

## THE EFFECT OF THE THERMAL STABILITY OF SOME SYNTHETIC $\text{MnO}_2$ SAMPLES ON THEIR ELECTROCHEMICAL AND CATALYTIC ACTIVITY

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### ABSTRACT

The effect of heat treatment of five synthetic  $\text{MnO}_2$  samples of various crystalline modifications on their O/Mn ratio, electrochemical activity (depolarising capacity), initial rate of catalytic decomposition of  $\text{H}_2\text{O}_2$  and BET surface area has been investigated. Because of its high thermal stability, the depolarising capacity of  $\beta$ - $\text{MnO}_2$  does not undergo much change even up to  $500^\circ\text{C}$  of calcination. Similarly,  $\alpha$  and  $\gamma$ - $\text{MnO}_2$  samples exhibit an appreciable depolarising capacity up to  $400^\circ\text{C}$  of calcination. On the other hand, like its thermal stability, the depolarising capacity of  $\delta$ - $\text{MnO}_2$  steadily decreases from  $110$  to  $500^\circ\text{C}$ . The rate of decomposition of  $\text{H}_2\text{O}_2$  shows two maxima; one at  $200^\circ\text{C}$  and the other at  $500$ – $600^\circ\text{C}$ : the former is attributed to the increase in surface oxygen content during dehydroxylation, the latter is attributed to the presence of a favourable  $\text{Mn}^{3+}$ – $\text{Mn}^{4+}$  couple at the transition temperature. The BET surface areas of all the samples show a gradual decrease from  $200$  to  $600^\circ\text{C}$ .

### INTRODUCTION

Manganese dioxide when heated in air undergoes several physico-chemical changes such as, (i) loss of physically adsorbed moisture, (ii) loss of chemically bound water or OH groups, (iii) change of metastable to stable phase, and (iv) loss of oxygen due to decomposition of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$  and then to  $\text{Mn}_3\text{O}_4$ . Each of these effects manifests itself in the physico-chemical properties of  $\text{MnO}_2$  particularly in relation to their electrochemical and catalytic activity. However, the extent of such influence depends upon the crystalline modification of  $\text{MnO}_2$ . Although thermal decomposition characteristics of  $\text{MnO}_2$  have been extensively studied [1–6] with the help of DTA, TG and DTG, little effort has been made to study the aspect of precalcination on their electrochemical and catalytic activity. In this paper an attempt has been made to study the thermal stability of some synthetic  $\text{MnO}_2$  samples and its effect on their depolarisation capacity and catalytic activity for the decomposition of  $\text{H}_2\text{O}_2$ .

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## EXPERIMENTAL

*MnO<sub>2</sub> samples*

For investigation of the effect of heat treatment, five samples belonging to different crystalline modifications were used. The methods of preparation and their physico-chemical characterization have been described in detail in an earlier communication [7]. The samples selected and their methods of preparation are summarised here. The Greek letters in parenthesis indicate their crystalline modifications.

*Sample 3 (α)*. δ-MnO<sub>2</sub>; which was prepared by the decomposition of hot KMnO<sub>4</sub> solution with HCl, was leached in 3 N HNO<sub>3</sub> at 90°C.

*Sample 4 (γ)*. Oxidation of Mn(NO<sub>3</sub>)<sub>2</sub> solution by NaClO<sub>3</sub> in a strong HNO<sub>3</sub> medium.

*Sample 7B (γ)*. Electrolytic oxidation of MnSO<sub>4</sub> in an acidic medium using a graphite anode.

*Sample 13 (δ)*. Oxidation of MnSO<sub>4</sub> by NaOCl in an alkaline medium.

*Sample 16 (β)*. A reagent grade sample of E. Merck (Germany) containing pyrolusite.

*Heat treatment*

Heat treatment of the samples was carried out in a cup-type furnace maintained at  $\pm 5^\circ\text{C}$ . The furnace was first heated to the requisite temperature and 3–4 g of sample were placed in a silica dish which was introduced into the furnace. After 2 h of heating the sample was withdrawn and stored in a dessicator. The particle size of all the samples was +240–200 mesh BSS.

