

An Observation of Homogeneous and Heterogeneous Catalysis Processes in the Decomposition of H_2O_2 over MnO_2 and $\text{Mn}(\text{OH})_2$

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The kinetics of peroxide decomposition by manganese dioxide (MnO_2) and manganese hydroxide ($\text{Mn}(\text{OH})_2$) have been studied in alkaline solutions. The activity for peroxide decomposition on $\text{Mn}(\text{OH})_2$ was generally higher than MnO_2 and the kinetics for the decomposition of H_2O_2 were first-order in the case of MnO_2 catalysts, but 1.3-order for $\text{Mn}(\text{OH})_2$ catalysts. It is suggested that H_2O_2 is mainly homogeneously decomposed by Mn^{2+} ions (in the form of HMnO_2^- ions in concentrated alkaline solutions) dissolved in the solution in the case of $\text{Mn}(\text{OH})_2$. Compared with the results reported for the decomposition of H_2O_2 in the presence of 1 ppm Co^{2+} ions, it is concluded that the kinetics of the homogeneous decomposition of H_2O_2 are directly influenced by the concentration of the active species in the solution. © 1991 Academic Press, Inc.

INTRODUCTION

Manganese oxide catalysts play a very important role in electrochemical processes. In the Leclanché type dry cell, where MnO_2 has long been used as cathode material, the life of the cell depends primarily on the quality of MnO_2 used. MnO_2 -based catalysts are also widely used for the oxidation of CO (1, 2) and various other organic compounds (3). The high activity of manganese oxides for the catalytic decomposition of H_2O_2 is well known. This includes not only manganese dioxide but also some non-stoichiometric oxides of manganese having formula MnO_x (where $2 > x > 1.5$) (2, 4, 5). It has been shown that the MnO_2 prepared by a wide range of methods is non-stoichiometric in nature (6). The non-stoichiometry in the composition is primarily due to the existence of Mn^{2+} and Mn^{3+} ions (6). However, all the previous studies proposed that hydrogen peroxide was heterogeneously decomposed on the active sites

of manganese oxides, and the reaction was considered to be first-order (2, 4). Little attention has been paid to the effect of the existence of Mn^{2+} and Mn^{3+} ions on the mechanism of the catalysis processes of the oxides, especially for the decomposition of H_2O_2 .

In a study of oxygen reduction on Teflon-bonded Co_3O_4 /graphite electrodes in alkaline solutions, it has been found (7, 8) that the dissolved Co^{2+} ions (in the form of dicobaltite ion HCoO_2^- in concentrated alkaline solutions (9)) are highly active for the decomposition of H_2O_2 , even at very low concentrations of about 1 ppm. The kinetics of decomposition of H_2O_2 in the presence of Co_3O_4 are controlled by the homogeneous catalytic reaction of the HCoO_2^- ions, and the heterogeneous redox reaction between HCoO_2^- ions in the solution and the Co^{3+} ions in the cobalt oxide spinel lattice sites. A fractional reaction order of about 1.2 was found for the decomposition of H_2O_2 in the presence of 1 ppm Co^{2+} ions with or without addition of high surface area graphite powders. From the Pourbaix diagram (9), it is known that Mn^{2+} ions, like Co^{2+} ions, are also thermodynamically stable in concen-

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trated alkaline solutions in the form of HMnO_2^- . The dissolution of Mn^{2+} ions is most likely in the case of manganese dioxides with non-stoichiometric composition. The purpose of this paper is to study the catalytic role of Mn^{2+} ions dissolved in the alkaline solution on the decomposition of H_2O_2 , and the kinetics of the heterogeneous as well as homogeneous decomposition reactions of H_2O_2 on the manganese oxide and manganese hydroxide catalysts. The significance of the participation of the homogeneous catalytic process of Mn^{2+} ions in the oxygen reduction on manganese oxide-based air electrodes is discussed.

