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THERMAL SOLID–SOLID INTERACTION BETWEEN POTASSIUM AND MANGANESE OXIDES

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ABSTRACT

The interaction between potassium and manganese oxides was studied using DTA, TG, DTG and X-ray diffraction techniques.

The results obtained revealed that potassium-treatment of $MnCO_3$ enhanced its thermal decomposition and underwent solid–solid interaction with the manganese oxides produced yielding potassium manganates. All the diffraction lines of KMn_8O_{16} were only detected in the X-ray diffraction patterns of $MnCO_3$ treated with 15 mol% KOH heated in air at 400°C. This compound resulted from the interaction between KOH and Mn_2O_3. The heating of the mixed oxide-solids at 750°C increased the crystallinity of the manganate phase with subsequent appearance of well-crystalline partidgeite Mn_2O_3 phase. Increasing the calcination temperature to 900°C led to the formation of well-crystalline $KMnO_2$ phase together with well-crystalline Mn_3O_4 and KMn_8O_{16} phases. $KMnO_2$ was produced via solid–solid interaction between K_2O and Mn_2O_3 and/or Mn_3O_4. The potassium manganates formed remained thermally stable to temperatures above 1000°C then decomposed at 1100°C yielding Mn_3O_4 and K_2O.

The potassium-treatment of manganese carbonate was found to decrease the decomposition temperature of $MnCO_3$, MnO_2 and Mn_2O_3 to an extent proportional to the amount of KOH added. The thermal dissolution of K^+ ions in the lattices of manganese oxides was too difficult due to the big difference between the ionic radii (r) of K^+ and manganese ions (r of K^+ ion is almost twice that of the ions of manganese oxides). The observed effect of K^+ ions on the thermal stability of manganese carbonate and manganese oxides was attributed to the chemical affinity of K^+ ions to interact with manganese oxides yielding potassium manganates.

INTRODUCTION

The role of foreign cations in the thermal stability of cobalt and manganese oxides forms the object of several investigations carried out in our laboratory [1–6]. It has been reported in our last investigations [7,8] that lithium and sodium brought some important changes in the thermal stability of manganese carbonate and the manganese oxides produced. These changes have been attributed to an effective dissolution of lithium and sodium ions in the lattice of different manganese oxides followed by corresponding alterations in their oxidation states which might play a decisive role in the thermal decomposition process of the treated oxides.

The effect of potassium ions in the thermal decomposition of manganese carbonate and manganese oxides forms the object of the present investigation. The techniques employed were DTA, TG, DTG and X-ray diffraction.

EXPERIMENTAL

Materials

Pure and treated manganese oxides were obtained by thermal decomposition of pure $MnCO_3$ and that mixed with different proportions of KOH (2–30 mol%). The decomposition temperature was varied between 400 and 1100°C and the time of heating was fixed at 6 h.

Techniques

DTA, TG and DTG analyses of pure and treated manganese carbonate were carried out using a Netzsch-Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10°C 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 behaviour of pure and potassium hydroxide-treated $MnCO_3$

Figures 1 and 2 represent DTA, TG and DTG curves of pure and treated manganese carbonate. The comparison of these figures reveals that the addition of 15 mol% KOH to $MnCO_3$ lowers its decomposition temperature, yielding MnO_2, from 420 to 400°C and also decreases the decomposition temperature of MnO_2, yielding Mn_2O_3, from 450 to 430°C and also decreases the decomposition temperature of Mn_2O_3, giving Mn_3O_4, from 950 to 910°C [7]. Indeed, the addition of 15 mol% KOH greatly increased the areas of the endothermic peaks corresponding to the previous thermal reactions. These results indicate, clearly, that potassium treatment greatly enhanced the thermal decomposition of each of $MnCO_3$, MnO_2 and Mn_2O_3. The addition of 30 mol% KOH to $MnCO_3$ resulted in important changes in its thermal behaviour. A strong broad endothermic peak extended between

