

## Decomposition of Hydrogen Peroxide by Nickel Oxide Powders

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**Summary:** The decomposition of hydrogen peroxide was studied in the presence of monodispersed nickel oxide powders, obtained from the nickel basic carbonate at the calcinations rates of 5, 10, 15, and 20 °C/min and on commercial nickel oxide powders. Effect of pH on the decomposition reaction was used to evaluate the mechanism of the decomposition reaction. It was observed that only the surface negative sites were responsible for the observed decomposition of hydrogen peroxide. Rates constants were calculated for the decomposition reaction in the temperature range of 35-50 °C and the activation energies were estimated from the Arrhenius plots for all the synthetic and commercial samples of nickel oxides.

### Introduction

It is generally agreed that most of the metal oxides act as catalysts in the variety of chemical processes [1-5]. However, the bulk and surface properties of these oxides have a significant effect on their catalytic properties. To get information about the catalytic activity of the catalyst, decomposition reactions of hydrogen peroxide have been used as a popular indicator [6-12]. An attempt has thus been made in this investigation to evaluate the catalytic properties of the synthetic nickel oxides by using decomposition reaction of hydrogen peroxide as the indicator.

This study describes the preparation, characterization and catalytic properties of uniform nickel oxide powders. The rate constants and the activation energies have been determined for the decomposition reaction of hydrogen peroxide on commercial as well as nickel oxide powders, prepared in this study.

### Results and Discussion

#### *Characterization*

XRD analysis revealed that the solids obtained from the calcination of nickel basic carbonate (SEM, Fig. 1) at different calcinations rates were found to be nickel oxide [NiO]. All the calcined samples had identical XRD patterns. Fig. 2 demonstrates a typical XRD pattern obtained with nickel oxide, produced at the calcinations rate of 20 °C/min. The nickel oxide powders obtained at the calcinations rates of 5, 10, 15, and 20 °C/min was

designated as S1, S2, S3, and S4, respectively in the text. Values of the point of zero charge of all the synthetic and commercial samples were in the pH range of 3.0-3.3. pH had no effect on their solubility in aqueous solutions.

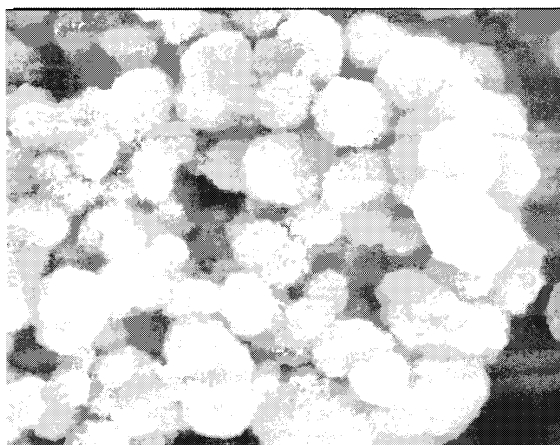


Fig. 1: Scanning electron micrograph [SEM] of nickel basic carbonate particles.

#### *Decomposition of Hydrogen Peroxide*

In order to test the catalytic properties of the nickel oxide powders, an attempt was made in this investigation to study the decomposition of hydrogen peroxide in aqueous solutions in the presence of this solid under different experimental conditions, described below.

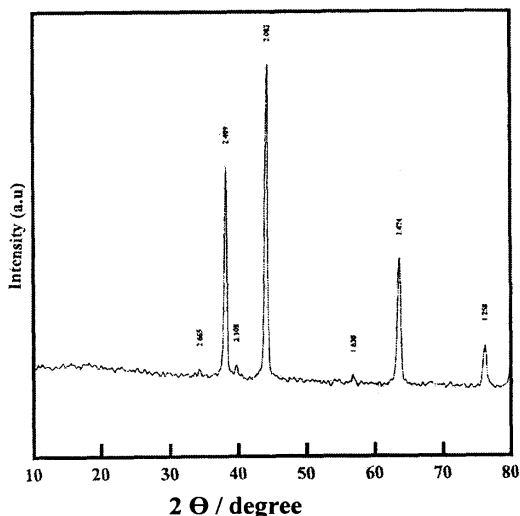


Fig. 2: X-ray diffraction [XRD] pattern of the NiO particles obtained from particles shown in Fig. 1.

#### Effect of pH

The decomposition of hydrogen peroxide was studied at the pH value of 10.77, 6.87, 5.12, and 3.07 in the presence and absence of S1, at 30 °C using HCl, HNO<sub>3</sub>, KOH, NaOH, and NH<sub>4</sub>OH solutions for adjusting pH of the reaction mixtures. It was observed that NaOH and KOH had a significant effect on the decomposition reaction of hydrogen peroxide in the absence of nickel oxide. Therefore, only either of the latter acids, and NH<sub>4</sub>OH was used for pH adjustment of the reaction mixture in the further study.