*Depolarising capacity*

This was determined by discharging a pellet (1 cm diameter) containing 0.15 g sample and 0.015 g acetylene black in 20% NH<sub>4</sub>Cl solution at 40 mA current. The details of the method have been described elsewhere [8].

*Catalytic activity*

The catalytic activity of the samples was determined from the rate of decomposition of H<sub>2</sub>O<sub>2</sub> at 30°C. The apparatus and procedure have also been discussed in an earlier communication [9].

*Surface area*

The surface area of the heat-treated samples was determined by a low-temperature ( $-196^\circ\text{C}$ ) nitrogen adsorption method with the help of a high

speed surface area analyzer (Micromeritics Instruments corporation, U.S.A., model No. 2200).

## RESULTS

### *Thermal stability*

Figure 1 illustrates that the O/Mn ratios of sample nos. 3 and 7B decrease slowly from 110 to 400°C and then sharply at 500°C. The figure shows that chemical grade  $\gamma$ -MnO<sub>2</sub> (sample no. 4) loses more oxygen at lower temperatures than electrolytic  $\gamma$ -MnO<sub>2</sub> (no. 7B). For sample no. 13 dehydration and loss of oxygen proceed almost simultaneously and no sharp loss in oxygen is observed. Sample no. 16 shows the highest stability with marginal loss of oxygen up to 500°C, but loses oxygen sharply at 600°C. In the temperature range 500–600°C all the samples excepting no. 3 attain the composition of Mn<sub>2</sub>O<sub>3</sub> as indicated by an O/Mn ratio of 1.50–1.52. In sample 3 some oxygen is held strongly by the alkali metals in the lattice thereby preventing the decrease of the O/Mn ratio below a certain value. Therefore, the thermal stability of the various modifications of MnO<sub>2</sub> decrease according to the order  $\beta$ -MnO<sub>2</sub> >  $\alpha$ -MnO<sub>2</sub> > electrolytic  $\gamma$ -MnO<sub>2</sub> > chemical  $\gamma$ -MnO<sub>2</sub> >  $\delta$ -MnO<sub>2</sub>

### *Depolarising capacity*

Figure 2 illustrates the change in depolarising capacity of different samples with increase in temperature of calcination. For sample 3, the depolaris-

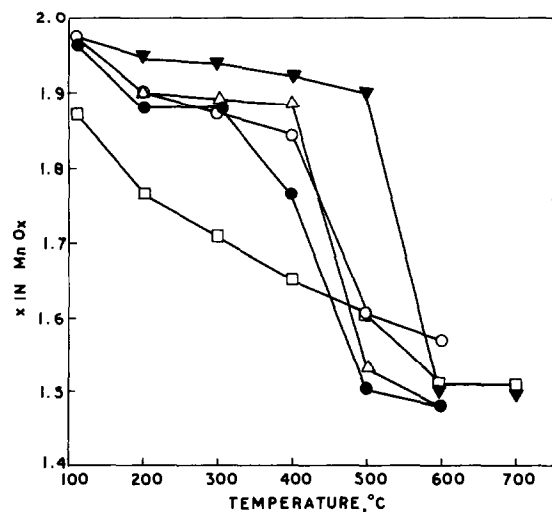


Fig. 1. Effect of calcination on the value of  $x$  in MnO <sub>$x$</sub>  of some MnO<sub>2</sub> samples. ○, Sample 3; ●, sample 4; △, sample 7B; □, sample 13; ▼, sample 16.

