

II — KINETICS OF THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTION BY MANGANESE DIOXIDE SAMPLES

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Summary

The catalytic decomposition rates of hydrogen peroxide solution by twelve MnO_2 samples have been shown to follow a similar order to those of the reduction rates by hydrazine. This suggests a correlation between the catalytic and battery activities of MnO_2 . Doping MnO_2 with Ga^{III} and Mo^{VI} increased the catalytic decomposition of H_2O_2 compared with the undoped sample, an effect which may be due to lattice distortion. In general, the catalytic decomposition rate of H_2O_2 was found to increase with the BET surface area. Acid-washing increased the rate of decomposition. This is believed to remove Mn^{II} ions, which probably inhibit, rather than participate in the catalytic decomposition, from the surface. The initial decomposition rates of H_2O_2 at pH 7.2 and 25 °C followed first order kinetics with respect to the peroxide. At pH values between 3 and 10, however, the decomposition rate was constant but at a pH of 12 it increased sharply. At even higher pH values the decomposition rate decreased. This last effect was attributed to the intrinsic instability of H_2O_2 in alkaline solutions, possibly enhanced by OH^- catalysis.

The difference in the catalytic decomposition rates of H_2O_2 over the various crystalline manganese dioxides may, in view of the proton diffusion rates, be explained by differences in the crystallographic structure. The catalytic decomposition rate increased as the particle size decreased, emphasising the importance of the real rather than the BET surface area. The low catalytic decomposition rates observed with partially reduced samples, compared with the rates for the unreduced samples, may be explained by the formation of surface Mn^{III} ions on reduction.

1. Introduction

The metal-catalysed decomposition of aqueous H_2O_2 has certain features which distinguish it from other heterogeneous reactions [1]. The correlation between the physico-chemical properties of the various manganese

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dioxide forms and their catalytic activity in the decomposition of H_2O_2 has been reported previously [2, 3] and the kinetics have been shown to be first order [4]. A correlation between the kinetic parameters and the degree of oxidation and surface structure of MnO_2 has also been found, and it was suggested that the active centres are aggregates rather than individual manganese ions [5].

The catalytic activity of manganese oxides may be determined by the local properties of the surface, as influenced by the number of available Mn^{IV} and Mn^{III} ions [6]. The initial decomposition rates of H_2O_2 by MnO_2 samples have been used to determine their catalytic activities [2] mostly resulting from the presence of Mn^{III} ions (dissociated from MnOOH) in the lattice. In the pH range 3 - 8 the active sites were thought to be Mn^{IV} ions, whereas Mn^{III} ions were presumed to be the active sites in the pH range 8 - 14 [3]. A correlation between the catalytic and the electrochemical activities of MnO_2 has been long suggested [7 - 11].

2. Experimental

Seven battery-active manganese dioxides, three International Common Samples of $\gamma\text{-MnO}_2$ (ICS4, ICS5 and ICS12), a commercial electrodeposited $\gamma\text{-MnO}_2$ (R2), and three fibrous $\epsilon\text{-MnO}_2$ samples were investigated in this study. The fibrous samples were precipitated by anodic oxidation from acidic solutions of manganese(II) sulphate, perchlorate or nitrate (FEMD-S, FEMD-P or FEMD-N, respectively). Four prepared manganese dioxide samples, doped with Specpure Ga^{III} and Mo^{VI} cations, together with a prepared, undoped sample for comparison, were also investigated. Details of the preparation of the doped and undoped samples are given elsewhere [12], as are the characteristics of all the MnO_2 samples used in this investigation [13]*.

2.1. Catalysed decomposition of hydrogen peroxide

The kinetics of the catalytic decomposition of H_2O_2 solutions by manganese dioxide were followed by recording the volume of oxygen evolved against time, which was monitored as described previously [13]. The experiment consisted of suspending a 2.0 g sample of MnO_2 in 20 ml of water at 25 °C to which 20.0 ml of diluted H_2O_2 was added. The H_2O_2 solution diluted from 35 wt.% A.R. hydrogen peroxide, was presaturated with oxygen before each kinetic run to prevent the liberated oxygen from being dissolved.