Fig. 3 shows the percent decomposition versus time curves for hydrogen peroxide at different pH values in the presence of nickel oxide sample (S1). It is clear from this figure that at the pH values, higher than the PZC, decomposition of hydrogen peroxide was measurable and increased with the increase in pH, whereas at the pH values less than PZC the decomposition was negligible. This suggested the fact that the positive surface sites were passive and only the negative surface sites were catalytically active for the decomposition of hydrogen peroxide. At the high pH values the surface carried high negative charge which caused enhanced decomposition. Thus on the basis of the above

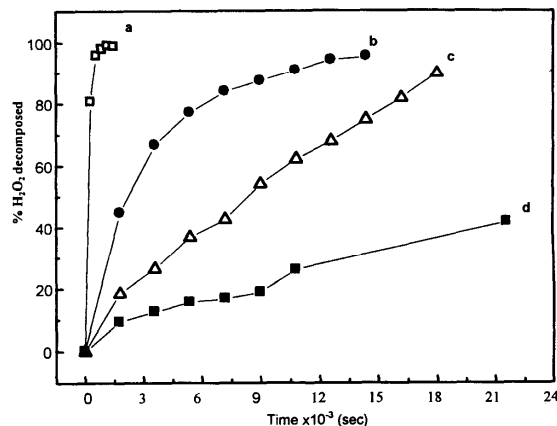
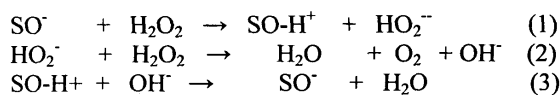


Fig. 3: Decomposition of hydrogen peroxide on nickel oxide (S1) as a function of time at different pH values: (a) 10.77: (b) 6.87 (c) 5.12 (d) 3.07.

observation, it was assumed that the decomposition of hydrogen peroxide on the negative sites proceeded through the following mechanism [9]:



where SO<sup>-</sup> represent the surface negative sites.

The net result of these reactions is the generation of oxygen, which was observed experimentally in the form of bubbles formation during the decomposition reaction. Furthermore, no change in the pH of the medium was observed during and after the decomposition reaction, which agreed well with the above mentioned proposed mechanism. Moreover, to see the activity of the regenerated negative sites *i.e.* SO<sup>-</sup>, the same solid was redispersed in hydrogen peroxide solution and the decomposition reaction was monitored under the same experimental conditions. It was observed that the solid was equally active and decomposed hydrogen peroxide to the same extent. Thus these observations supported the mechanism of decomposition reaction, described above.

The rate of decomposition of hydrogen peroxide, as estimated from the data of Fig. 3, indicated that the first order rate equation holds good in all cases, as linear plots were obtained by plotting log (a/a-x) versus time (Fig. 4). The rate constants

thus estimated at different pH values are given in Table-1.

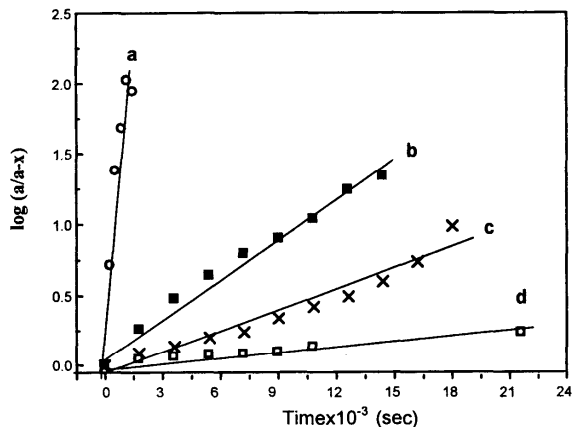


Fig. 4: Plots of  $\log(a/a-x)$  versus time (t) for the decomposition of hydrogen peroxide on nickel oxide (S1) at different pH values: (a) 10.77: (b) 6.87: (c) 5.12: (d) 3.07.

Table-1:

S. No	pH	Rate const. / $k \times 10^4$ ( $\text{sec}^{-1}$ )
1.	3.07	0.228
2.	5.12	0.998
3.	6.87	5.072
4.	10.77	38.449

As can be seen, the value of the rate constant increased with the increase in pH of the reaction medium, which may be attributed to the high negative surface charge at the high pH values.

