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Hydrated Oxides of Manganese Supported on Magnesium Hydroxide as Catalysts for Hydrogen Peroxide Decomposition

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Three catalytic systems were studied: Mn, supported on magnesium oxide; Mn, supported on magnesium hydroxide prepared by coprecipitation; and Mn, supported on magnesium hydroxide prepared by impregnation. The rate of decomposition of H_2O_2 was used as a measure of the catalytic activity of the catalysts. Results indicated that the use of MgO as a carrier for the manganese oxides gave a highly active catalytic system as compared with that of manganese oxides or magnesium oxide alone.

The Mn-supported on $Mg(OH)_2$ system proved to have a better catalytic activity and to give better experimental reproducibility than the oxide system. The catalyst prepared by impregnation was found to be more active than a similar one prepared by coprecipitation; in the latter the $Mn(OH)_2$ is assumed to be fixed in the lattice of $Mg(OH)_2$ so that the surface concentration of manganese is lower than in catalysts prepared by impregnation.

The importance of the surface of the carrier was investigated by carrying out experiments with $Mg(OH)_2$ having different specific surface areas. Some solids were found to have micropores which were not available for the reaction. The activity was found to increase with the increase of the external surface area rather than with the total area.

A mechanism is suggested based on the continuous formation of an unstable manganese peroxy-complexes which break on the surface of magnesium hydroxide and undergo a cycle of oxidation and reduction resulting in the decomposition of H_2O_2 into O_2 and H_2O.

INTRODUCTION

During the last two decades, catalysts formed of mixed oxides and hydroxides have received much attention (*1–19*). In particular, Krause and coworkers (*5–17*) have made a wide coverage of different oxides and hydroxides. However, the heterogeneous system manganese–magnesium hydroxide has not received much of their care. In homogeneous catalysts, an aqueous solution of $Mg(OH)_2$ and divalent manganese were shown by Krause and Plura (*17*) to have much stronger decomposing activity on H_2O_2 as compared to cupric ions.

Despite the numerous studies on the catalytic decomposition of hydrogen peroxide using simple or mixed heterogeneous catalysts, the catalytic phenomena are not yet understood. The exact nature of the active centers and even the role of the metal present in small doses and the carrier are not satisfactorily known. The order of the reaction and the mechanism seem to be debatable.

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Explanations based on the interaction of $Mg(OH)_2$–H_2O_2 and Zr_2O_2–H_2O_2 to form a peroxy-compound was suggested by Krause (*17*) for the first system and by Jalaj and Ghosh (*2*) for the second system. Formation of an unsaturated and highly energetic complex of an unstable nature between H_2O_2 and $Mg(OH)_2/Co^{2+}$ system was also assumed (*17*). Decomposition through a reduction–oxidation cycle was considered by some authors (*2*).

The presence of metal ions, such as manganese, in various states of valency is considered to be favorable for redox reactions. Therefore, it was of interest to investigate systematically the systems of manganese supported on magnesium oxide or hydroxides. The need of an efficient catalyst for the decomposition of H_2O_2 is of great demand, especially with the development of fuel cells in which H_2O_2 is formed as an undesirable side reaction during the reduction of O_2.

EXPERIMENTAL

Materials

Hydrogen peroxide. B.D.H. microanalytical reagent (100 volumes) was used. Solutions of the required concentrations were prepared by dilution and estimated titrimetrically by a freshly standardized $KMnO_4$ solution. Other chemicals used were Analar B.D.H. products. $Mg(NO_3)_2 \cdot 6H_2O$ was a Baker Analyzed reagent. Catalysts were prepared using one of the following carriers:

Carrier I. Magnesium oxide. Heavy MgO (B.D.H.) was used without further treatment.

Carrier II. Magnesium hydroxide. This was prepared by three different methods and referred to as carrier IIA, B, and C, respectively.

Carrier IIA. Magnesium hydroxide precipitated by sodium hydroxide. More than the stoichiometric amount of 5% NaOH solution was added at a rate of 20 drops per minute to the boiling solution containing 60 g of $Mg(NO_3)_2 \cdot 6H_2O$/liter. The precipitate was washed thoroughly then dried at 110°C until constant weight.

Carrier IIB. Magnesium hydroxide precipitated by ammonium hydroxide. The same procedure was followed as for carrier IIA. Excess ammonia was expelled by boiling the mixture.

Carrier IIC. Prepared by the hydrolysis of magnesium methoxide. A small ribbon of about 1 g of magnesium metal was refluxed with 250 ml of dry and freshly distilled methanol (fraction boiling at 64.7°C was used). Boiling under reflux was continued until dissolution of magnesium was complete. Distilled water was added to the magnesium ethoxide formed, where a white precipitate of $Mg(OH)_2$ appeared. The precipitate was washed and dried as the previous carriers.