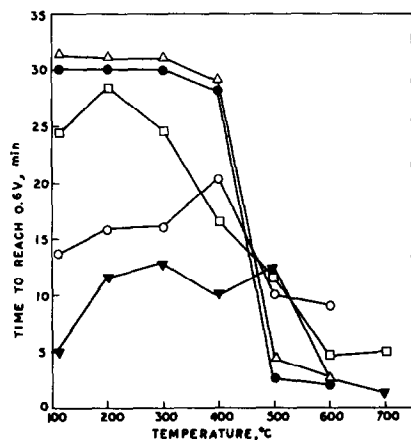


Fig. 2. Effect of calcination on the depolarisation capacity of some  $\text{MnO}_2$  samples. ○, Sample 3; ●, sample 4; △, sample 7B; □, sample 13; ▼, sample 16.

ing capacity rises slowly from 110 to 300°C, attains its maximum value at 400°C and decreases sharply thereafter. On the other hand, the depolarising capacity of sample 16 increases slowly from 110 to 300°C, falls slightly at 400°C and then exhibits a maximum at 500°C. For both the  $\gamma\text{-MnO}_2$  samples, the depolarising capacity remains almost constant up to 400°C but decreases abruptly at 500°C because of the loss of oxygen. In conformity with the nature of oxygen loss on heating, the depolarising capacity of sample no. 13 decreases steadily from 200 to 600°C. Similarly, while all other samples become almost inactive at 500–600°C of calcination, sample 3 retains some activity even at 600°C. It may be mentioned here that for all the samples except no. 16, the initial voltage drops sharply from 110 to 200°C and then falls almost linearly up to 600°C. For sample 16 the initial cell voltage remains almost constant at 1.15 V up to 500°C and then drops but remains constant up to 700°C of calcination. All these results are in close conformity with the variation of the O/Mn ratio at different calcination temperatures.

### *Catalytic activity*

Figures 3A and B show the plots of the initial rate of decomposition of  $\text{H}_2\text{O}_2$  vs. the temperature of calcination of  $\text{MnO}_2$  samples. For almost all the samples the rate of decomposition of  $\text{H}_2\text{O}_2$  increases from 110 to 200°C. Since the surface area of most of the samples does not increase from 110 to 200°C, the reason for this enhanced activity lies in the change of surface oxygen composition of the samples. Beyond 200°C a gradual decrease in catalytic activity is observed for all the samples because of the loss of such loosely-bound or extra lattice oxygen. However, the interesting feature is

