Effect of pH and Temperature on the Catalytic Properties of Manganese dioxide

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Summary: Manganese dioxide was studied for its catalytic activity under different experimental conditions such as pH (3 -10) and temperature (30 -70°C). Decomposition of hydrogen peroxide is used as an indicator reaction for the catalyst. The kinetics of the reaction was analyzed by first order equation and rate constants were determined from the slopes of the straight lines. It was observed from the experimental results that the decomposition rate constant was found to be dependent on pH and temperature. The high rate constants at high pH values for the decomposition reaction demonstrated the fact that negative surface sites are responsible for the decomposition of hydrogen peroxide. The same trend in the percent decomposition of hydrogen peroxide was observed while using $NaNO_3$ as a background electrolyte. It was further noted that high temperature enhanced the catalytic activity of MnO_2. Activation energy for the decomposition reaction at different pH was estimated from the slope of Arrhenius plot.

Introduction

The production of most industrially important chemicals involves catalysis. Research into catalysis is a major field in applied science and involves many areas of chemistry, especially in materials science and organometallic chemistry. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced of waste generated (1). Many transition metals and transition metal oxides are used in catalysis (2-4). A catalyst provides an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has lower activation energy than the reaction route in the absence of the catalyst. It is found that about 90% of all commercially produced chemical products involve catalysts at some stage in the process of their production (5).

Most of the heavy metal oxides are used for their catalytic activity in various types of chemical reactions (6-9). It is found that the catalytic activity of these oxides is greatly affected by the surface and bulk properties of the metal oxides. Manganese oxide in pure form as well as in combination with other catalyst has been used for different catalytic reactions by many researchers (10-12). In order to study the catalytic activity of different catalysts, decomposition of H_2O_2 is used by different scientists and research workers as a well-liked indicator reaction (13-19) as the conversion of H_2O_2 to water and oxygen is strongly affected by the catalyst.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (1)$$

The hydrogen peroxide rapidly reacts according to reaction 1 upon the addition of a small quantity of manganese dioxide (20). This effect is readily seen by the effervescence of oxygen (21).

An effort has thus been made in the present research to investigate the effect of pH and temperature on the catalytic activity of commercial MnO_2 by using H_2O_2 decomposition as an indicator reaction. This piece of work consists of washing, characterization and catalytic activity of MnO_2 under different experimental conditions. The rate constants and activation energy are determined for the decomposition reaction of H_2O_2 on the surface of MnO_2.

Results and Discussion

Most of the researchers had found that the decomposition of H_2O_2 proceeds in accordance with the first order kinetics (22, 23). In order to investigate the effect of pH and temperature on the kinetics of catalytic decomposition of H_2O_2 on commercially available manganese dioxide from Merck and also to propose a mechanism for the catalytic reaction, decomposition of hydrogen peroxide on the surface of MnO_2 was carried out under different experimental conditions. The data was analyzed by applying first order kinetics and the rate constants were determined from the slopes of the straight lines.

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Characterization

The catalyst was examined for its surface morphology by Scanning Electron Microscope. The irregular shaped particles can be seen from the images at different magnifications in Fig. 1 and 2.

Fig. 1: Scanning electron micrograph of MnO_2 with 100,000 magnification.
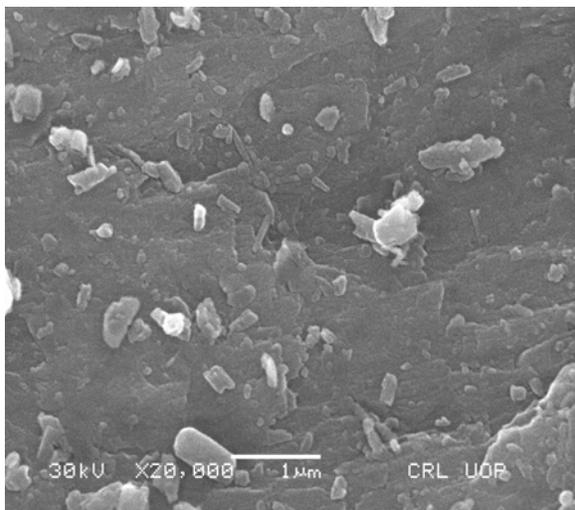
Fig. 2: Scanning electron micrograph of MnO_2 with 20,000 magnification.