3. Results and discussion

The kinetic curves for the decomposition of the hydrogen peroxide solution at 25 °C, catalysed by four different $\gamma\text{-MnO}_2$ samples and recorded as volumes of oxygen liberated in arbitrary units against time, are depicted in

*Ref. 13 is Part I of this paper.

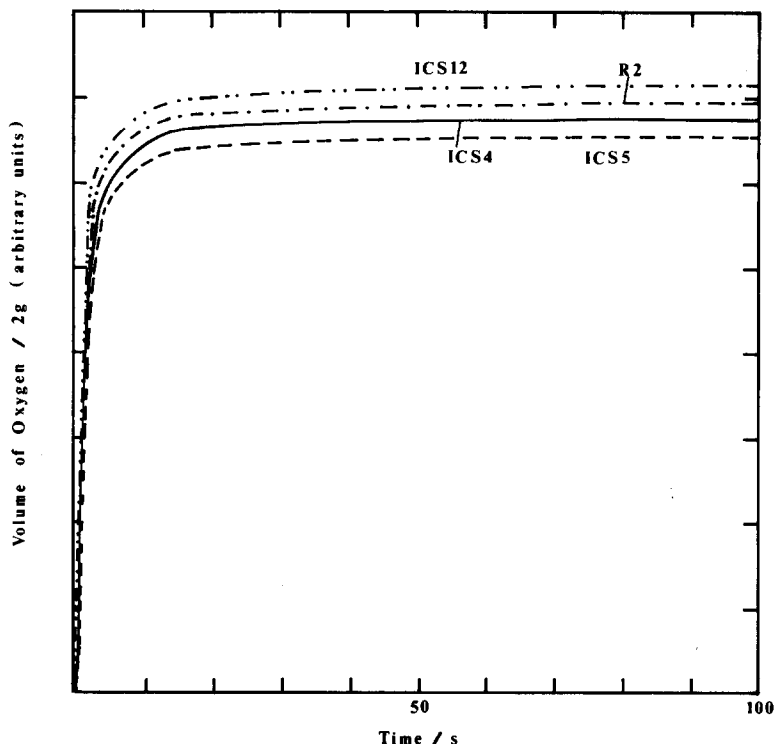


Fig. 1. Kinetic curves of oxygen liberated *vs.* time for the decomposition of hydrogen peroxide solution at 25 °C catalysed by the different γ -MnO₂ samples; [H₂O₂] = 3.24₅ × 10⁻¹ mol dm⁻³.

Fig. 1. The apparatus was not calibrated in absolute volume as it was unnecessary for the purpose of comparison, but the error in the relative values did not exceed $\pm 1.6\%$. The volume of O₂ recorded after the first 10 s (as an O₂ evolution rate) may be assumed to be equivalent to the decomposition rate during the initial stages of the reaction. The catalytic decomposition rates of H₂O₂ by the different γ -MnO₂ samples followed the order: ICS12 > R2 > ICS4 > ICS5, which is nearly the same order as that for the rates of reduction of the same samples by N₂H₄ [13]. The kinetic curves for the catalysed decomposition, however, are close to each other, although the separation is double the experimental error. If the reduction rates by N₂H₄ are assumed to be indicative of the battery activity, the results of H₂O₂ and N₂H₄ show the correlation between the catalytic activity and the battery activity of MnO₂, which has been discussed earlier [11] and which is not unexpected. Increased catalytic activity with increased electrochemical activity has been found for γ -MnO₂ samples [3], and a similar correlation between the two activities for β - and ϵ -MnO₂, as well as for γ -MnO₂, has also been reported [14].

