September, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2181—2185 (1974)

Linear Free Energy Relationships in Heterogeneous Catalysis. XII.[1] Interpretation of the Catalytic Activity of Decomposition of Hydrogen Peroxide over Nickel Oxide on the Basis of Oxidation Power Distribution

Toshio Uchijima and Yukio Yoneda

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113

(Received November 10, 1972)

Kinetic studies have been carried out on the heterogeneous decomposition of hydrogen peroxide over several nickel oxide catalysts calcined at different temperatures. Kinetic parameters such as reaction order and apparent activation energy depend somewhat on the reaction conditions, but show practically no change with catalyst. The catalytic activity changes with calcination temperature, becoming minimum at 550 °C and maximum at 600 °C. The trend does not change with pretreatment of the catalyst, resembling the behavior of surface excess oxygen having a relatively higher oxidation power. Thus the distribution of oxidation power is closely related to catalytic activity for the decomposition of hydrogen peroxide. We therefore applied the regional analysis assuming that the surface excess oxygen represents active sites for catalysis, and a specific regional activity corresponds to each regional oxygen. It was found that the fifth region (the range of free energy change of adsorption of oxygen being from -11.1 to -12.6 kcal/mol) markedly contributes to the reaction rate, and the calculated rates agree with the observed ones. The nature of the active site was discussed as regards pretreatment of the catalyst.

Of the reactions studied extensively on various catalytic materials including heterogeneous and homogeneous systems,[2] the catalytic decomposition of hydrogen peroxide is one of the most typical. Investigations were carried out with several metal oxide catalysts, aimed at understanding the catalysis on the basis of semiconductive properties,[3] activity order,[4] and the correlation between catalytic activities and the amounts of excess oxygen.[5,6] The amounts of excess oxygen are valuable for account for the catalytic activities of pure or doped, supported or unsupported chromium oxides[5] and the γ-irradiated nickel oxides.[6] Such correlation is reasonable in this reaction, since hydrogen peroxide acts as a reducing reagent as well as an oxidizing one.

A large number of metal oxides have more or less heterogeneous surfaces, certain parts of which contribute to catalysis as active sites. We developed a method to determine the distribution of oxidation power on the oxide surfaces, and applied it to a series of nickel oxide catalysts.[7] In the present study, we measured the catalytic activities for hydrogen peroxide decomposition in an aqueous solution under various reaction conditions using the same lots of nickel oxide catalysts. We found that they possess a similar pattern against the calcination temperature as in the surface excess oxygen of relatively higher oxidation power. This suggests that the distribution of oxidation power is closely related to catalytic activity for the decomposition of hydrogen peroxide. Regarding the regional surface excess oxygen as an active site having a specific activity characteristic of the respective region, the catalytic activities were analyzed by the regional analysis method[8] to estimate the most effective region for catalysis. The nature of the active site was discussed in reference to the fact that pretreatment such as reduction or oxidation affects the catalytic activities, giving rise to deactivation during the course of catalysis.

Experimental

Catalysts and Reagents. The same lots of catalysts as described previously,[7] *i.e.*, a series of pure nickel oxide and Li_2O-doped catalysts, were used. The oxidation power distribution of these oxides has been determined by the aqueous reduction method using hydrazine and KI(pH x) systems.[7] 30% hydrogen peroxide containing no stabilizer (Mitsubishi-Edogawa Co., Ltd.) was used. All the other reagents were commerical products of G.R. grade.

Procedures. The reaction rates of hydrogen peroxide decomposition were determined by following the pressure changes due to oxygen gas evolved, with a conventional reactor of constant volume (about 150 ml). The hydrogen peroxide solution (50 ml) was introduced into the reactor containing a weighed amount of catalyst at a constant temperature (within ± 0.2 °C). The speed of stirring was chosen so as to provide a state in which true reaction rate was obtained but not the diffusion-controlled one. The reaction was carried out at temperatures 10—50 °C and concentrations 0.1—10 mol/l H_2O_2. In some cases, pure hydrogen peroxide solution was used without any additives, and in other cases, the solution buffered with potassium hydroxide or sodium tetraborate solution in the pH range 6—11.5.

When necessary, the catalysts were pretreated *in vacuo* or in oxygen gas of 1 atm at 300 °C in the reactor, and their effects on catalytic activities were examined.