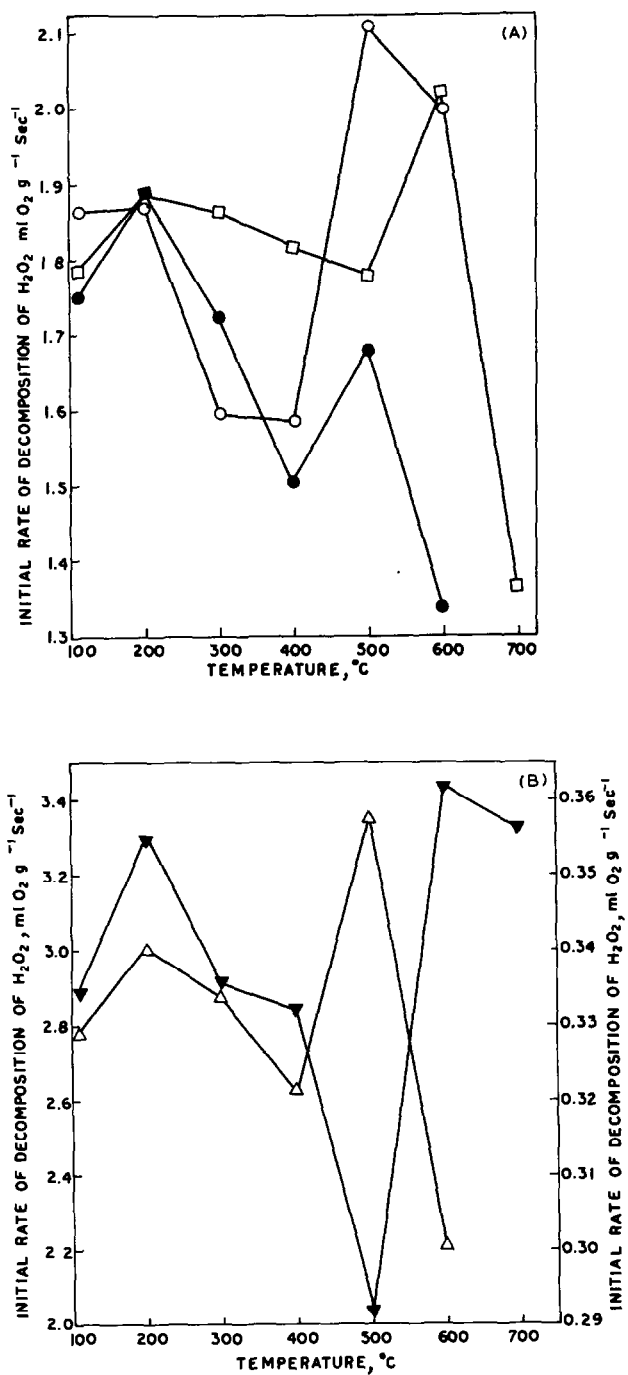


Fig. 3. Effect of calcination on the initial rate of decomposition of  $H_2O_2$  at  $30^\circ C$ . Initial concentration of  $H_2O_2 = 0.8642 \times 10^{-2} M$ . (A)  $\circ$ , sample 3;  $\bullet$ , sample 4;  $\square$ , sample 13. (B)  $\triangle$ , sample 7B;  $\blacktriangledown$ , sample 16.

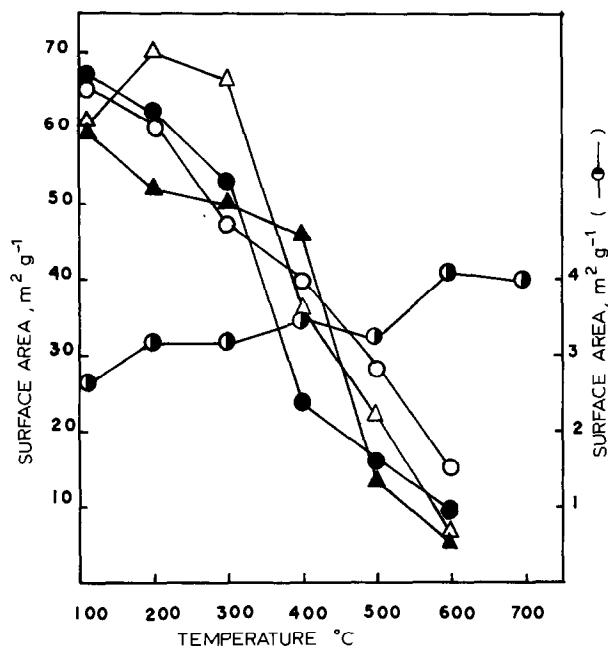


Fig. 4. Effect of calcination on the surface area of some  $\text{MnO}_2$  samples. ○, Sample 3; ●, sample 4; ▲, sample 7B; △, sample 13; ◐, sample 16.

that a sharp rise in activity is observed for all the samples again at 500–600°C depending upon the nature of the samples. After this second rise in activity  $\alpha$  and  $\beta$ - $\text{MnO}_2$  retain some activity, but  $\gamma$  and  $\delta$ - $\text{MnO}_2$  lose their catalytic activity almost completely.

### Surface area

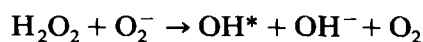
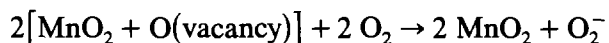
The results of the effect of heat treatment on the surface area of different samples are presented in Fig. 4. The surface area of sample 13 increases from  $60 \text{ m}^2 \text{ g}^{-1}$  at 110°C to  $70 \text{ m}^2 \text{ g}^{-1}$  at 200°C, but decreases marginally at 300°C. Above 300°C calcination, this fall is so sharp that at 600°C the area is about  $6.4 \text{ m}^2 \text{ g}^{-1}$ . In contrast, sample 16 maintains a trend showing a small increase up to 500°C, beyond which a sharp fall is observed at 600°C and then remains almost constant at 700°C. This unique behaviour of the  $\beta$ -variety is reflected in the catalytic activity towards the decomposition of  $\text{H}_2\text{O}_2$  as discussed earlier. While sample 3 exhibits a steady decrease in surface area from 110 to 600°C, samples 4 and 7B show a sharp fall from 300 and 400°C, respectively. Unlike some previous authors [10,11], we have not observed any rise in surface area for  $\gamma$ - $\text{MnO}_2$  in the temperature range 200–250°C. This is probably because the samples were already dried at 110°C for 2–3 h during which all the surface moisture was essentially removed.