Carrier III. Brucite. The naturally occurring $Mg(OH)_2$ mineral was crushed, powdered, and sieved to pass between 100 and 120 mesh.

Catalysts

Four catalysts were tested, further referred to as catalyst 1, 2, 3, and 4.

Catalyst 1. Manganese oxides. About 5% solution of $MnSO_4 \cdot 4H_2O$ was precipitated by the addition of 5% NaOH solution. The precipitate was thoroughly washed, dried at 110°, and calcined at 550°C for 6 hr.

Catalyst 2. Manganese oxides supported on magnesium oxide. One gram of $MnSO_4 \cdot 4H_2O$ and 10 g of heavy MgO were mixed thoroughly with 500 ml of distilled water. A solution of 5% NaOH was added rapidly at room temperature with continuous stirring until it became alkaline to litmus. The precipitate was washed, dried, and calcined as catalyst 1.

Catalyst 3. Manganese hydroxide supported on magnesium hydroxide prepared by coprecipitation. A solution was prepared containing 128.216 g/l of $Mg(NO_3)_2 \cdot 6H_2O$ and 2 g/l of $MnSO_4 \cdot 4H_2O$. The solution was heated to boiling and stirred mechanically. A 10% NaOH solution was added at a rate of 60 drops per minute until the solution became alkaline to litmus. The precipitate was thoroughly washed, dried at 110° until constant weight. The dried material was homogenized for about 10 min in a porcelain ball mill. A series of samples was prepared using different amounts of manganese sulfate. The catalyst was kept under vacuum.

Catalyst 4. Manganese hydroxide supported on magnesium hydroxide prepared by impregnation. To a definite weight of the $Mg(OH)_2$ the calculated volume of manganese sulfate solution containing 0.139 mg Mn^{2+}/ml was added to give the required concentration of divalent manganese. About 5 ml of distilled water was also added and the mixture was mechanically shaken, filtered, and washed.

The manganese content in the catalyst was analyzed polarographically, using a Fisher Electropode Model 65. An accurate weight of about 100 mg of the Mn-doped catalyst was dissolved in the least amount of dilute sulfuric acid solution. A few milliliters of 0.1 *N* sodium oxalate solution were added in order to reduce all the manganese to the easily soluble Mn^{2+} ions. The solution was evaporated almost to dryness to get rid of the excess acid. The contents were dissolved and quantitatively transferred to a 100 ml measuring flask with 1 *M* NH_4Cl–NH_4OH mixture. A sample was deoxygenated and polarographed. The wave height was compared with a standard solution of manganous sulfate dissolved in the same medium as the catalyst.

The decomposition of H_2O_2 was followed titrimetrically. A known weight of the catalyst was inserted in a conical flask clamped to a Griffin flask shaker placed in an air thermostat adjusted to the required temperature. The H_2O_2 solution and the reaction vessel with the catalyst were placed in the thermostat for sufficient time to take the ambient temperature, then mixed together. At suitable time intervals 1 ml was withdrawn and rapidly added to 5 ml of about 2 *N* ice cold sulfuric acid and immediately titrated with permanganate. Several aliquots were withdrawn in each experiment in order to minimize the error caused by the reduction of the initial volume. Unless stated the system was thermostated at 35 ± 0.2°C.

The specific surface areas of the carriers were measured by the BET method using N_2 (*20*). The external surface of carrier IIA, IIB, and IIC was determined by adsorption from solution, at 25°C, of the surface active bulky molecule Aerosol OT (sodium di-2-ethylhexyl sulfosuccinate) of cross-sectional area of 70Å^2/molecule (*21*). The relative density of the different carriers was obtained by measuring the heights of a definite weight of each preparation placed in a narrow cylindrical glass vessel.

EPR spectra were recorded at room temperature using a Varian V-4502 *X*-band spectrometer. X-Ray powder diffraction patterns were obtained using a General Electric XRD-6 diffractometer with Cu radiation.