Figure 2 shows the kinetic curves for the decomposition of H₂O₂ catalysed by the fibrous samples (ϵ -MnO₂). Comparison of Figs. 1 and 2, which

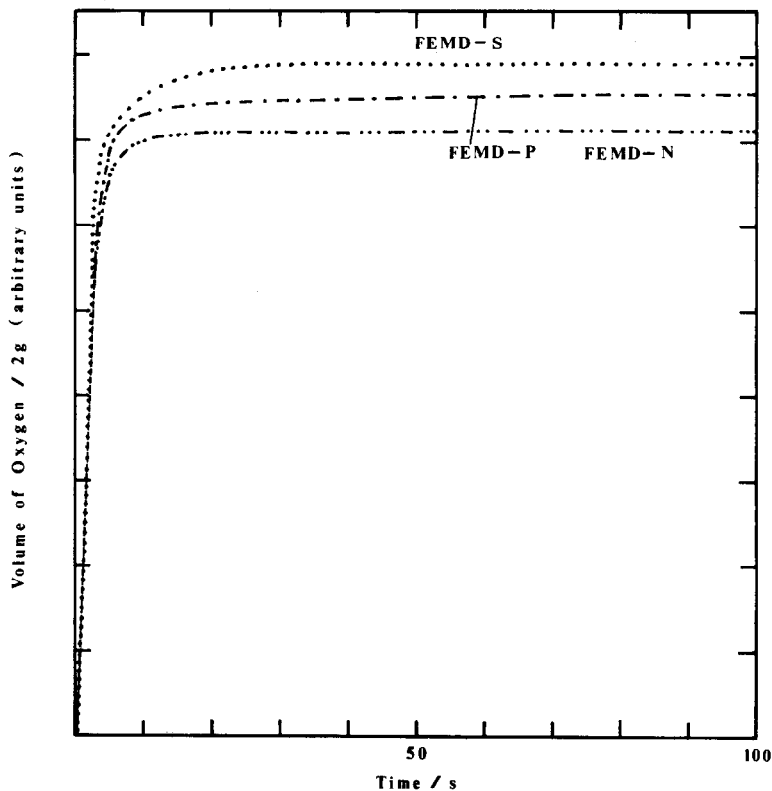


Fig. 2. Kinetic curves of oxygen liberated *vs.* time for the decomposition of hydrogen peroxide solution at 25 °C catalysed by the different fibrous samples; $[\text{H}_2\text{O}_2] = 3.245 \times 10^{-1} \text{ mol dm}^{-3}$.

have the same scale of arbitrary units, shows that the oxygen evolution rate (assumed to be equivalent to the decomposition rate) for the catalytic decomposition of H_2O_2 by $\epsilon\text{-MnO}_2$ is greater than that by $\gamma\text{-MnO}_2$. The reported higher electrochemical reactivity of $\epsilon\text{-MnO}_2$ compared with that of $\gamma\text{-MnO}_2$ [15], suggests that the crystallographic structure of the surface is more important than the surface area in determining the electrochemical reduction rate. It is suggested that it may also determine the catalytic decomposition rate of H_2O_2 . The BET surface areas of $\epsilon\text{-MnO}_2$: FEMD-S, FEMD-P, and FEMD-N were found to be 52, 48.5 and 45 $\text{m}^2 \text{g}^{-1}$, respectively [13], which is the same order as the catalytic decomposition rate of H_2O_2 by the different $\epsilon\text{-MnO}_2$ samples in Fig. 2. Increasing BET surface area corresponds to increasing catalytic decomposition rate.

Figure 3 illustrates the kinetic curves for the catalytic decomposition of H_2O_2 solution by an undoped, and differently doped, MnO_2 samples. These show that doping MnO_2 with different levels of the Mo^{VI} cation tends to increase the catalytic decomposition rate compared with that of the undoped sample, although some of the curves are close enough to each other