*Effect of Calcinations Rate*

As mentioned in the experimental section, the precursors of the NiO powder was calcined at 700 °C for 1h at the heating rates of 5, 10, 15, and 20 °C/min in order to see the effect if any on the catalytic properties of NiO batches, S1, S2, S3, and S4, respectively. Decomposition data of hydrogen peroxide on these solids was recorded as a function of time in the temperature 308-323K and at the pH 6.87. In all cases, the data fitted the first order rate law and the rate constants thus calculated from the plots of  $\log(a/a-x)$  versus time are illustrated in Fig. 5. As can be seen from Fig. 5, at all the temperatures, effect of calcinations rate of the solid on the extent of decomposition was small in the range 5-15 °C/min. However, the nickel oxide powder

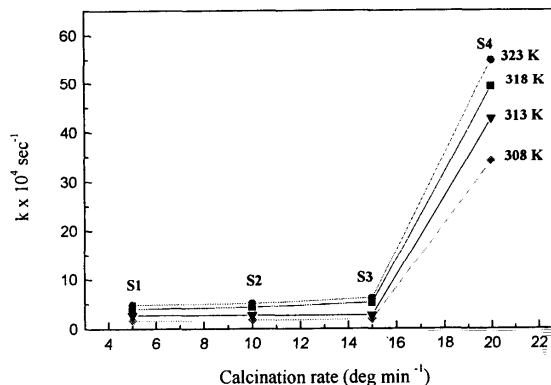


Fig. 5: Variation in rate constants (k) for the decomposition of hydrogen peroxide on nickel oxide samples (S1, S2, S3 and S4) at different temperatures *i.e.*, 308 K, 313K, 318K and 323K.

prepared from the precursor powder at the calcinations rate of 20 °C/min, S4, showed enhanced catalytic activity at all the temperatures. This may be attributed to the fact that calcinations of nickel basic carbonate at the rate of 20° C/min resulted solid having large number of negative surface sites (Fig. 6) most probably due to smaller particles (SEM, Fig. 7) which could be held responsible for the enhanced catalytic activity of this solid.

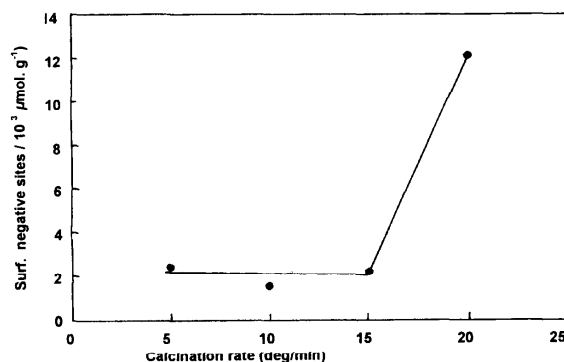


Fig. 6: Negative surface sites for the nickel oxide samples, S1, S2, S3, and S4, obtained at different calcinations rates.

Furthermore, activation energies of the decomposition reaction were calculated from the Arrhenius plot (Fig. 8) and are summarized in

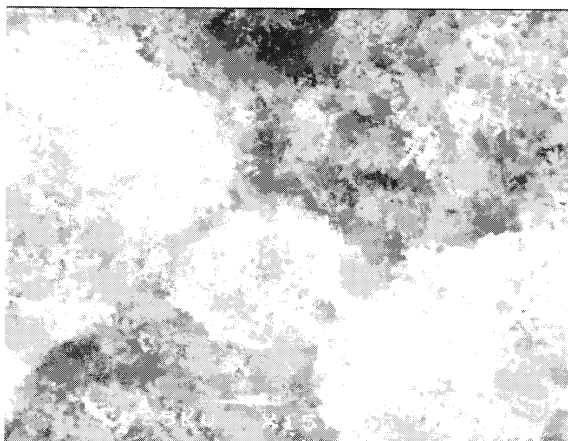


Fig. 7: Scanning Electron Micrograph (SEM) of the particles obtained, when the particles shown in Fig. 1 was calcined (S4) at the heating rate of 20 °C/min.

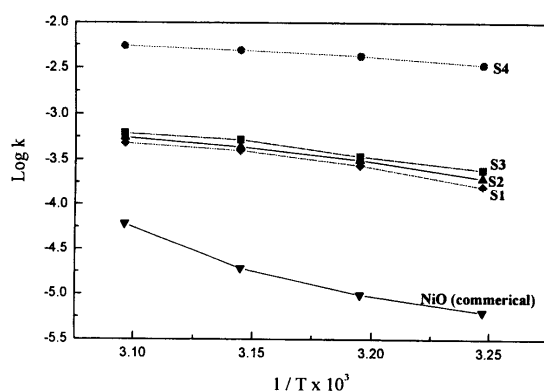


Fig. 8: Arrhenius plots showing log k Vs 1 / T for S1, S2, S3, S4 and NiO commercial.