Results and Discussion

Catalysts 1 and 2

The decomposition of H_2O_2 at 35°C was studied using different oxides and their mixtures. Figure 1 shows the results of decomposition using 250 mg of pure MgO (carrier I), 2 mg of manganese oxides (catalyst 1), and 250 mg of 0.23% Mn-doped MgO (catalyst 2). The results show that catalyst 2 gave nearly complete decomposition after 55 min while for the same period of time the manganese oxide (catalyst 1) resulted in 15% decomposition. The activity of catalyst 2 is higher than those of the two oxides, which shows

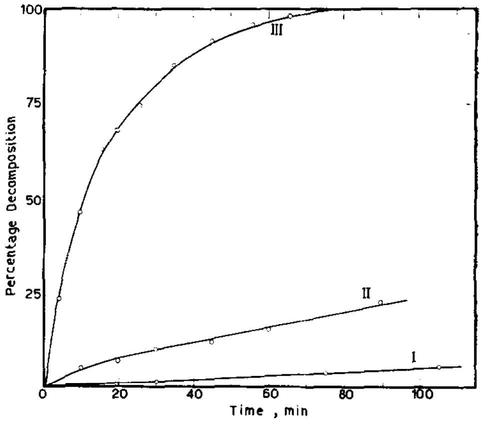


FIG. 1. Catalytic decomposition of 0.37 *N* H_2O_2. I. 250 mg MgO (carrier I), II. 2 mg of manganese oxide (catalyst 1), III. 250 mg of 0.23% Mn-doped MgO (catalyst 2).

that it has acquired synergistic catalytic properties.

Several experiments were carried out under the same experimental conditions using 250 mg of 1.02% Mn-doped MgO (catalyst 2). The results (Fig. 2) show little divergence at the early stages of decomposition, but noticeable differences are obtained at the later stages. These divergences are not easy to explain but might be due to the lack of homogeneity in the preparation of the catalyst, or differences in the concentration of manganese at the surface of the carrier.

Catalyst 3

Catalyst 3 showed good reproducibility for duplicate experiments (Fig. 2, II) and for two separate preparations of the catalyst having the same content of Mn (Fig. 2, III). Its activity was greater than that of catalyst 2. Thus, when 250 mg of catalyst 2 and 3 having the same concentration of Mn (0.23% Mn by weight) were used to decompose 100 ml of 0.72 *N* H_2O_2, 90% decomposition was reached in 27 min with the hydroxide system as compared to 44 min with the oxide system. The higher reactivity of the hydroxide might be due to the ease of oxidation and reduction and complexation with H_2O_2 (see Discussion).

The Effect Of Temperature

This was studied at four different temperatures using two different amounts of catalyst 3 of different Mn content. The first was 0.025 g, containing 1.35% Mn, and the second, 0.500 g containing 0.356% Mn. The energy of activation calculated from the approximately constant rate at the early region of decomposition was 11.2 kcal/mol for the first catalyst and 7.1 kcal/mol for the second. These values are comparable with values obtained by other authors whether the decomposition of H_2O_2 is carried out in a homogeneous medium (*22*) (19.4 kcal/mol using $CoCl_2$ in sodium acetate) or heterogeneously (*4*) (6.97 kcal/mol using manganese sesquioxide surfaces).

Effect Of Initial Concentration Of H_2O_2

The concentration of H_2O_2 used varied between 0.27 to 1.22 *N*. Generally the rate

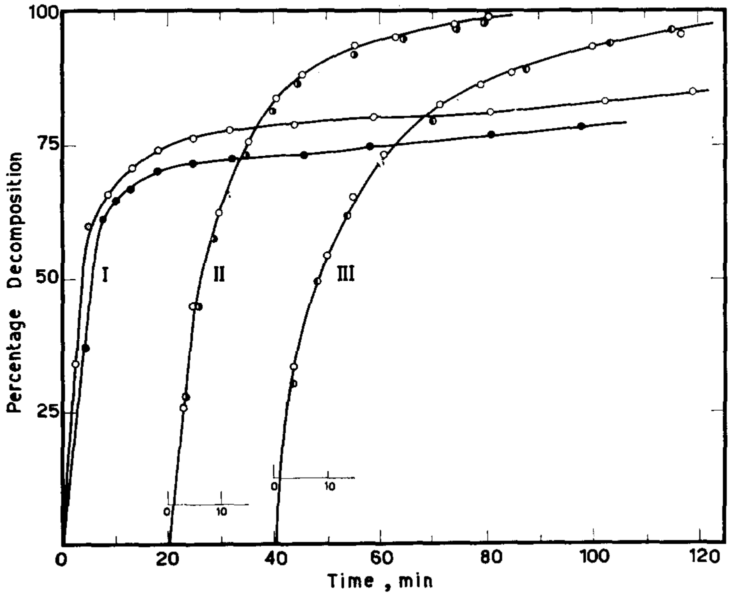


FIG. 2. Test for the reproducibility of the catalysts: I. 250 mg of 1.02% Mn-doped MgO (catalyst 2); H_2O_2, 0.65 *N*. First run (○). Second run (●) using the same catalyst. II. 250 mg of 0.23% Mn-doped $Mg(OH)_2$ (catalyst 3); H_2O_2, 0.74 *N*. First run (○). Second run (◑) using the same catalyst. III. 500 mg of 0.35% Mn-doped $Mg(OH)_2$ (catalyst 3), H_2O_2, 0.54 *N*. First catalyst (○), second catalyst (◐).

