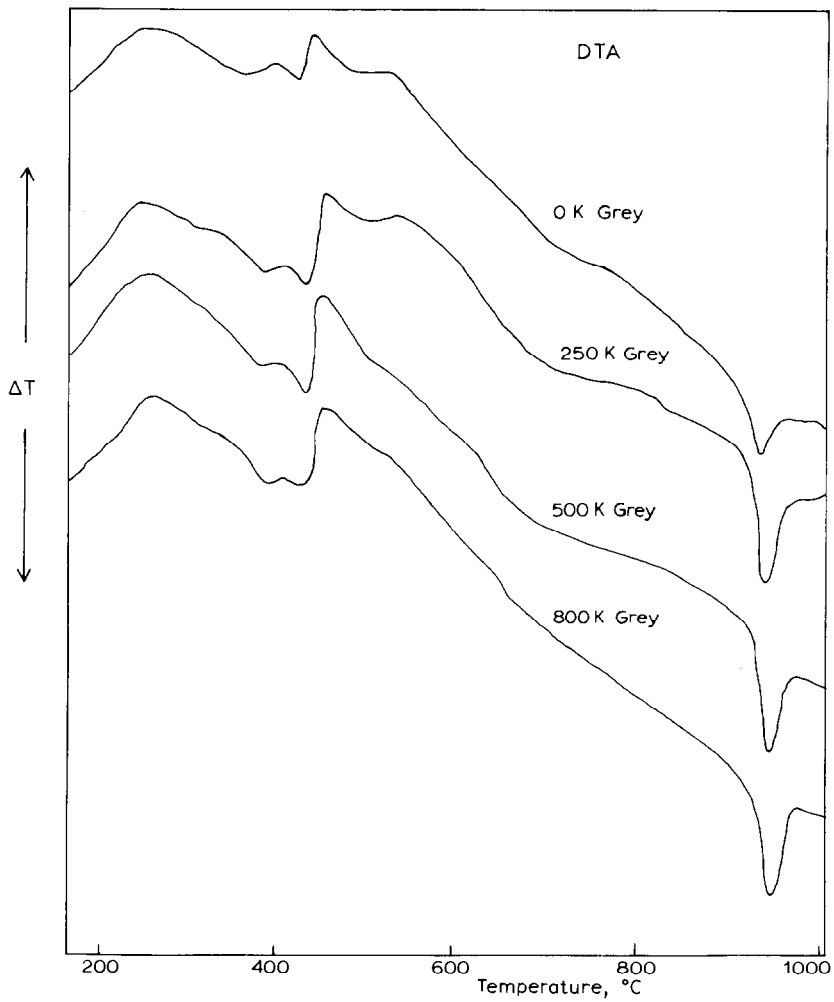

Fig. 2. DTA curves of unirradiated and γ-irradiated samples of $MnCO_3$ solid.

peaks had maxima at 400 and 440°C for all the solid specimens. The third peak, sharp and strong, extended between 910 and 930°C. The first two endothermic peaks indicated the decomposition of $MnCO_3$ to MnO_2 which underwent simultaneous decomposition giving Mn_2O_3 [11]. The Mn_2O_3 produced remained thermally stable until the air temperature on heating reached 900°C, when it decomposed yielding Mn_3O_4 [11]. Such a process is indicated by the third endothermic peaks of Fig. 2.

Since the weight of unirradiated and γ-irradiated manganese carbonate specimens was constant in each run, the area of each endothermic peak for each solid could be regarded as a measure of the amount of solid undergoing a chemical change (decompositions: $MnCO_3 \rightarrow MnO_2$; $MnO_2 \rightarrow Mn_2O_3$; and $Mn_2O_3 \rightarrow Mn_3O_4$) [10–14]. The first two peaks were so close that it was

TABLE 1

Effect of γ-irradiation on the peak area of DTA curves of the thermal decomposition of $MnCO_3$ and Mn_2O_3

Solid	Radiation dose (K Grey)	Temperature range of the endo. peak (°C)	Peak area (arb. units)	Change in area of endo. peak (%) [a]
$MnCO_3$	0.0	370–440	15.5	0.0
	250	370–440	26.5	−70.9
	500	370–440	28.0	−80.6
	800	370–440	29.6	−90.9
Mn_2O_3	0.0	910–930	12.8	0.0
	250	910–930	17.4	−35.9
	500	910–930	18.7	−36.1
	800	910–930	22.6	−76.6