EXPERIMENTAL

MnO_2 and $\text{Mn}(\text{OH})_2$ were chosen as manganese oxide catalysts for this study. $\text{Mn}(\text{OH})_2$ was prepared by addition of excess of 5 M KOH solution to aqueous MnCl_2 solution. The solution was continuously stirred by bubbling nitrogen. The brown precipitate of $\text{Mn}(\text{OH})_2$ was filtered off, washed free of alkali, and then dried at 110°C . A portion of the precipitate product was heated at 460°C for 24 h. It was found that there were no further weight losses as the heating temperature increased, indicating that $\text{Mn}(\text{OH})_2$ had been fully decomposed to MnO_2 at 460°C . Samples were ground and kept in air-tight bottles.

The decomposition reaction of H_2O_2 on MnO_2 and $\text{Mn}(\text{OH})_2$ was measured by a conventional gasometric method. The peroxide solution was injected into the reaction vessel using a 5-ml syringe. The volume of oxygen decomposed, V , was determined in a gas burette at atmospheric pressure and room temperature. The gasometric apparatus and measurement procedure were described elsewhere (7). The concentration of H_2O_2 was determined by titration with standard KMnO_4 solution in acidic media. The electrolyte, 5 M KOH, was made from potassium hydroxide pellets and distilled deionized water. All chemicals used were analytical grade (BDH). The experiments were carried out at 20°C and the solution

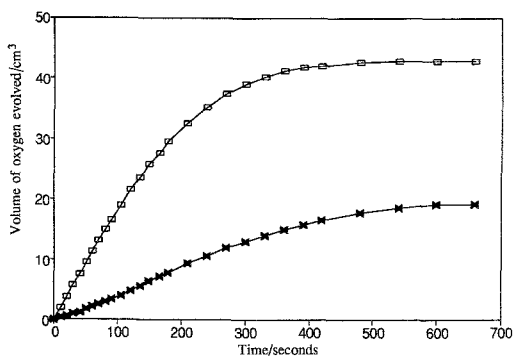


FIG. 1. Decomposition of peroxide catalyzed by $\text{Mn}(\text{OH})_2$ and MnO_2 at initial peroxide concentration of 0.0304 M in 5 M KOH. (\square) $\text{Mn}(\text{OH})_2$, (\times) MnO_2 .

was stirred using a magnetic stirrer. The solution volume and the catalyst weight were 50 ml and 50 mg, respectively.

RESULTS

Solubility of MnO_2 and $\text{Mn}(\text{OH})_2$

A small quantity of the MnO_2 and $\text{Mn}(\text{OH})_2$ powder samples was added to 5 M KOH solution under bubbling nitrogen for 48 h. The solution was then filtered twice. The concentration of Mn^{2+} dissolved was determined by atomic absorption spectroscopy. The concentration of Mn^{2+} ions in 5 M KOH was 0.267 ppm for $\text{Mn}(\text{OH})_2$ and 0.167 ppm for MnO_2 , respectively. The solubility of the manganese oxides is much lower than that of cobalt oxides (which is about 1 ppm) in the same conditions (7). This accounts for the fact that manganese dioxides are much more stable than cobalt oxides in alkaline solutions. Nevertheless, the solubility of $\text{Mn}(\text{OH})_2$ is generally higher than MnO_2 .

Catalytic Activity for the Decomposition of H_2O_2

Figure 1 shows the decomposition curves of H_2O_2 by MnO_2 and $\text{Mn}(\text{OH})_2$ in 5 M KOH at an initial peroxide concentration of 3.04×10^{-2} M. By comparison, $\text{Mn}(\text{OH})_2$ shows much better catalytic performance for the peroxide decomposition. The much higher

activity of $\text{Mn}(\text{OH})_2$ for the decomposition of H_2O_2 indicates the possibility of the participation of the homogeneous catalytic process of dissolved Mn^{2+} ions. The homogeneous catalytic process generally shows very high activity even at very low concentration of the participating ions (7). Assuming first-order reaction kinetics for the decomposition of H_2O_2 , the linearity of the first-order reaction was generally observed in both cases (Fig. 2). In the figure, V is the volume of oxygen decomposed at time t and V_{max} is the final volume of oxygen when all the H_2O_2 has been decomposed. The rate constant, k_f , calculated from the slope of the linear regression line, was $1.2 \times 10^{-4} \text{ s}^{-1}$ for MnO_2 and $5.7 \times 10^{-4} \text{ s}^{-1}$ for $\text{Mn}(\text{OH})_2$, respectively. The reaction rate constants obtained are in the same magnitude range as reported by Kanungo *et al.* (4).