of reaction increases slightly with the increase of the initial concentration of H_2O_2. However, the time of half-change ($t_{0.5}$) does not show much difference. For example, the highest concentration of H_2O_2 ($1.22\,N$) gave a $t_{0.5} = 7$ min and the lowest concentration ($0.27\,N$) gave 10.1 min.

Order Of The Reaction

The analysis of the previous results of experiments on the rate of decomposition of H_2O_2 shows that the reaction does not obey the first order equation during the whole range of decomposition, as established by several authors (*2, 6, 23*). Attempts to find a general simple order of reaction with whole or fractional numbers were not successful. It seems probable that the decomposition does not follow one and the same order under different conditions of catalyst and H_2O_2 concentration, for the equation which could fit one set of experiments was found to fail to represent another set.

The results of experiments carried out with catalysts having relatively high percentage of Mn, namely 1.35%, obey the first order equation except in the early and last stages of decomposition, but the study of the effect of the initial concentration does not support the assumption of a simple first order reaction. Deviations from the first order law are clearly observed when the concentration of Mn in the catalyst decreases.

Catalyst 4

Several experiments were carried out to investigate the optimum conditions under which manganese catalyzes the decomposition of H_2O_2. The catalytic action of Mn^{2+} ion (0.27 mg/100 ml of $0.51\,N$ H_2O_2) alone was investigated, and the results illustrated in Fig. 3 show little catalytic activity. On the other hand, when the same amount of $MnSO_4$ solution was added to H_2O_2 containing an almost saturated solution of $Mg(OH)_2$ but free from solid $Mg(OH)_2$, the rate of decomposition became more rapid (curve II). The rate was much faster in presence of solid $Mg(OH)_2$, catalyst 4 (curve III).

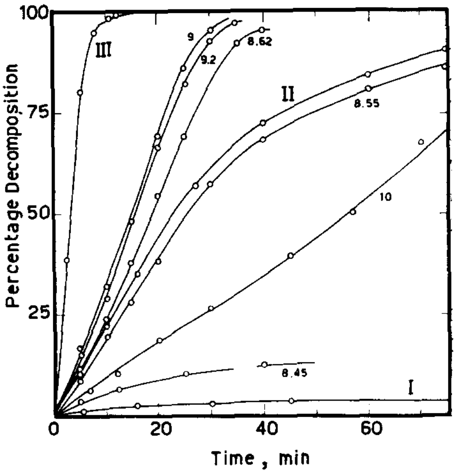


FIG. 3. Catalytic decomposition of $0.51\,N$ H_2O_2 in presence of 0.279 mg Mn^{2+} added as $MnSO_4$ solution in different media. I. $MnSO_4$ solution, II. Saturated solution of $Mg(OH)_2$, III. 100 mg of solid $Mg(OH)_2$. The other curves represent results of experiments at the pH values indicated on the diagram.

The addition of solid $Mg(OH)_2$ introduced two variables in the system simultaneously: (i) the variation of pH due to the dissolution of a little $Mg(OH)_2$, and (ii) the presentation of a large surface area for the reaction to take place.

(i). The effect on the rate of decomposition of changing the pH value of the H_2O_2 solution between 8.45 and 10.0 was studied by the dropwise addition of very dilute NaOH solution (Fig. 3). The rate increases with NaOH concentration until a maximum is reached when the initial pH value of the solution is about 9. Slight alterations at lower pH values produce greater differences in the decomposition rate than at higher pH values. This might be attributed to the quantity of manganese hydroxide precipitated, which depends on the amount of NaOH added. However, it is not clear why the presence of excess NaOH, when the pH of the solution becomes higher than 9, inhibits the reaction; this might be due to the disturbance in the equilibrium $H_2O_2 \rightleftharpoons H^+ + HO_2^-$, or to the rapid formation of a precipitate of $Mn(OH)_3$ which changes to less active Mn_2O_3. (See catalyst 1). No attempt was made, at this stage, to present a detailed study of such a phenomenon.