## DISCUSSION

The results show that on prolonged heating all synthetic  $\text{MnO}_2$  samples, irrespective of their crystalline modification, lose some oxygen before their actual decomposition to  $\text{Mn}_2\text{O}_3$ . Such a loss of oxygen is highest for  $\beta$ - $\text{MnO}_2$  samples and lowest in the case of  $\delta$ - $\text{MnO}_2$ . Whereas the decomposition of  $\alpha$  and  $\gamma$ - $\text{MnO}_2$  samples as indicated by a sharp loss of oxygen occurs in the temperature range of 400–500°C, for  $\beta$ - $\text{MnO}_2$  this occurs at 600°C. These decomposition temperatures are a little lower than those observed by DTA and TG studies, because a longer period of heating at a particular temperature, as carried out in the present work, results in more weight loss than that recorded by a thermoanalytical instrument at the heating rate of  $10^\circ\text{C min}^{-1}$  [14].

The results of the present investigations indicate that the depolarising capacity is not much deteriorated by prolonged heating up to 400°C for all the samples except 13. In fact, samples 3 and 16 show their highest activity at 400 and 500°C, respectively. These observations apparently go contrary to the belief that depolarising capacity is related to combined water content of  $\text{MnO}_2$ . Therefore, although completely dehydrated at 400°C, the samples must be rehydrated when immersed in an electrolyte solution during discharge capacity measurement. In the case of sample 13 ( $\delta$ - $\text{MnO}_2$ ), however, at 300°C or above a phase change takes place (to  $\alpha$ - $\text{MnO}_2$ ). As a result, this sample does not regain its original depolarising capacity even when immersed in an electrolyte medium.

During calcination around 200°C extensive surface dehydroxylation takes place resulting in the creation of oxygen vacancies which are subsequently replenished by oxygen adsorbed from air. During this process some excess oxygen is chemisorbed on the surface which acts as catalytically active centres for initiating the decomposition of  $\text{H}_2\text{O}_2$  through the formation of  $\text{OH}^*$  radicals [9]. This chemisorbed excess oxygen occurs in a highly reactive and mobile state because of its loose bonding with the surface [12,13]. The possible reactions may be represented by



The rise in catalytic activity of the samples at 500°C is probably a phenomenon of secondary activation just before complete decomposition of  $\text{MnO}_2$  and recrystallisation to a new phase ( $\text{Mn}_2\text{O}_3$ ). An examination of the O/Mn ratio of the samples will show that the values are slightly above the theoretical value of 1.5. This indicates that some randomly dispersed  $\text{Mn}^{4+}$  centres are present in the domain of the  $\text{Mn}^{3+}$  ions. As a result, a suitable  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$  couple exists, thereby enhancing the rate of catalytic decom-

position of  $\text{H}_2\text{O}_2$ . Similar behaviour has been observed by Mooi and Selwood [15] who have shown that a favourable couple of  $\text{Mn}^{4+}$  is necessary for the catalytic activity of  $\text{H}_2\text{O}_2$  through electron exchange.

## CONCLUSIONS

Summarising, it may be concluded that, although prolonged heating reduces the O/Mn ratio of most of the samples before the decomposition to  $\text{Mn}_2\text{O}_3$ , electrochemical activity remains unchanged or even increased in some instances up to 340–400°C. The electrochemical activity pattern with increase in temperature of calcination is more or less in conformity with the thermal stability behaviour of the samples. Similarly, the change in catalytic activity is also in conformity with the behaviour of thermal change.

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