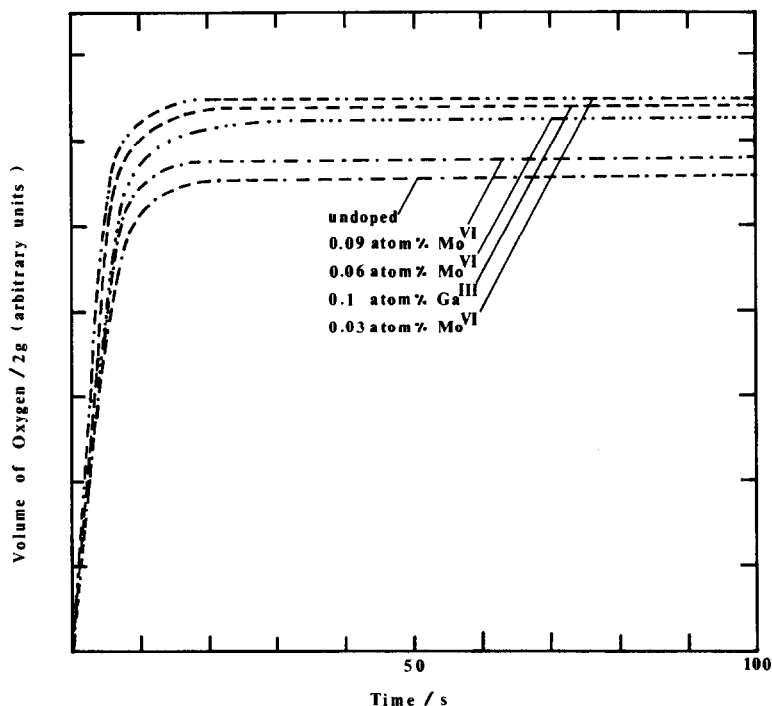


Fig. 3. Kinetic curves of oxygen liberated *vs.* time for the decomposition of hydrogen peroxide solution at 25 °C catalysed by doped manganese dioxides with different levels of doping; $[H_2O_2] = 3.245 \times 10^{-1} \text{ mol dm}^{-3}$.

to be within the experimental error. The curve for gallium(III) doped MnO_2 , however, was significantly higher (14%) than that of the undoped sample: in agreement with the previously reported work [14]. The higher catalytic activity of the doped, compared with the undoped sample (Fig. 3), may be due to lattice distortion caused by the replacement of manganese ion from the solid by a dopant cation of a different radius and/or charge. The decomposition rates of H_2O_2 catalysed by the different MnO_2 samples (Figs. 1 - 3) are given in Table 1.

A redox type mechanism has been reported [3] for the catalytic decomposition of H_2O_2 over MnO_2 . In the pH range 8 - 14, the active site for the dissociation process is assumed to be Mn^{3+} ion. The suggested reaction steps may be represented by:



TABLE 1

Catalytic decomposition rates of H₂O₂ solution by different MnO₂ samples

No.	Sample	10 × Rate of decomposition (≡ 10 × O ₂ evolution rate) (ml s ⁻¹ g ⁻¹) (approx. values)
1	ICS4	32
2	ICS5	31
3	ICS12	34
4	R2	33
5	FEMD-S	38
6	FEMD-P	37
7	FEMD-N	35
8	Mo ^{VI} -doped (0.03 at.%)	31
9	Mo ^{VI} -doped (0.06 at.%)	29
10	Mo ^{VI} -doped (0.09 at.%)	27
11	Ga ^{III} -doped (0.1 at.%)	30
12	undoped	26



where k_n represents the rate constants and $K_{\text{HO}_2 \cdot (a)}$ is the dissociation constant of HO₂· radical in the adsorbed phase. The higher rate of proton diffusion into the lattice of γ -MnO₂ compared to that into β -MnO₂ has been reported [16]. In the case of H₂O₂ decomposition over β -MnO₂, where the concentration of protons is expected to be higher in solution, equilibrium (3) is expected to shift to the left. Accordingly, reaction (4) proceeds at a slower rate, leading to a reduced liberation of O₂. The forward reaction (5) proceeds at a higher rate, leading to a higher transformation of Mn³⁺ to Mn⁴⁺, i.e., a slower reduction of MnO₂ to MnOOH. On the other hand, in the case of decomposition over γ -MnO₂ the reverse is expected. The present results (Figs. 1 and 3 and Table 1) showed that the rates of O₂ evolution in the H₂O₂ decomposition catalysed by the β -MnO₂ samples were relatively slower than those found in the case of the γ -MnO₂ samples. These results are in agreement with the relative proton diffusion rates into the lattice of the two structures of MnO₂. In the pH range 3 - 8, the possible active site is assumed to be the Mn⁴⁺ ion and the suggested reaction steps may be represented by:





Equilibrium (3) is assumed to govern the rate of O_2 evolution via reaction (7). The above argument also applies in this case.