(ii). In order to show that the high catalytic activity is associated with the precipitation of manganese hydroxide at the surface of $Mg(OH)_2$ rather than its mere precipitation by the alkalinity it induces, the following experiment was carried out. The same amount of Mn^{2+} (0.279 mg) was added to H_2O_2 solution containing 0.100 g of $Mg(OH)_2$. The decomposition curve (Fig. 3, curve III) is the highest among all other curves. It was also noticed that the supernatant liquid became free from Mn^{2+}; the alkaline suspension of $Mg(OH)_2$ ($pH > 9.0$) practically precipitated all the manganous ions at its surface.

These experiments made it clear that the catalytic activity depends on the pH value of the medium. Nevertheless, the presence of solid $Mg(OH)_2$ is found to increase the catalytic activity to a far greater extent than would be expected from the pH it induces.

The Role Of Mg $(OH)_2$ As A Carrier In Catalysts Prepared By Impregnation And Coprecipitation

The results obtained by impregnated catalysts are apparently not in harmony with similar runs carried with catalysts prepared by coprecipitation. Table 1 summarizes these results: as 80% of the decomposition follows a first order law, $t_{0.5}$ can be taken as a measure of the catalytic activity. Examination of the table shows that impregnated catalysts are more active than the coprecipitated catalysts having the same amount of $Mg(OH)_2$ and equal or even less manganese content. This property is a general feature as long as the weight of Mn and $Mg(OH)_2$ are comparable.

TABLE 1
DEPENDENCE OF $t_{0.5}$ ON THE TYPE OF CATALYST

Catalyst	Weight of catalyst (mg)	Mn content (mg)	$t_{0.5}$ (min)
Coprecipitated	100	0.356	19
Impregnated	100	0.279	4.5
Coprecipitated	25	0.338	9
Impregnated	25	0.279	7.5

The explanation of this apparent anomaly is understood if we recall the fact that the $Mn(OH)_2$ is isomorphous with $Mg(OH)_2$ (*24*). The preparation of the catalyst by coprecipitation permits much of the Mn^{2+} to enter as hydroxide in the formation of the $Mg(OH)_2$ crystal lattice and become fixed in its structure. This suppresses further oxidation and permits only the small amount of $Mn(OH)_2$ present at the surface to give a variety of oxidation products (mainly non-Daltonide compounds) which are important factors increasing the catalytic activity.

On the other hand, in the case of catalysts prepared by impregnation, the Mn^{2+} ions precipitate mainly on the surface as $Mn(OH)_2$. Being less fixed in the lattice of the carrier and more exposed to the atmosphere, the $Mn(OH)_2$ is easily transformed to higher hydroxides thus increasing the number of active centers at the surface.

Dependence Of Activity Of The Catalyst On The Method Of Preparation Of Mg$(OH)_2$ Carrier

Since large areas of the carrier should present a better exposure for manganese hydroxides in catalysts prepared by impregnation, an attempt was made to vary the specific surface area of $Mg(OH)_2$ by preparing it on different ways (Carriers IIA, IIB, IIC, and III).

The rate of decomposition of H_2O_2 using 100 mg of the catalysts which have the same amount of Mn^{2+} (0.279 mg/100 ml of 0.54 *N* H_2O_2) as Mn-doped impregnated carriers followed the order: Carrier IIB > carrier IIC > carrier IIA > carrier III. The specific surface areas are: 73, 48, 38, and 0.5 m^2/g for carriers IIA, IIB, IIC, and III, respectively. It seems that the higher the surface area, the higher the catalytic activity. $Mg(OH)_2$ prepared by precipitation with NaOH (carrier IIA) is an exception. It might be that some of the surface area measured by N_2 adsorption does not contribute to the catalytic decomposition because of the presence of micropores which are not available for the catalytic process.

The measurement of the external surface area gave an area amounting to 35 m^2/g for carrier IIA, B, and C. This result could explain why carrier IIA, in spite of its high nitrogen area (73 m^2/g), did not possess the highest catalytic activity, and indicates that it is rather the external area and not the total area which plays the more important role in the rate of the catalytic reaction.

The role played by the external area has been further proved by measurement of the bulk density. For a given weight of a carrier, the smaller the bulk density the higher is the effective external area; consequently the Mn^{2+} ions will be precipitated and spread over a large area. The relative bulk densities were 1:3.41:3.58:7.02 for carrier IIB, IIC, IIA, and III, respectively. This order is in agreement with the catalytic activity.

X-ray Diffraction and EPR Studies

The X-ray diffraction patterns for a variety of preparations were determined before and after catalysis; they were all identical with the pure brucite pattern, even with Mn up to 1.35%. This is to be expected since manganese hydroxide crystallizes in the same lattice as that of brucite. The manganese hydroxide lines could not be detected because of its low concentration.