It has been shown (7) that the linear correlation of the first-order reaction equation does not prove a first-order kinetics for the reaction. In order to confirm the validity of the first-order reaction kinetics in the case of peroxide decomposition by manganese oxide catalysts, the reaction was performed at various initial peroxide concentrations. Figure 3 shows the plots of the first-order rate constants against the initial concentration of H_2O_2 . In the case of MnO_2 , the reaction rate constant is virtually independent of the initial concentration of H_2O_2 . However,

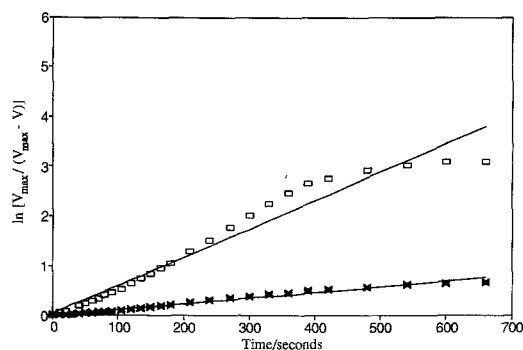


FIG. 2. First-order plots of peroxide decomposition catalyzed by $\text{Mn}(\text{OH})_2$ and MnO_2 at 0.0304 M H_2O_2 concentration. (\square) $\text{Mn}(\text{OH})_2$, (\times) MnO_2 .

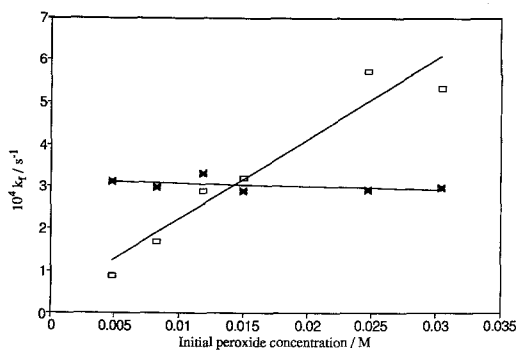


FIG. 3. Plots of first-order rate k_f versus the initial concentration of H_2O_2 in the presence of $\text{Mn}(\text{OH})_2$ and MnO_2 catalysts. (\square) $\text{Mn}(\text{OH})_2$, (\times) MnO_2 .

the first-order reaction rate constant increases with the increase of the initial concentration of H_2O_2 in the case of $\text{Mn}(\text{OH})_2$. For a true first-order reaction, the reaction order should be independent of the initial peroxide concentration. This clearly shows that in the case of $\text{Mn}(\text{OH})_2$, the kinetics of the reaction are different. This also means that in the case of decomposition of H_2O_2 by $\text{Mn}(\text{OH})_2$, the reaction is not a simple first-order reaction.

Order of the Reaction

Therefore, it is necessary to use other methods to determine the reaction kinetics. The initial-rate method was used to evaluate the actual order of the reaction. Figure 4 shows the log-log plots of the initial rate vs initial concentration of H_2O_2 . The order of the reaction was obtained from the slope of the plots, which was 1.02 in the presence of MnO_2 and 1.29 in the presence of $\text{Mn}(\text{OH})_2$, respectively. The reaction order for the decomposition of H_2O_2 in the presence of MnO_2 is very close to unity and is in good agreement with the observation that the first-order reaction rate is independent of the initial concentration of H_2O_2 . This again confirms that the peroxide decomposition by MnO_2 is a first-order reaction and the decomposition reaction is a heterogeneous process.