Comparison of the results in Figs. 1 - 3 with those reported for N_2H_4 reduction ([13], Figs. 9 - 11), shows that the correlation between the catalytic and electrochemical activities discussed earlier is generally observed for all the MnO_2 samples investigated. The effect which the BET surface area has on the decomposition rate of H_2O_2 catalysed by the different MnO_2 samples at 25 °C is shown in Fig. 4, in which the sample numbers are the same as those in Table 1 and Table 1 of ref. 13. Generally, an increase in the decomposition rate with increasing catalyst surface area is suggested from the plot (see Table 1 in ref. 13). Clear deviations in the case of some samples ($\gamma\text{-MnO}_2$) indicate, however; that there are additional factors needing investigation. In view of this ICS5 was washed with dilute hydrochloric acid solution then repeatedly rinsed with water and decanted before the addition of the H_2O_2 solution. The acid-washed sample exhibited a higher catalytic decomposition rate than did the unwashed sample. It is known that most of the battery-active MnO_2 samples contain variable amounts of Mn^{II} ions on the surface during the manufacturing process [17]. The proposed mechanism for the heterogeneous decomposition of H_2O_2 [3] suggested that divalent

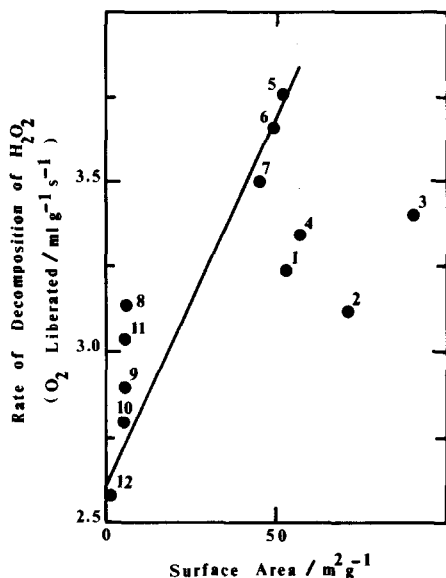


Fig. 4. Decomposition rate of hydrogen peroxide solution at 25 °C catalysed by the different (numbered) manganese dioxide samples *vs.* surface area.

manganese does not take part in the catalytic activity of the sample and, therefore, a fraction of the surface containing Mn^{II} ions will not be catalytically effective. It has also been reported that Mn^{II} ions act as inhibitors for the MnO_2 -catalysed decomposition of H_2O_2 [18]. The higher rate obtained for the H_2O_2 decomposition catalysed by the acid-washed sample compared to that of the unwashed sample can, therefore, be explained.

Measurements of the catalytic decomposition rates of different concentrations of H_2O_2 solution were made to determine the order of the reaction. Five concentrations of H_2O_2 , whose molarities were determined by titration using a standardised KMnO_4 solution, were used. For these diluted concentrations the sensitivity of the gas measuring system was increased, since the volume of oxygen liberated from the reaction mixture was expected to be small. In a control experiment, 1.0 g of ICS5 was suspended in 10 ml of distilled water and the pH of the suspension was found to be 7.21 prior to the addition of 10.0 ml of diluted H_2O_2 solution. The kinetic curves for the decomposition of the different H_2O_2 concentrations at 25 °C and pH 7.21 catalysed by ICS5 were recorded and the initial decomposition rates are shown in Table 2.