The EPR spectra of catalyst 3 having 1.35, 0.356, and 0.088% Mn each gave the six characteristic signals of divalent manganese. Representative curves of the catalyst and of the pure carrier IIA are shown in Fig. 4, curve II. Although it is known that Mn $(OH)_2$ rapidly turns to higher states of oxidation, the presence of the well-developed six peaks denotes that a percentage of manganese has been fixed in the solid in the divalent state. The well resolved signals indicate that magnetic interaction between Mn^{2+} ions are small and hence the Mn^{2+} are far apart.

Catalyst 4, using carrier IIA and IIC, gave also the six characteristic signals of Mn^{2+} (Fig. 4, III). The hyperfine structure and the small line-width show that the Mn^{2+} exists in an environment which differs from that of the coprecipitated samples, probably due to a higher concentration of Mn^{2+} at the surface resulting in a stronger Mn^{2+}–Mn^{2+} interaction. This is expected since the majority of the Mn^{2+} ions are precipitated mainly on the surface of the carrier, whereas the majority of Mn^{2+} ions in the coprecipitated samples went into the bulk.

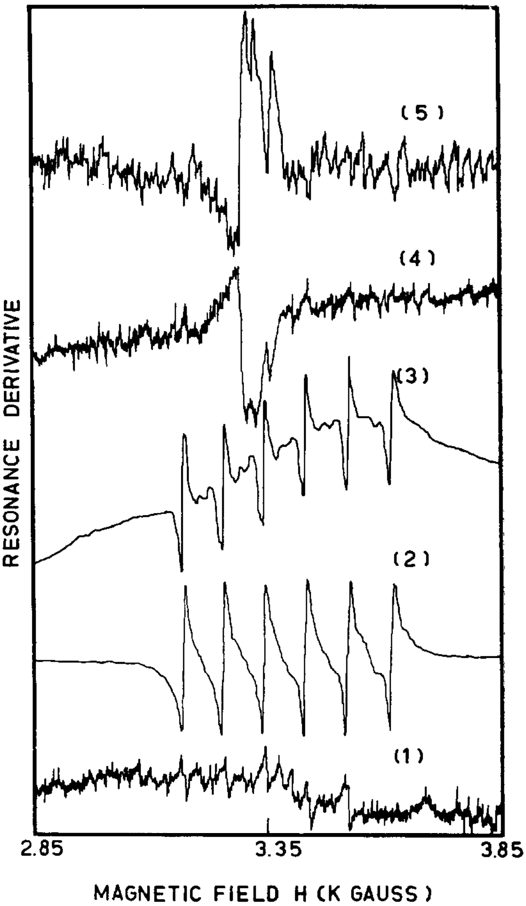


FIG. 4. EPR spectra: 1. $Mg(OH)_2$ precipitated by NaOH (carrier IIA). 2. 0.35% Mn-doped $Mg(OH)_2$ prepared by coprecipitation using NaOH; 3. 0.558% Mn-doped $Mg(OH)_2$ prepared by impregnation of carrier IIA; 4. $Mg(OH)_2$ precipitated by NH_4OH [carrier (IIB)]; 5. 0.558% Mn-doped $Mg(OH)_2$ prepared by impregnation of carrier IIB.

The spectrum of catalyst 4 using carrier IIB and the spectrum of the pure carrier are shown as curves 5 and 4, respectively.

These curves were recorded using a higher sensitivity than the previous ones to detect any trace of divalent manganese. The spectrum of the catalyst has somewhat similar shape to that of the carrier; both show a large peak at nearly the same *g* value, which probably indicates that the carrier contains defects. However, the most important feature is the absence of the six signals of Mn^{2+} ions. It is probable that the surface of the carrier has a higher alkalinity than the others due to the adsorbed NH_4^+ ions at its surface (see method of preparation), thus helping the precipitation of all the Mn^{2+} ions at the surface of the carrier, and that the precipitate was then oxidized to higher valencies with atmospheric oxygen. This interpretation is in agreement with the high rate of catalytic decomposition of H_2O_2 obtained with this system.

The EPR spectrum for a solution obtained by the action of 6% H_2O_2 over pure manganese hydroxides was also recorded. Figure 5 shows clearly six characteristic peaks of divalent manganese, especially in curve (b) using higher sensitivity.