However, in the case of the decomposi-

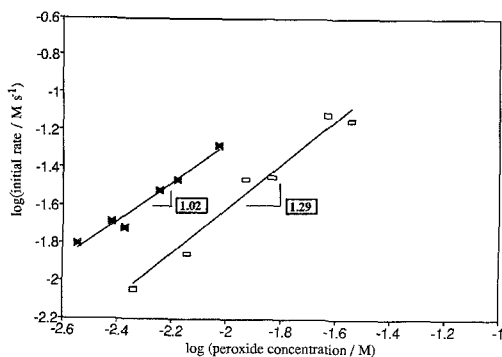


FIG. 4. Log-log plots of initial rate of peroxide decomposition versus initial concentration of H₂O₂. (□) Mn(OH)₂, (x) MnO₂.

tion of H₂O₂ in the presence of Mn(OH)₂ catalysts, the reaction order was found to be ~1.3. More significantly, the magnitude of this fractional order rate is the same as the one found in the case of peroxide decomposition by Co²⁺ ions (1 ppm) in the presence of high surface area graphite (7), even though the concentration of Mn²⁺ ions in the solution is about four times lower. The concentration of the catalytic ions has little effect on the mechanism of the homogeneous decomposition of H₂O₂ in alkaline solutions. H₂O₂ could also be predominantly decomposed by Mn²⁺ ions dissolved from Mn(OH)₂ in alkaline solutions. By considering the reaction order to be 1.3, the 1.3-order reaction rate could be evaluated from the 1.3-order reaction law

$$dx/dt = k_{1.3}(a - x)^{1.3}, \quad (1)$$

where $k_{1.3}$ is the 1.3-order reaction rate constant and a and x are the initial and decomposed concentration of H₂O₂, respectively. The reaction rate constants $k_{1.3}$ were therefore obtained from the slopes of the linear regression plots from Eq. (1). In Fig. 5, the reaction rate constants $k_{1.3}$ were plotted against the initial concentration of H₂O₂ in the case of Mn(OH)₂. It is shown that the reaction rate constant is generally independent of the initial concentration of peroxide.

This therefore confirms the fractional order for the decomposition of H₂O₂ in the presence of Mn(OH)₂. This also implies that H₂O₂ is most probably homogeneously decomposed by Mn²⁺ ions as Mn(OH)₂ has a tendency to dissolve in concentrated alkaline solutions.

DISCUSSION AND CONCLUSIONS

In the study of the decomposition of H₂O₂ over various MnO₂ catalysts prepared by different methods, the reaction order was found to vary between 1 and 1.5 by Kanungo *et al.* (4). It can be seen from the results of the chemical analysis of the samples that the MnO₂ catalysts generally contain rather large quantities of Mn²⁺ and Mn³⁺ in the case of fractional orders (6). It seems that the occurrence of the fractional order for the decomposition of H₂O₂ is more or less dependent on the existence of Mn²⁺ and Mn³⁺ in the MnO₂ with non-stoichiometric composition.

The existence of the fractional order clearly demonstrates that the decomposition of H₂O₂ over Mn(OH)₂ and MnO₂ with non-stoichiometric composition is a multi-step reaction. As in the case of peroxide decomposition by cobalt oxides (7), the mechanism could also involve the homogeneous decomposition of H₂O₂ by HMnO₂⁻ ions in the solution, and the heterogeneous reaction between the HMnO₂⁻ ions in the

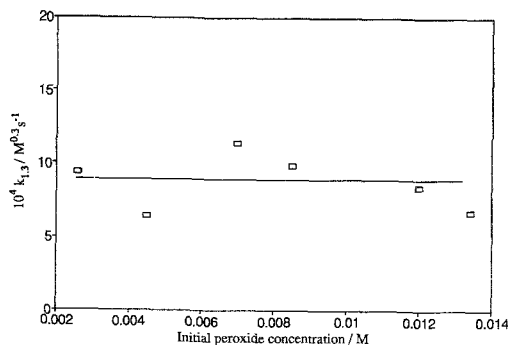


FIG. 5. Relationship between the 1.3-order rate constant $k_{1.3}$ and the initial concentration of peroxide in the presence of Mn(OH)₂.