Results

Reaction Order. The reaction curves can be analyzed on the basis of a certain reaction order except for their initial unsteady parts. The reaction orders for hydrogen peroxide were also obtained by varying its initial concentration. These values depend largely on the type of solution (additives or pH) and the conditions of pretreatment whereas they are mostly constant among the catalysts except for a few cases. The mean values of reaction order are given in Table 1. For

Table 1. Reaction orders of decomposition of hydrogen peroxide under various conditions (30°C)

Reaction orders were obtained from analysis of the reaction curves (method 1) and also by varying the initial concentration of hydrogen peroxide (method 2).

Catalyst pretreatment	Solution	Reaction order[a)]	
		Method 1	Method 2
Untreated	No additives	0.4	0.4[b)]
Untreated	0.1 N KOH	0.6	—
Untreated	0.005 N $Na_2B_4O_7$	0.6	0.6[c)]
Evacuated at 300°C	No additives	0.1[d)]	—

a) Unless otherwise stated, the mean values are listed since variation among catalysts is relatively small. b) Ni-2-350-8. c) Ni-2-500-8. d) For Ni-2-600-8 and Ni-2-700-8 only, the reaction follows the order of 0.5 during the first run but gives the value of 0.1 after the second run.

example, the values of the untreated catalysts are 0.57—0.62 in a solution buffered with 0.005 mol/l sodium tetraborate. The only exception is the case of the first run on Ni-2-600-8 and Ni-2-700-8, subjected previously to evacuation at 300 °C, which yield much higher values than the others. The cause of this anomaly is not clear.

Table 1 also shows good agreement between the values obtained by the two independent methods. The kinetic curve would accompany the effect due to the changes of pH and the deactivation of catalysts during reaction. Both effects may compensate each other, yielding the agreement.

The reaction orders are reasonably lower than unity in all the cases and the reduced state is accompanied by the much lower order as compared with the oxidized one.

Dependency on pH. The decomposition rate of hydrogen peroxide varies with pH, where pH was controlled with potassium hydroxide or sodium tetraborate–potassium hydroxide solution. The additives affect the reaction rate not only through the pH changes but also through other effects possibly due to complex formation. In 1 mol/l H_2O_2 solution, addition of 10^{-5} M potassium hydroxide retards the rate slightly, while a remarkable accelerating effect is found above 10^{-4} M. A satisfactory linear relationship exists between log(rate) and log(H^+) in the concentration range 10^{-4}—10^{-1} M potassium hydroxide, yielding a value of -0.17 as the order with respect to (H^+). Similarly, pH was changed from 8.7 to 9.5 by the addition of potassium hydroxide to the solution buffered with sodium tetraborate of constant concentration. Analysis of the results gives a value of -0.31. Retardation of the reaction by hydrogen ion is in line with the well-examined case in homogeneous metal ion-catalyzed systems.[2)]

A comparison of the system containing potassium hydroxide as an additive with that containing sodium tetraborate and potassium hydroxide each with the same pH shows that the rate of the latter is much lower. This suggests that the added ion blocks the active sites according to its coordination tendency.

Table 2. Variation of catalytic activity due to various pretreatments of catalyst

Catalyst; Ni-2-350-8. Temperature; 30°C. Solution; 1 mol/l H_2O_2 solution

Pretreatment	Initial rate (10^{-2} mol/min·g)
Untreated	0.83
Evacuated at 200°C for 1 hr	2.23
Evacuated at 300°C for 1 hr	3.04
Treated with oxygen of 600 mmHg at 300°C for 14 hr after evacuation at 300°C for 9 hr.	0.61

Pretreatment Effects and Deactivation during Catalysis. Variation of catalytic activity due to pretreatment such as evacuation and oxidation at high temperature, which is comparable with the case of untreated catalysts, is shown in Table 2. The catalytic activity is largely enhanced after evacuation at high temperature. By oxidation of the evacuated catalyst in one atmospheric oxygen at 300 °C, the activity decreases to a level slightly lower than that of the untreated catalyst.

After the first run was completed on the catalyst evacuated at 300 °C using an unbuffered 1 mol/l H_2O_2 solution, 5 ml of 10 mol/l H_2O_2 solution was added and the reaction was then repeated under the same conditions. The variation of catalytic activity during these repeated runs is presented in Fig. 1. The activity declines gradually with each run and approaches a certain level which is approximated to the value of the fully oxidized catalyst. This might help clarify the nature of active sites.