TABLE 2

$10^2 \times [\text{H}_2\text{O}_2]$ (mol dm^{-3})	$10^2 \times$ initial decomposition rate ($\equiv 10^2 \times \text{O}_2$ evolution rate) ($\text{ml s}^{-1} \text{m}^{-2}$) (approx. values)
0.786 ₈	0.45
1.57 ₄	0.94
2.36 ₀	1.66
2.69 ₇	1.88
3.14 ₇	2.35

The approximate values of the slopes used to calculate the initial rates of decomposition in Table 2 are independent of the units (arbitrary or otherwise) used to calculate the volumes of oxygen liberated during the reaction. Figure 5 shows that there is a linear relationship in the log/log plot of the initial catalytic decomposition rates *versus* H_2O_2 concentration, and the order of the reaction, calculated from the slope, was close to unity. Thus the catalytic decomposition of hydrogen peroxide is first-order with respect to the H_2O_2 concentration at the initial stages, in agreement with the literature [3, 4].

The effect which the pH of the solution has on the decomposition rate of H_2O_2 catalysed by ICS5 was also studied. Two gram samples of ICS5 were suspended in 20 ml of H_2O (pH 7.21). This was then either lowered or raised to cover a range of measured values. After adding 20.0 ml of a $3.24_5 \times 10^{-1} \text{ mol dm}^{-3}$ H_2O_2 solution, the oxygen liberated was recorded as a function of time. The decomposition rates of the H_2O_2 solution at 25 °C, as catalysed by

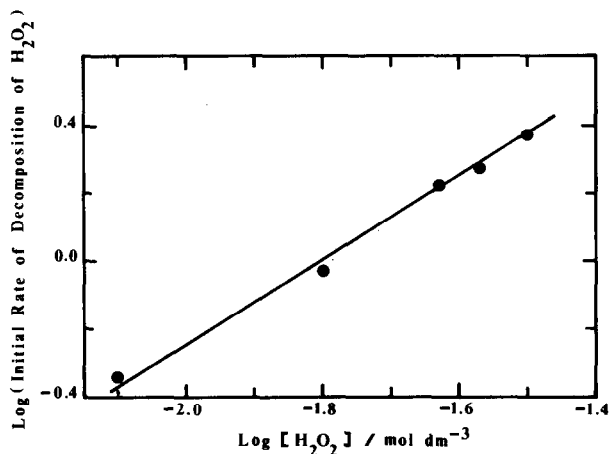


Fig. 5. Initial decomposition rate of hydrogen peroxide solutions at 25 °C catalysed by ICS5 vs. molar concentration of hydrogen peroxide.

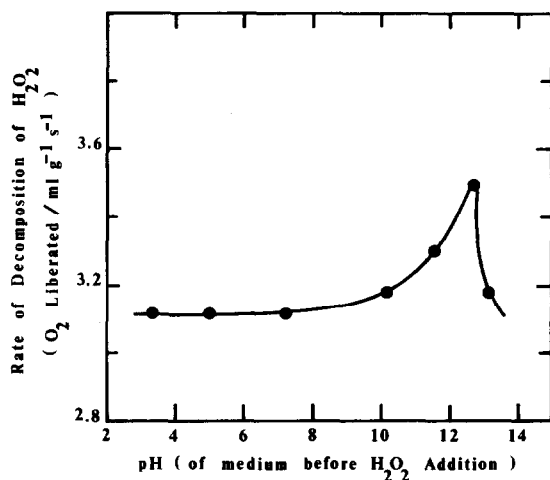


Fig. 6. Decomposition rate of hydrogen peroxide solution at 25 °C catalysed by ICS5 vs. the pH of the medium; $[H_2O_2] = 3.24_5 \times 10^{-1} \text{ mol dm}^{-3}$.

ICS5 at the different pH values, were calculated from the corresponding kinetic curves, and the results are shown in Fig. 6. There was no appreciable change in the decomposition rate below a pH value of about 10. Above pH 10 the rate increased to a sharp peak at a pH of about 12.2 before decreasing. Similar behaviour has been reported for different crystalline modifications of MnO₂ [3] and for cobalt-iron oxides [19]. The drop in reaction rate at the higher pH values may be ascribed to the intrinsic instability of H₂O₂ in alkaline medium in addition to base catalysis by OH⁻ ions [19]. Alternatively, it has been suggested that intermediates formed on the active catalyst surface during the decomposition reaction are less stable in acid

solution. The decomposition rates would therefore be generally lower in acid than in alkaline media [20].