solution and the Mn^{3+} and Mn^{4+} ions in the solid lattice state. The kinetics of the reaction are therefore controlled by the relative rates of both homogeneous and heterogeneous catalytic reactions. As the quantities of the Mn^{2+} and Mn^{3+} ions are at large dependent on the preparation methods (6), the relative rates of the homogeneous and heterogeneous catalytic reactions are inevitably influenced by the nature of the MnO_2 samples. In the case of MnO_2 with negligible amount of Mn^{2+} and Mn^{3+} ions, H_2O_2 is predominantly decomposed by the heterogeneous process and the reaction can be satisfactorily described by first-order reaction kinetics. However, as the non-stoichiometry in the composition of manganese oxides increases, the participation of Mn^{2+} ions dissolved from the manganese oxides would play an increasing important role in the decomposition of H_2O_2 . In the extreme case of $\text{Mn}(\text{OH})_2$, the homogeneous decomposition of H_2O_2 by dissolved Mn^{2+} becomes a predominant process. The homogeneous decomposition reactions are typically characterized by the fractional order kinetics (7).

The fractional order reaction rate ($k_{1,3}$) for the peroxide decomposition by $\text{Mn}(\text{OH})_2$ is of the same order of magnitude as the $k_{1,2}$ value found in the case of 1 ppm Co^{2+} ions (7). In the case of $\text{Mn}(\text{OH})_2$, $k_{1,3}$ is found to be $\sim 0.85 \times 10^{-3} \text{ M}^{-0.2} \text{ s}^{-1}$, which is about three times lower than the $k_{1,2}$ value ($2.4 \times 10^{-3} \text{ M}^{-0.2} \text{ s}^{-1}$) found in the case of the decomposition of H_2O_2 by Co^{2+} ions in the presence of high surface area graphite (7). This could be explained by the fact the solubility of $\text{Mn}(\text{OH})_2$ is about four times lower than 1 ppm which is the solubility of Co_3O_4 in alkaline solutions (7). The results suggest that the kinetics of the homogeneous catalytic reactions are directly influenced by the concentration of the active species in the solution. The kinetics of such homogeneous catalytic reactions are also affected by the relative rate of the redox reaction between the lower and higher metal ions couple (e.g., Mn^{2+} in solution and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ion in the

oxide lattice). Detailed elucidation of the homogeneous-heterogeneous mechanism for the decomposition of H_2O_2 over manganese dioxide catalysts could be much more difficult as both the composition and crystalline structure vary. In conclusion, it is unjustified to simply use the first-order reaction law to evaluate the kinetics and mechanism of the peroxide decomposition in the presence of MnO_2 , especially in the case of MnO_2 with non-stoichiometric compositions. The participation of dissolved Mn^{2+} ions could be one of the main reasons for the difficulties in the attempts to correlate the physicochemical properties of the MnO_2 -based catalysts with their electrochemical as well as catalytic activities (2, 4, 10).

In the situation where H_2O_2 is formed as intermediate during O_2 reduction on MnO_2 -based electrodes, the efficiency of the peroxide decomposition can be significantly increased by promoting the homogeneous decomposition process. This can be achieved by increasing the non-stoichiometry in composition, thus increasing the percentage of the Mn^{2+} and Mn^{3+} ions. As the homogeneous decomposition reactions of H_2O_2 are most likely localized near the active sites of the electrodes (8), the efficiency of the homogeneous catalytic reactions is also significantly dependent on the interfacial distribution of the $\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$ ions on the catalyst supports. One solution is to deposit the manganese oxide/hydroxide catalysts onto the porous electrode *in situ*. Such an *in situ* deposition method, apart from ensuring the uniform distribution of the catalysts, can also greatly increase the efficiency of the homogeneous catalytic reactions (11).

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