Mechanism of Decomposition of H_2O_2

The results achieved in this work lead to the following conclusions:

1. $Mg(OH)_2$ alone is not catalytically active.
2. Neither the Mn^{2+} (aquo) ions nor the OH^- ions alone are responsible for the higher catalytic activity.
3. The role of pH is to give rise fundamentally to the formation of manganese hydroxides. The more these are formed the higher is the catalytic activity up to a maximum at about pH 9.
4. $Mg(OH)_2$ presents a favorable alkaline solid which plays a major role in the decomposition of H_2O_2 both by acting as a buffering source with sufficient supply of OH^- ions needed for the precipitation of manganese hydroxides and by offering a suitable surface at which the reaction proceeds more easily.
5. The precipitate of $Mn(OH)_2$ is adsorbed by $Mg(OH)_2$ solid used as a carrier imparting to the latter a buff, then brownish, color which indicates its oxidation to higher states. The catalytic activity in-

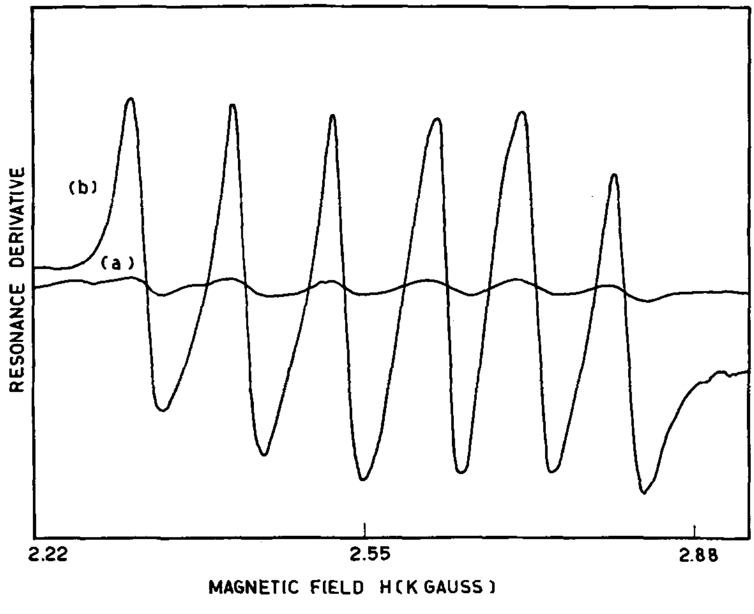


FIG. 5. EPR spectrum for a solution of manganese hydroxides (about 10 mg) in 200 ml of 6% H_2O_2 solution: (a) frequency modulation: 0.8, gain: 200; (b) frequency modulation: 8.0, gain: 400.

creases with the increase of the brown coloration.

Experiments have also shown that when an excess of H_2O_2 is added to a freshly precipitated $Mn(OH)_2$, or to a chemically pure hydrated MnO_2 (Prolabo), a vigorous reaction with effervescence of gaseous oxygen occurred with two noticeable changes: (a) the color of the $Mn(OH)_2$ precipitate turns from buff to dark brown; (b) the brown precipitate, as well as the pure sample of MnO_2, dissolves and the reaction subsides with the formation of a clear solution. It was of interest to notice that the reaction did not come to an end because of the complete decomposition of hydrogen peroxide, but due to the disappearance of the brown precipitate. The reaction could continue by (i) adding new amounts of the freshly precipitated manganese hydroxide, or hydrated MnO_2, or (ii) inducing alkalinity by the addition of few drops of dilute NaOH solution, and (iii) inducing alkalinity by the addition of solid $Mg(OH)_2$. In the latter case, the surface of $Mg(OH)_2$ is covered with a brown precipitate and the decomposition of H_2O_2 becomes vigorous and reaches completion.

This state of affairs suggests that the decomposition of H_2O_2 occurs in more than one way:

$$\text{(a)}\quad 2H_2O_2 + \underset{\text{(buff)}}{Mn(OH)_2} \rightarrow \underset{\text{unstable}}{[2Mn(OH)_3 + 2OH^-]} \rightarrow \underset{\text{(brown)}}{Mn_2O_3 \cdot 3H_2O} + \tfrac{1}{2}O_2 + H_2O$$

This reaction is responsible for the formation of the brown coloration at the beginning.

(b). H_2O_2 is known to have both oxidizing and reducing properties depending on the reagent with which it comes into contact. Strong oxidizing reagents will oxidize H_2O_2. It is probable that manganese hydroxides of valencies higher than two behave towards H_2O_2 in a similar way as the MnO_4^- ion.

$$H_2O_2 + 2Mn(OH)_3 \rightarrow 2Mn(OH)_2 + O_2 + 2H_2O$$
$$H_2O_2 + Mn(OH)_4 \rightarrow Mn(OH)_2 + O_2 + 2H_2O$$

When all the brown hydroxide has been consumed the reaction subsides.