[a] The data in this column were obtained by subtracting the area of the endothermic peak for each solid from 15.5 and 12.8 (the values of unirradiated $MnCO_3$ and Mn_2O_3, respectively). The negative sign indicates a decrease in thermal stability of irradiated solids.

difficult to separate them from each other and the total area of both peaks was measured for each solid and considered as a measure of the decomposition $MnCO_3 \rightarrow Mn_2O_3$ for each solid. Data on the areas of endothermic peaks indicating various decomposition processes for unirradiated and γ-irradiated solids are given in Table 1. This table also includes the percentage change in area of the endothermic peaks due to γ-irradiation. It can be seen from Table 1 that γ-irradiation of $MnCO_3$ effected a decrease in its thermal stability to an extent proportional to the dose employed. However, a decrease of 70% was attained at a dose of 250 K Grey, reaching 90% at a dose of 800 K Grey. Furthermore, the effect of irradiation was not restricted to $MnCO_3$, which has only been subjected to γ-rays, but extends to the Mn_2O_3 produced effecting a decrease in its thermal stability. The observed decrease in thermal stability was, however, less pronounced in the case of Mn_2O_3. It has been reported by two of the authors [10] that γ-irradiation decreases the thermal stability of Co_3O_4; a maximum decrease of 60% in the thermal stability of cobaltic oxide was attained when the dose reached 300 K Grey. The decrease in thermal stability of Co_3O_4 due to γ-irradiation has been attributed to a decrease in oxidation character of the irradiated solid resulting from desorption of chemisorbed oxygen [10]. The observed decrease in thermal stability of $MnCO_3$ due to γ-irradiation could be related to a possible increase in the degree of ordering and nucleation of manganese carbonate crystallites. It has been recently shown by two of the authors that lithium doping effects an important decrease in the thermal stability of Mn_2O_3 [11]. Such a decrease has been attributed to an effective decrease in the concentration of its charge carriers, in other words, a decrease in the

oxidation state of the doped solid. These charge carriers could be regarded as lattice defects. It might be argued that γ-irradiation effects a decrease in concentration of lattice defects in Mn_2O_3 or a decrease in its oxidation state. Such a decrease might lead to a corresponding decrease in the thermal stability of solid Mn_2O_3.

REFERENCES

1 J.M. Caffrey and A.O. Allen, J. Phys. Chem., 62 (1958) 33.
2 H.R. Leider, Phys. Rev., 101 (1956) 56.
3 Y. Saito and Y. Makishima, Nature (London), 183 (1959) 388.
4 H.W. Kohn and E.H. Taylor, J. Phys. Chem., 63 (1959) 966.
5 V. Mucka, Collect. Czech. Chem. Commun., 41 (1976) 2159; 42 (1977) 391; 44 (1979) 1003, 1015.
6 M.J. Smith, J. Appl. Phys., 34 (1963) 2879.
7 M. Pospisil and M. Tvrznik, Collect. Czech. Chem. Commun., 44 (1979) 1023.
8 R. Kudlacek and A. Judlova, Collect. Czech. Chem. Commun., 49 (1984) 1933.
9 G.A. El-Shobaky, N. Petro, T. Gahzy and A.M. Dessouki, Surf. Technol., 19 (1983) 17.
10 G.A. El-Shobaky, N.M. Ghoneim and A.M. Dessouki, Thermochim. Acta, 72 (1984) 297.
11 G.A. El-Shobaky and K.A. El-Barawy, Thermochim. Acta, 89 (1985) 53.
12 G.A. El-Shobaky, N.M. Ghoneim, U.F. Hewaidy and I.M. Morsi, Thermochim. Acta, 61 (1983) 107.
13 G.A. El-Shobaky, N.M. Ghoneim and I.M. Morsi, Thermochim. Acta, 67 (1983) 293.
14 G.A. El-Shobaky and N.M. Ghoneim, Thermochim. Acta, 89 (1985) 63.