The sample was analyzed by X- ray diffractometery and a typical XRD pattern obtained for the oxide is shown in Fig. 3. XRD analysis revealed that the solids used for the decomposition reaction was found to be manganese dioxide as reported elsewhere (24).
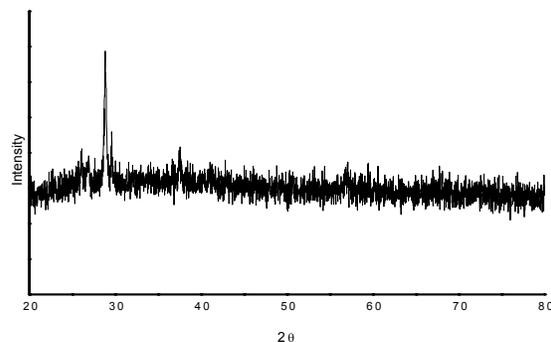
Fig. 3: XRD pattern of MnO_2.

The BET surface area determined in the presence of nitrogen atmosphere for manganese oxide catalyst ($6.5 m^2/g$) was comparable with that reported in literature for other commercial oxides (25)

Decomposition of Hydrogen Peroxide

Catalytic processes that involve transition metal ions, particularly manganese, lead to the decomposition of peroxide under alkaline conditions. Manganese dioxide is one of the more stable species among the different oxidation states of manganese. Therefore, the aim of the present study was to check the catalytic ability of commercial manganese dioxide and to investigate the pH and temperature for the best catalytic activity of this catalyst.

Effect of pH

The decomposition of H_2O_2 in the presence of 0.333g/L of MnO_2 catalyst was studied at pH 3, 5, 6.35, 8 and10 in aqueous solution at 30°C. The pH of the solution mixture was adjusted by dilute solutions of HCl and NH_4OH. The experimental data was plotted in the form of percent decomposition vs. time as shown in Fig. 4. It is clear from this figure that decomposition of hydrogen peroxide was measurable at the pH values higher than the PZC and increased with the increase in pH, whereas at the pH values less than PZC the decomposition was negligible. This suggested the fact that only the negative surface sites were catalytically active for the decomposition of hydrogen peroxide and the positive surface sites were passive (19). At the high pH values above PZC the surface carried high negative surface charge which caused enhanced decomposition. Thus on the basis of the above observation, it is assumed that the decomposition of hydrogen peroxide over the negative surface sites adopted the following mechanism (26).
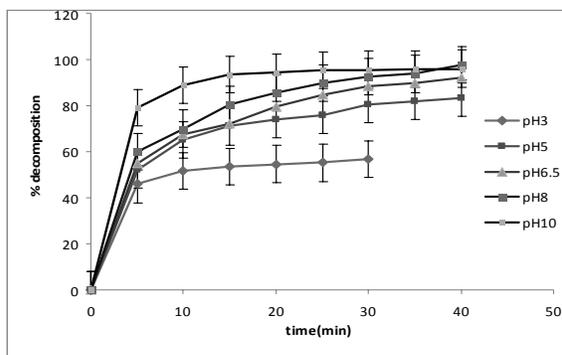
Fig. 4: Decomposition of hydrogen peroxide on MnO$_2$ as a function of time at different pH values in aqueous medium.

$$SO^- + H_2O_2 \rightarrow SO\text{-}H^+ + HO_2^- \qquad (2)$$

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \qquad (3)$$

$$SO\text{-}H^+ + OH^- \rightarrow SO^- + H_2O \quad (4)$$
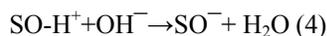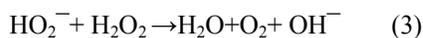
where, SO$^-$ represents the surface negative sites and SOH$^+$ represents the surface positive sites.

The net result of these reactions is the generation of oxygen, which was observed in the form of bubbles formation during the decomposition reaction. Furthermore no change in pH was observed during and after the reaction. Similarly, no changes were observed in the solid after the reaction, thus these two observations supported the above proposed mechanism.

The same trend was observed Fig. 5 when decomposition was carried out in the presence of 0.01 moldm^{-3} NaNO$_3$ as a background electrolyte. Most researchers had found that the decomposition of H$_2$O$_2$ proceeds through first order kinetics. In order to investigate the kinetics of the reaction, the present data was analyzed with first order kinetics in the same manners as those of earlier works (22, 23). The straight lines obtained from the relationship between log (a-x) vs. t (Fig. 6 and 7) reveal that the kinetics of the decomposition reaction on the surface of MnO$_2$ catalyst also follows first order behaviour. Furthermore, the rate constants observed in the electrolytic medium were slightly higher than that in the aqueous medium at the same pH values (Table-1). It may be due to the fact that oxides and hydroxides develop surface electrical charges by the protonation and deprotonation of the surface groups when immersed in aqueous electrolyte solution (27). Therefore, decomposition of H$_2$O$_2$ enhanced in the presence of NaNO$_3$ solution as compared to aqueous medium, it will be further investigated for other electrolytes with different concentrations.