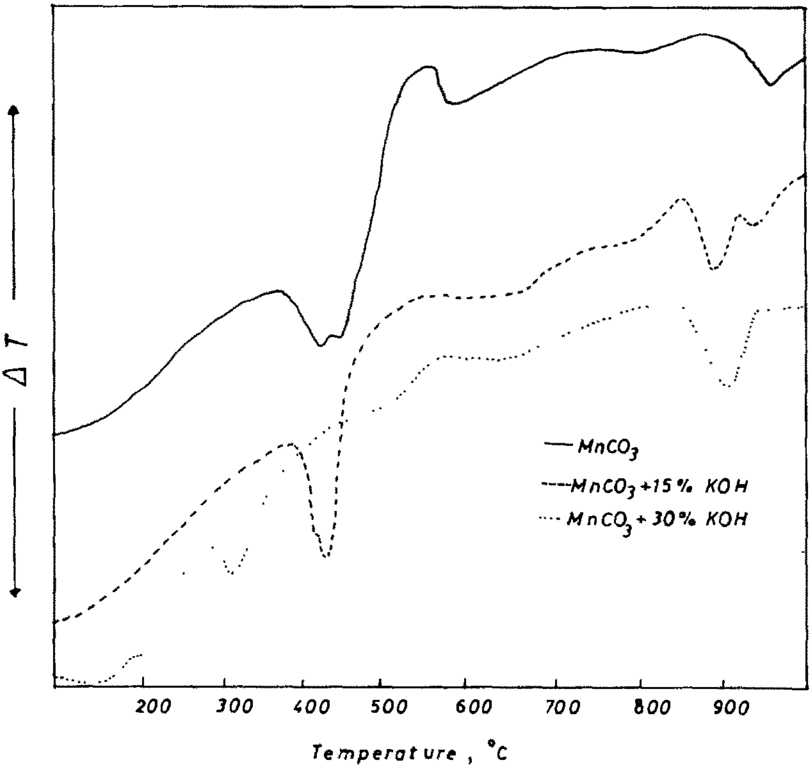

Fig. 1. DTA curves of pure and potassium-treated $MnCO_3$.

100 and 200°C, followed by 11% loss in weight, was observed in the DTA curve of the solid treated with 30 mol% KOH. Such a peak which corresponds to departure of physisorbed water indicates an important increase in the hygroscopic nature of the treated solid. Two other endothermic peaks were detected in the DTA curve of the solid treated with 30 mol% KOH having their maxima at 320 and 900°C, respectively. The first is sharp and the second is very strong and sharp. These two peaks were accompanied by loss in weight attaining 13 and 3.7%, respectively. The two successive endothermic peaks at 400 and 420°C in the DTA curve of $MnCO_3$ + 15% KOH were accompanied by a total weight loss of 22.2% instead of 32% in the case of pure $MnCO_3$. One can add that the loss in weight accompanying the endothermic peak ($Mn_2O_3 \rightarrow Mn_3O_4$) at 900–950°C increased from 0.75 to 1.7 and 3.7%, for pure $MnCO_3$ and that treated with 15 and 30 mol% KOH, respectively. The important changes in the thermal behaviour of manganese carbonate and manganese oxides due to potassium treatment could reflect possible solid–solid interactions between potassium and manganese oxides. Such speculation may find its verification via an X-ray investigation of the thermal products of pure and treated manganese carbonate.