Table-2:

Samples	Activation energy (J mol <sup>-1</sup> .)
S1	63.759
S2	47.867
S3	38.294
S4	31.784
NiO(commercial)	95.735

Table-2 for the nickel oxide powders obtained from the nickel basic carbonate at the calcinations rate of 5, 10, 15, and 20 °C/min, respectively.

Similarly, for comparison purposes, decomposition of hydrogen peroxide was measured also on commercial nickel oxide under the same

experimental conditions, as adopted for the synthetic nickel oxide samples, mentioned above. The activation energy of the decomposition reaction on this sample was found to be 95.735 J mol<sup>-1</sup> as given in table 2 which was high as compare to all the samples of nickel oxide, prepared in this study.

## Experimental

### Reagents

All the reagents used were of analytical grades. Doubly distilled water was used for making all solutions. Commercial nickel oxide powder was obtained from Merck.

### Preparation and Characterization of Nickel Oxide

Precursors of the nickel oxide powder, *i.e.*, nickel basic carbonate was prepared by the method described [13]. Following this method, a solution which was 0.026 mol. dm<sup>-3</sup> in nickel (II) sulfate and 0.4 mol. dm<sup>-3</sup> in urea was aged in a glass stoppered pyrex glass vessel at 85 °C for 5h. The solid obtained at the end of the aging period was calcined at 700 °C for 1 h at the calcinations rates of 5, 10, 15, and 20 °C/min in a furnace (Nabertherm M7/11. with program controller C19) in a static air atmosphere for conversion into nickel oxide powder. The composition of the calcined samples was confirmed by X-ray diffractometry (XRD, JEOL, JDX-7E) with Cu-K radiation. Similarly, IR spectra of the samples were recorded by using Perkin Elmer, 16PC, FT-IR, whenever required.

### Determination of Surface Negative Site

Suspension, containing 0.03 g of the desired sample of nickel oxide in 50 cm<sup>3</sup> of 0.01 mol. dm<sup>-3</sup> of HNO<sub>3</sub> was allowed to stay for 48 h with occasional stirring after which time the suspension was filtered and the filtrate was analyzed for the remaining acid. The amount of acid taken up by the sample was then estimated from the difference between the initial and final concentration of the solid.

### Determination of Point of Zero Charge

Values of the point of zero charge of the nickel oxide samples were evaluated by the salt addition method [13]. Following this method, 0.5g of the desired sample of nickel oxide was transferred to

500 cm<sup>3</sup> volumetric flask containing small volume of 0.01 mol. dm<sup>-3</sup> NaNO<sub>3</sub> solution. The volume of the suspension was made up to the mark with NaNO<sub>3</sub> solution of the same concentration. The flask was put in an ultrasonic bath for 30 min for the uniform dispersion of the solid in the suspension. The suspension was allowed to equilibrate for 24 h with occasional stirring. At the end of the equilibration period, 50 cm<sup>3</sup> aliquotes were withdrawn from the stirred suspension, transferred them to 100 cm<sup>3</sup> titration flasks, and adjusted to various pH values with 1.0 mol. dm<sup>-3</sup> NaOH or HNO<sub>3</sub> solutions. After 30 min of equilibration, pH of these suspensions were noted as initial pH values, and then 1 g of NaNO<sub>3</sub> was added to each suspension and stirred them for additional 30 min. pH of these suspensions were then measured as the final pH values. All the pH measurements were made with Orion Model 900A pH meter, equipped with a combination glass electrode.

#### Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide in the presence of the nickel oxide powders was studied at different temperatures and pH. In each experiment, 0.0206 g of the solid catalyst was transferred to 100 ml double-walled glass vessel, containing 60 ml of 0.002 mol. dm<sup>-3</sup> solution of hydrogen peroxide, adjusted to the desired value of the pH with 0.1 M solution of HCl or HNO<sub>3</sub>, NaOH, or NH<sub>4</sub>OH. Temperature of the vessel was adjusted to the desired temperature by circulating water through the double 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 suitable interval of times, a known amount of the reaction mixture was withdrawn from the double-walled vessel and was rapidly added to 5 cm<sup>3</sup>

of ice cooled 5 mol. dm<sup>-3</sup> sulfuric acid solutions. The solid was separated from a mixture by centrifugation, and the centrifugate was then titrated against 0.02 mol. dm<sup>-3</sup> KMnO<sub>4</sub> solutions. From this the amount of the decomposed hydrogen peroxide was estimated. In all cases, blanks experiments were also performed in the absence of the solid in order to evaluate the effect, if any, of the experimental conditions on the decomposition of hydrogen peroxide.

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