Table-1: Rate constant K (min^{-1}) for the decomposition reaction of H$_2$O$_2$ at different pH and temperature.

pH	K (min^{-1}) aqueous Medium	K (min^{-1}) electrolytic Medium	Temperature ^{o}C	K (min^{-1}) aqueous Medium
3	0.009	0.011515	30	0.04935
5	0.02878	0.031	40	0.0511
6.5	0.038	0.04935	50	0.0575
8	0.051	0.057575	60	0.0657
10	0.058	0.0767	70	0.0767
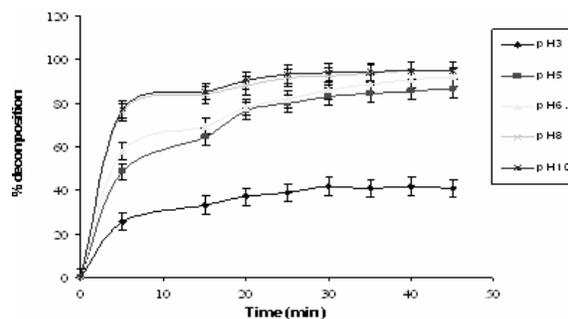
Fig. 5: Decomposition of hydrogen peroxide on MnO$_2$ as a function of time at different pH values in electrolytic medium.
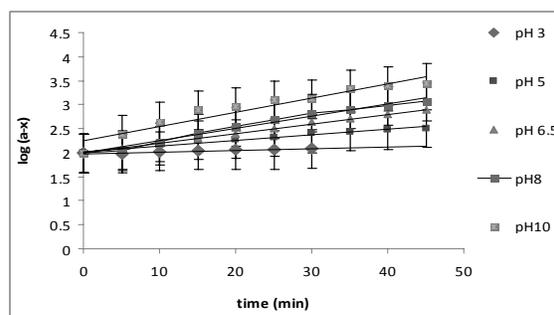
Fig. 6: log (a-x) versus time (t) for the decomposition of hydrogen peroxide on MnO$_2$ at different pH values in aqueous medium:
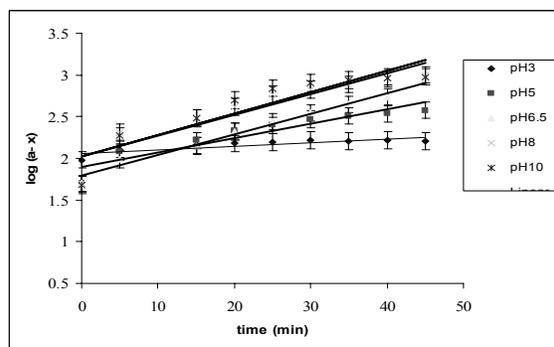
Fig. 7: log(a-x) versus time (t) for the decomposition of hydrogen peroxide on MnO$_2$ at different pH values in Electrolytic medium

Effect of Temperature

The influence of temperature on decomposition reaction was studied at 30, 40, 50, 60, and 70°C at pH 3, 5, 6.35, 8 and 10. It was found that the rate of decomposition of H_2O_2 at a given pH increased with the increase in temperature (Fig. 8) and the enhanced catalytic activity with temperature was also observed for other oxides in the literature (19). High temperature increase the surface negativity by decreasing the PZC value of the oxide (28) which could be held responsible for the decomposition of H_2O_2 reaction according to the proposed mechanism. The reaction obeys first order kinetics at these temperatures and the straight lines observed are given in Fig. 9. The rate constants for all the reactions were calculated from the slopes of the straight lines of Log (a-x) vs. t and are arranged in Table-1. It was further noted that the rate constant increased with the increase in temperature in accordance with the Arrhenius equation (Table-1). The energy of activation for H_2O_2 decomposition on the catalyst was determined from the slope of the Arrhenius plot of log k vs. 1/T in the temperature range of 30-70°C at different pH. The activation energies thus estimated are arranged in Table-2. The energy values reported in the study was comparable with the literature (23, 29-31) for the decomposition of the same reaction on the surfaces of different oxides. It is clear from the table that activation energy decreased with the increase in pH. The lower value of activation energy at high pH values in Table-2 demonstrated the fact that pH above PZC improved the catalytic activity due to increase in surface negativity of MnO_2 for the decomposition reaction of H_2O_2.

Table-2: Activation energy at different pH for decomposition of H_2O_2 on MnO_2.