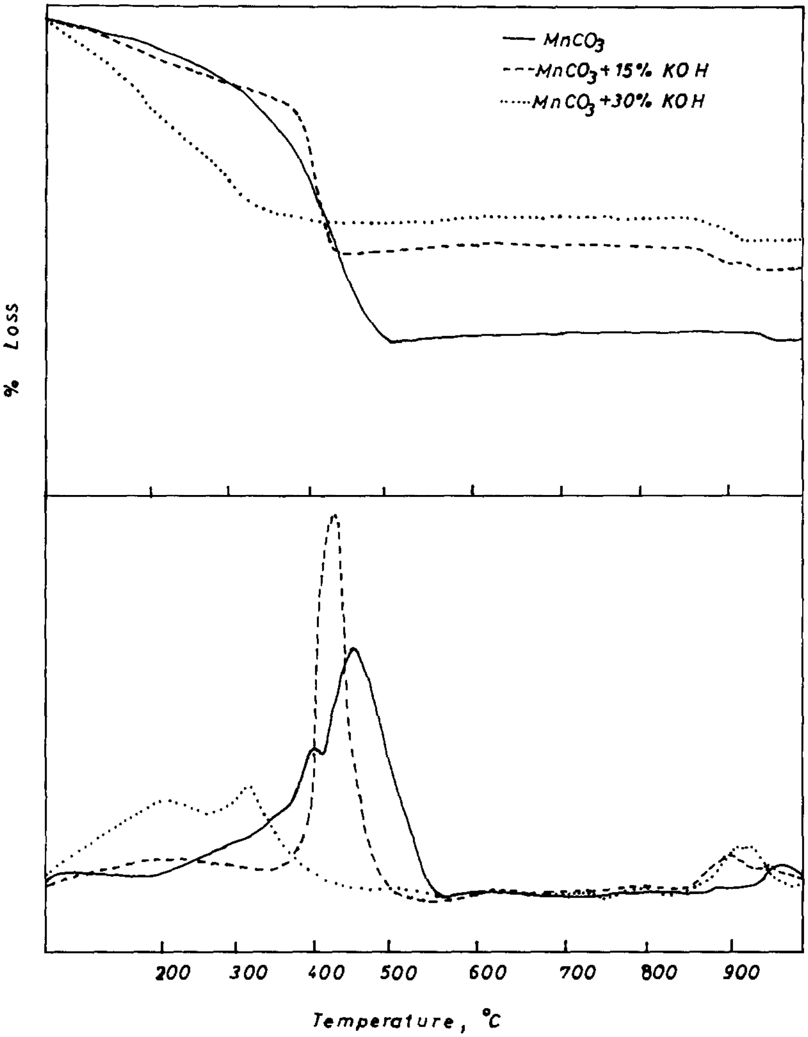

Fig. 2. TG and DTG of pure and potassium-treated $MnCO_3$.

X-ray investigation of the thermal products of manganese carbonate treated with different proportions of KOH

Figure 3 represents the X-ray diffraction patterns of $MnCO_3$ treated with 15 mol% potassium hydroxide and heated in air for 6 h at 400, 750 and 900°C. The patterns of the solid heated at 1100°C were carried out but not given in Fig. 3. Six diffraction lines of reasonable intensity were detected in the diffraction patterns of the solid calcined at 400°C. The *d* spacings of these lines were calculated and found to be 3.11_x, $2.40_{0.8}$, $1.83_{0.5}$, $4.97_{0.4}$, $6.98_{0.4}$ and $2.16_{0.3}$.

These lines corresponded to the potassium manganate phase, KMn_8O_{16}

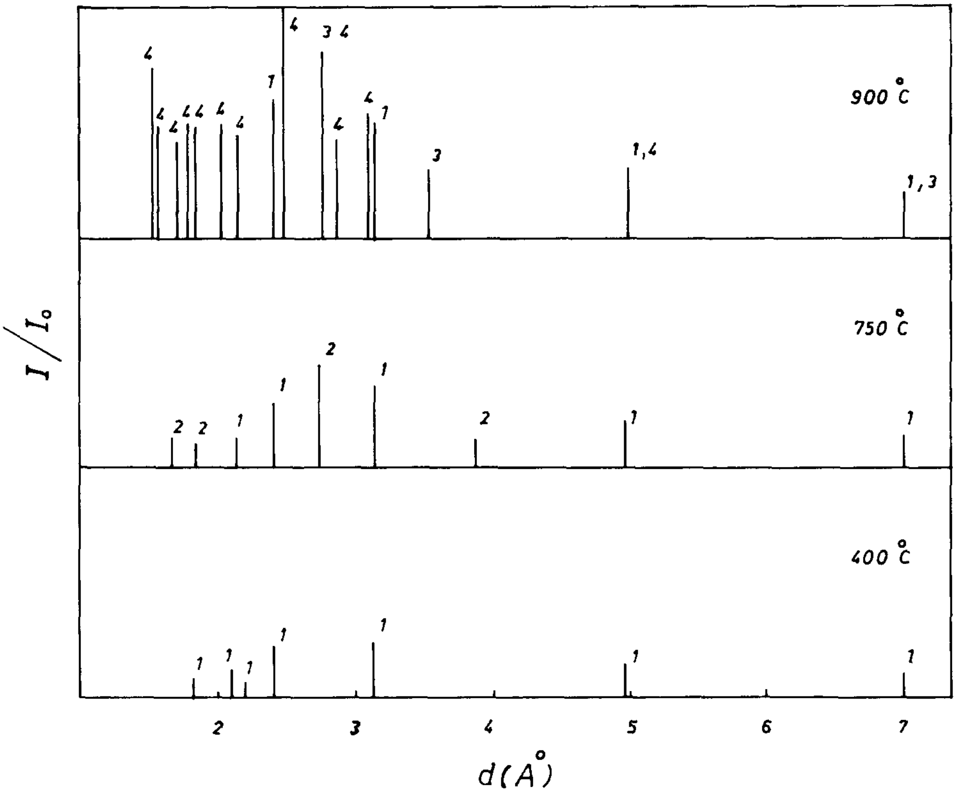

Fig. 3. X-ray diffraction patterns of the thermal products of potassium-treated $MnCO_3$; (1) KMn_8O_{16}; (2) partidgeite Mn_2O_3; (3) $KMnO_2$; (4) Mn_3O_4.