At relatively low pH values, the rate-law suggested for the heterogeneous decomposition of H_2O_2 [3] was:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = \text{constant} \cdot [\text{H}_2\text{O}_2]_t \quad (9)$$

where $[\text{H}_2\text{O}_2]_t$ is the total analytical concentration of H_2O_2 . This indicates that the reaction follows first-order kinetics with respect to H_2O_2 during the initial stages of decomposition and would be constant up to a pH of 8. The present results are in agreement with eqn. (9). The rates at higher pH values in the range 8 - 14 [3] are also in agreement with the observed first-order kinetics with respect to hydrogen peroxide during the initial stages of decomposition.

Grading the ICS5 sample showed that the catalytic decomposition rate of H_2O_2 increased as the particle size decreased. The magnitude of the effect was, however, less than in the case of reduction by N_2H_4 [13]. This result demonstrates the importance of the real external surface area rather than the BET surface area.

The catalytic activity of MnO_2 for decomposing H_2O_2 has been found to depend on the number of available Mn^{IV} and Mn^{III} ions on the surface [3, 6, 21, 22]. To study the effect which partial reduction of $\gamma\text{-MnO}_2$ has on its catalytic activity, samples were prepared using slow reduction by hydrazine solution, as given elsewhere [23]. The reduced powder was washed with water, dried under reduced pressure and stored in a vacuum desiccator at a temperature $\leq 30^\circ\text{C}$. The total manganese and available oxygen were determined by a modified Gattow's method [24, 25]. Figure 7 illustrates the kinetic curves for the decomposition of H_2O_2 at 25°C , catalysed by the three partially reduced samples FEMD-S ($\text{MnO}_{1.867}$), FEMD-N ($\text{MnO}_{1.844}$), and ICS4 ($\text{MnO}_{1.789}$), compared to the corresponding unreduced samples FEMD-S ($\text{MnO}_{1.929}$), FEMD-N ($\text{MnO}_{1.934}$), and ICS4 ($\text{MnO}_{1.862}$). The lower oxygen evolution rate (assumed to be equivalent to the decomposition rate) observed for each partially reduced sample may be explained as follows. MnOOH is the primary product of the reduction of $\gamma\text{-MnO}_2$ by hydrazine. It has been reported that the MnOOH thus formed may be dissociated into Mn^{III} and OH^- ions [26]. Large numbers of Mn^{III} ions are known to degrade the catalytic activity in the $\text{H}_2\text{O}_2/\text{MnO}_2$ reaction [3]. Figure 7 shows that the difference in the amount of oxygen evolved between the partially reduced and the unreduced samples varied in the following order:



The Mn^{III} ion content in the bulk of the partially reduced sample may be calculated, assuming the formula for the non-stoichiometric MnO_2 to be represented by:

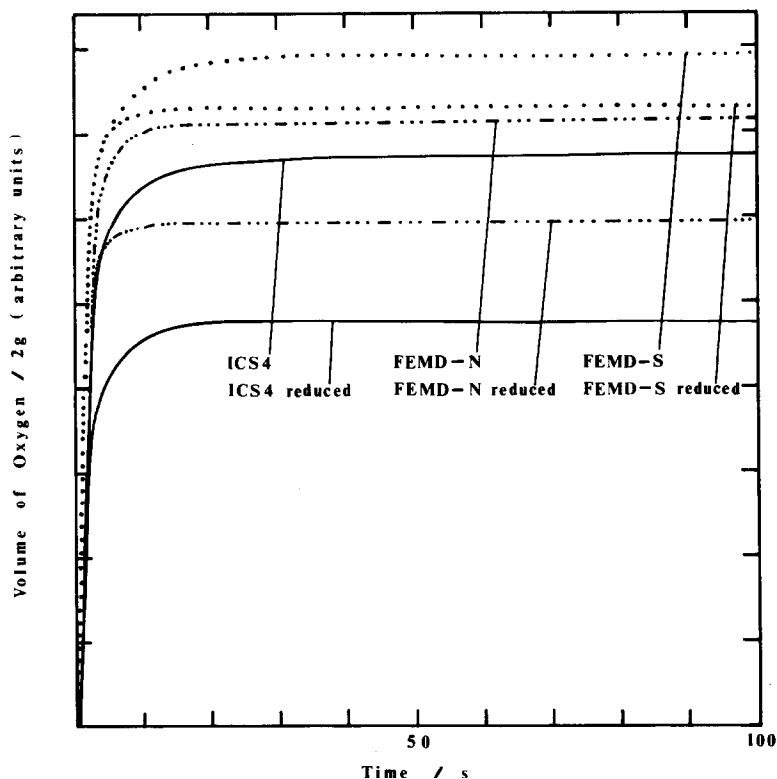
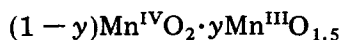