S.NO	pH	Activation energy(kJ/ mol)
1	3	20.31
2	5	9.50
3	6.5	8.26
4	8	7.15
5	10	6.01
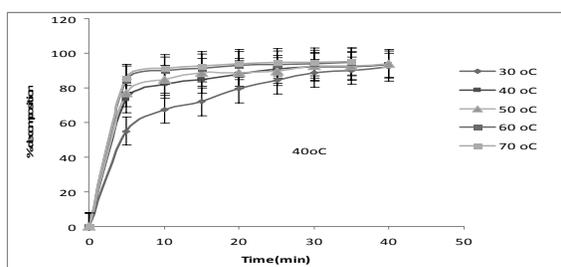
Fig. 8: Decomposition of hydrogen peroxide on MnO2 as a function of time at different temperatures in aqueous medium

Experimental

Reagents Used

The reagents used in this study were of analytical grades. The solutions were made in doubly distilled water. The commercial solid catalyst, MnO_2, was obtained from Merck.
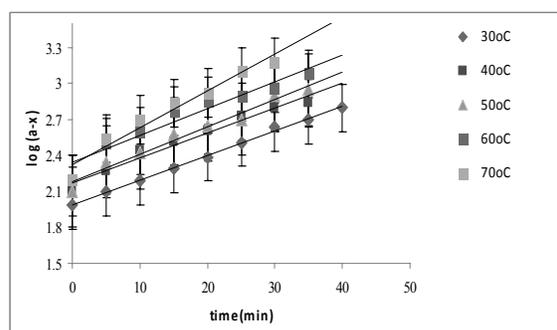
Fig. 9: Log (a-x) versus time (t) for the decomposition of hydrogen peroxide on MnO_2 at different temperatures in aqueous medium.

Washing of MnO_2 Sample

Commercially available MnO_2 obtained from Merck was washed with doubly distilled water and $0.1mol\ dm^{-3}$ NaOH solution to refresh the active surface sites of the sample. The solid sample of MnO_2 was dispersed in doubly distilled water and was kept for nearly 48 hours with continuous stirring using Teflon coated magnetic bar. The suspension was then filtered and the solid obtained was redispersed in $0.1mol\ dm^{-3}$ NaOH solution for 24 hours. It was then filtered and dried in desiccators. The washed sample was then used for further study.

Characterization

The bulk nature of the sample was characterized by X-ray diffractometery, (XRD, JEOL, JDX-7E) with Cu-K radiation. The surface morphology of the sample was checked from the images by scanning electron microscope model-JEOL, JSM-5910.

The role played by surface area measurements of a catalyst in the field of surface chemistry and catalysis is very important. The surface area of the catalyst was determined by nitrogen adsorption at 77.4 K; using Quanta Chrom NOVA 2200c, USA. Prior to adsorption measurements, respective catalyst was degassed at

373 K for a period of 1 hour in nitrogen atmosphere. The BET surface area of the sample was determined by nitrogen adsorption in the range of P/Po ≈0.15

Decomposition of H_2O_2

The decomposition of hydrogen peroxide was studied in the presence of MnO_2 at different temperatures and pH. As H_2O_2 is sensitive to light therefore, all the experiments were performed in the absence of light by wrapping the black paper around the vessels to minimize the error. The method applied was the same as reported in the literature (19). The amount of solid catalyst used in each experiment was 0.333 g/L. The concentration of H_2O_2 was adjusted to 0.02mol dm^{-3} in all cases. The pH of the mixture was set to the desired value by using dilute solutions of HCl or, NH_4OH. Temperature of the vessel was adjusted by circulating water through the doubled walled jacket of a thermostated water bath. The content of the vessel was stirred uniformly by means of a magnetic stirrer using Teflon coated magnetic bar. After an interval of 5 min about 5ml of the reaction mixture was withdrawn from the double walled vessel and was rapidly added to 5ml of ice cooled 5mol dm^{-3} H_2SO_4 solutions. The solid was separated from a mixture by centrifugation, and the centrifugate was then titrated against 0.002mol dm^{-3} $KMnO_4$ solution. From this, the amount of the decomposed H_2O_2 was estimated. In all cases blank experiments were also performed in the absence of the solid in order to investigate the effect, if any of the experimental conditions on the decomposition of H_2O_2. The schematic of the experimental setup is shown in Fig. 10 [32-34].
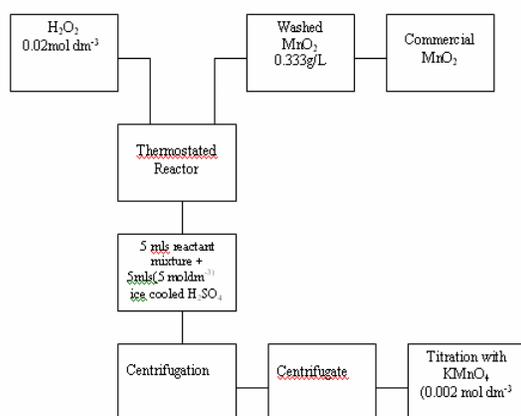
Fig. 10: Schematics of experimental setup.

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