[9]. The reaction leading to the formation of this compound might proceed according to

$$8\ Mn_2O_3 + 2\ KOH + 3.5\ O_2(g) \xrightarrow{300-400°C} 2\ KMn_8O_{16} + H_2O(g) \qquad (1)$$

On this basis, the endothermic peak at 320°C observed in the DTA curve of the treated manganese carbonate (Figs. 1 and 2) corresponded to the formation of KMn_8O_{16} according to the mechanism given by reaction (1). This reaction is accompanied by a net gain in weight. Such a gain in weight could account for the observed changes in the loss in weight of pure and treated manganese carbonate in the temperature range 300–450°C (32, 22.2 and 13% for pure $MnCO_3$ and that treated with 15 and 30 mol% KOH, respectively). It has been shown in a previous investigation [8] that the solid–solid interaction between sodium and manganese oxides, yielding sodium manganate $Na_4Mn_9O_{18}$, did not proceed at temperatures below 900°C. The fact that the formation of potassium manganate KMn_8O_{16} by an interaction between potassium and manganese oxides occured at relatively low temperatures of 300–400°C indicated the big difference in the reactivity of potassium and sodium oxides towards the formation of alkali manganates.

Figure 3 also shows that the mixed-oxide solid calcined in air at 750°C is composed of well-crystalline KMn_8O_{16} and partidgeite Mn_2O_3 phases. The increase in the calcination temperature of the mixed oxide from 400 to 750°C increased the degree of crystallinity of potassium manganate phase with subsequent formation of a partidgeite Mn_2O_3 phase. These results might indicate that potassium interacted more favourably with poorly crystalline γ-Mn_2O_3, which persisted at 400–500°C, to give KMn_8O_{16}. When the calcination temperature reached 900°C, the diffraction lines of $KMnO_2$ together with those of KMn_8O_{16} and Mn_3O_4 were observed in the diffraction patterns of the mixed-oxide solid (Fig. 3). These results revealed the thermal stability of KMn_8O_{16}. The formation of another potassium manganate compound $KMnO_2$ [9] at 900°C might take place according to

$$Mn_2O_3 + K_2O \xrightarrow{850\text{–}900°C} 2\ KMnO_2 \qquad (2)$$

and/or

$$Mn_3O_4 + K_2O + \tfrac{1}{2}O_2(g) \xrightarrow{850\text{–}900°C} 6\ KMnO_2 \qquad (3)$$

The diffraction lines of Mn_3O_4 and a few lines of K_2O were only detected in the diffraction patterns of the mixed-oxide solid roasted in air at 1100°C indicating the thermal decomposition of potassium manganate compounds. The decomposition process could take place according to

$$6\ KMn_8O_{16} \xrightarrow{1100°C} 16\ Mn_3O_4 + 3\ K_2O + 14.5\ O_2(g) \qquad (4)$$

$$6\ KMnO_2 \xrightarrow{1100°C} 2\ Mn_3O_4 + 3\ K_2O + 0.5\ O_2(g) \qquad (5)$$

The detection of the diffraction lines of free K_2O phase in the patterns of the treated solid heated at 1100°C might indicate the absence of an appreciable solubility of this oxide in Mn_3O_4 even at such high temperature.

DISCUSSION AND CONCLUSIONS

The results obtained, in the present investigation, show that potassium-treatment of manganase carbonate greatly decreased the thermal stability of $MnCO_3$ and the manganese oxides produced. The dissolution of some foreign cations of different valence states in the lattice of Co_3O_4 has been shown by one of the authors to greatly affect its thermal stability [1–6]. The addition of Li^+ and Na^+ to manganese oxides has been found to modify their thermal stability [7,8]. The observed changes in the thermal stability of cobalt and manganese oxides due to treatment with foreign cations have been explained in terms of an effective dissolution of some of the added foreign cations in the lattice of the treated solids with subsequent alterations in their oxidation states [1–6]. In all the cases investigated the ionic radii of the foreign cations were in the same order of magnitude of the host cations of the treated oxides [1–6]. The ionic radius of potassium cations being 1.33 Å is very big as compared with those of manganese cations of manganese oxides which vary between 0.66 and 0.80 Å [10]. Such a big difference in the ionic radii of K^+ and manganese cations might exclude an appreciable dissolution of K^+ ions in the lattice of manganese oxides. Such a speculation has been verified experimentally in this investigation. The fact that potassium interacted readily with Mn_2O_3, in the solid state, at low temperatures (300–400°C) to give KMn_8O_{16} might account for the observed decrease in the thermal stability of $MnCO_3$ which decomposed to give $MnO_2 \rightarrow Mn_2O_3$. Similarly, the observed decrease in the thermal stability of Mn_2O_3 (which gives Mn_3O_4 upon decomposition) due to potassium-treatment could also be attributed to an energetic chemical interaction between Mn_3O_4 and K_2O to produce $KMnO_2$.

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