Fig. 7. Kinetic curves of oxygen liberated by the decomposition of hydrogen peroxide at 25 °C catalysed by partially reduced manganese dioxide samples vs. time; $[\text{H}_2\text{O}_2] = 3.24_5 \times 10^{-1} \text{ mol dm}^{-3}$.



where y represents Mn^{III} ions which have replaced some normal Mn^{IV} sites. The calculated amounts of Mn^{III} ions in the bulk of each of the three partially reduced samples were found to be in the following order:

reduced FEMD-S < reduced FEMD-N < reduced ICS4

The oxygen evolution rates and the number of Mn^{III} ions in the bulk, therefore, follow the same order, although the catalytic activity is believed to be, primarily, a surface phenomenon.

The Mn^{III} and Mn^{IV} ion contents in the bulk of the twelve MnO_2 samples investigated in the present study have been calculated, and a log/log plot of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ ratio versus the specific rate constant for the decomposition of H_2O_2 catalysed by the different samples is depicted in Fig. 8. This shows that the specific rate constant attained a maximum at a $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ ratio of 0.16. A similar optimum value was reported for the decomposition

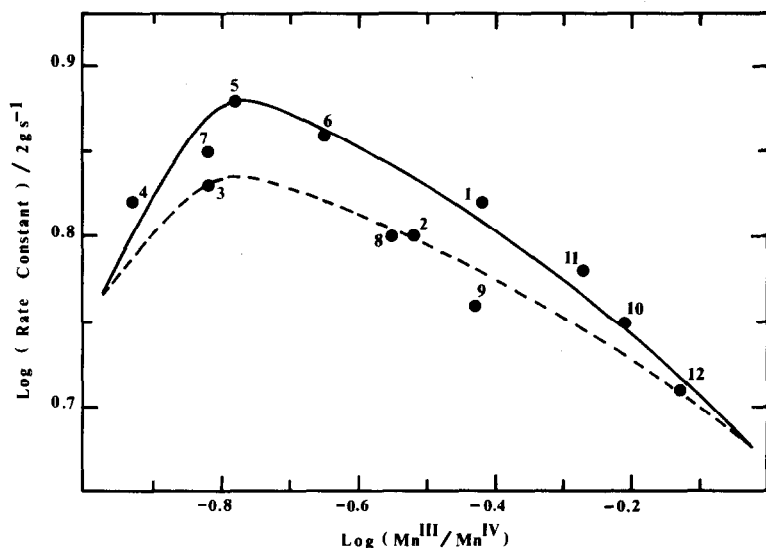


Fig. 8. The $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ ratio vs. the specific rate constant for the decomposition of hydrogen peroxide solution at 25 °C catalysed by the different manganese dioxide samples; $[\text{H}_2\text{O}_2] = 3.24_5 \times 10^{-1} \text{ mol dm}^{-3}$.

of H_2O_2 over different crystalline modifications of MnO_2 [3]. The latter authors have used the surface area, density, and unit cell parameter data to calculate the total number of manganese atoms and, hence, the number of Mn^{III} or Mn^{IV} atoms on the surface, from a knowledge of the fraction of each species in the sample, although the latter is known to be a bulk phenomenon.

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