The divalent manganese hydroxide formed has been prevented from precipitation by the formation of a soluble kind of complex in presence of an excess of H_2O_2.

To check the validity of the reduction of the mixed manganese hydroxides of valencies higher than two to the divalent state and their stabilization through complexation with H_2O_2, a freshly precipitated $Mn(OH)_2$ (obtained by the action of NaOH on $MnSO_4$ solution) was oxidized by a few drops of 6% H_2O_2. The buff precipitate immediately changed to brown, and the latter was washed thoroughly until it became free from SO_4^{2-} and OH^- ions. A few milligrams of the brown washed hydroxides were acted upon by the same solution of H_2O_2. A vigorous reaction took place and the brown precipitate dissolved to give a slight brown solution. When the gas evolution subsided, the EPR spectrum of the solution was recorded (Fig. 5). The graph shows clearly the six characteristic peaks of the divalent manganese in the solution, which proves that the brown hydroxides have been reduced to the divalent state and kept in solution by complexation with H_2O_2. The brown color of the solution might be due to a trivalent Mn–H_2O_2 complex; such a complex has already been reported in the literature (*25*). The percentage of divalent manganese peroxide complex and its stabilization increases with the increase in acidity. The latter was achieved by very dilute perchloric and acetic acid, both of which are known to have very weak complexing properties.

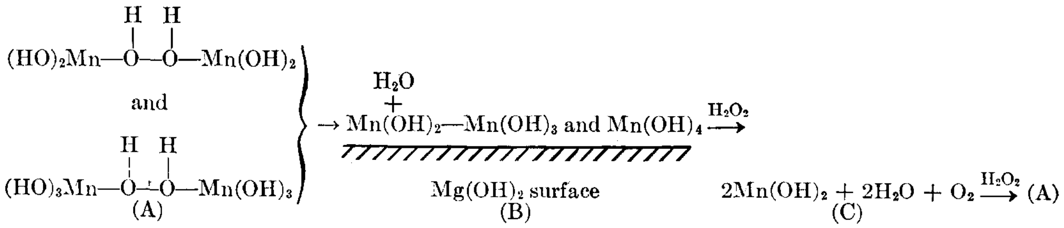
Mn(II) and Mn(III) peroxide complexes are of a low stability and are easily broken down by the addition of solid $Mg(OH)_2$; the latter by virtue of its alkalinity and adsorptive power will extract the manganese ions from their complexes.

The process repeats itself starting with step (a) till there is complete consumption of H_2O_2.

The oxidation process of $Mn(OH)_2$ precipitate is not as simple as represented in (a) but is rather complicated by the presence of dissolved oxygen in the aqueous media and by the evolution of nascent O_2 at the early stage of oxidation. Similarly the Mn^{III}(aquo) ion is not simply reduced by H_2O_2, as in step (b), since it is known that this ion even in the absence of a reducing agent is subject to disproportionation to give Mn^{2+} and MnO_2, the latter being a known catalyst for H_2O_2 decomposition.

The contribution of each process is difficult to establish. It is the ensemble of all processes which is responsible for the catalytic decomposition of H_2O_2. This probably explains why the reaction does not follow a simple order. The major part of the reaction is due to step (b) which suggests that the decomposition rate is a first order rate as considered by several authors. The rate determing step seems to depend on stability of the Mn–peroxide complexes.

The mechanism of decomposition can be schematically represented as follows:



$$\left.\begin{array}{c}(HO)_2Mn\text{—}\overset{H}{\underset{|}{O}}\text{—}\overset{H}{\underset{|}{O}}\text{—}Mn(OH)_2\\ \text{and}\\ (HO)_3Mn\text{—}\overset{H}{\underset{|}{O}}\text{—}\overset{H}{\underset{|}{O}}\text{—}Mn(OH)_3\\ \text{(A)}\end{array}\right\} \rightarrow \underset{\substack{Mg(OH)_2\ \text{surface}\\ \text{(B)}}}{\overset{H_2O\ +}{Mn(OH)_2\text{—}Mn(OH)_3\ \text{and}\ Mn(OH)_4}} \xrightarrow{H_2O_2} \underset{\text{(C)}}{2Mn(OH)_2 + 2H_2O + O_2} \xrightarrow{H_2O_2} \text{(A)}$$

The complexes have probably part (A) in their structures. The alkalinity and the strong adsorptive forces of $Mg(OH)_2$ surface extract the manganese from its complexes as represented in (B).

The brown hydroxides represented in (B) are reduced to give (C), which in the presence of an excess of H_2O_2 gives (A) again and the process proceeds until decomposition of hydrogen peroxide is complete.

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