Effects of Catalyst Variations. Catalyst activity, plotted against calcination temperature (a) and the amount of the doped lithium (b), is shown in Fig. 2. The results are obtained on the untreated catalysts using a 1 mol/l H_2O_2 solution with no additives at 25 °C. The curves show a complex dependency on

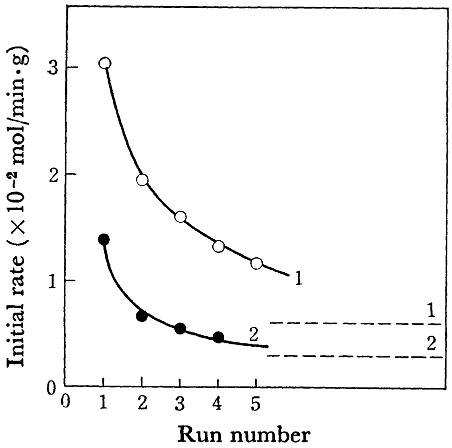

Fig. 1. Deterioration of the catalytic activities during repeated runs

The catalysts are pretreated at 300 °C *in vacuo* for 1 hr. Dotted lines show the rates over the fully oxidized catalysts.

Solution; 1.0 mol/l H_2O_2, Temperature; 30 °C, 1; Ni-2-350-8, 2; Ni-2-450-8

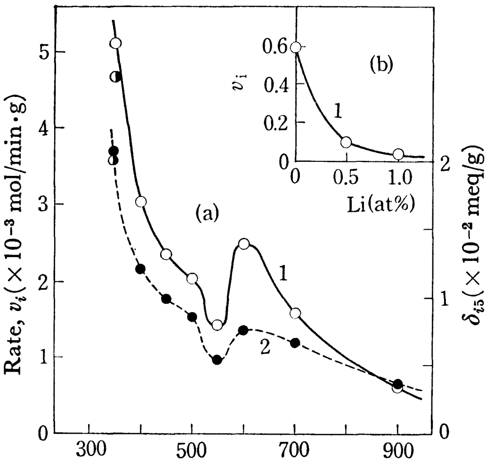

Fig. 2. Dependency of the catalytic activity on the calcination temperature (a) and the lithium content (b) of nickel oxide
Solution; 1.0 mol/l H_2O_2, Reaction temperature; 25 °C
Curve 1 shows the reaction rate, v_i, and curve 2 the amount of the surface excess oxygen of the fifth region, δ_{i5}. The values of the catalyst calcined for 16 hr are marked as ◑.

the calcination temperature characterized by a minimum at 550 °C and a maximum at 600 °C. As the lithium content is increased, the activity decreases monotonously. This is in line with the case of surface excess oxygen with relatively higher oxidation power, *e.g.*, the regional oxygen given as a difference between the ones measured by the KI (pH 10.8) and KI (pH 11.3) methods, which is also plotted in Fig. 2. Similar curves were obtained for both calcination temperature and lithium content under other reaction conditions such as in a buffered or unbuffered solution on the pretreated or untreated catalysts. The absolute values differ largely according to the reaction conditions.

The activation energies are obtained on several catalysts using a solution buffered with sodium tetraborate at temperatures 30—50 °C. The results are summarized in Table 3. The catalyst variations do not seem to affect activation energy, addition of lithium oxide having little effect.

TABLE 3. APPARENT ACTIVATION ENERGIES FOR DECOMPOSITION OF HYDROGEN PEROXIDE OVER SOME NICKEL OXIDES

Solution; 0.1 mol/l H_2O_2, 0.005 mol/l $Na_2B_4O_7$.

Catalyst	Activation energy (kcal/mol)
Ni-2-350-8	17.2
Ni-2-500-8	17.5
Ni-2-600-8	16.8
Ni-2-900-8	16.8
Ni-2-Li-0.5-900-8	16.1

Discussion

In order to account for the catalytic activity of metal oxides for oxidation catalysis, a number of parameters such as dissociation pressure of oxide,[9] enthalpy change of formation of oxide,[10] homomolecular isotope exchange of oxygen,[11] reducibility of oxide[12] and excess oxygen[5,6] have been extensively examined. The surface of most metal oxides has been generally accepted to be of more or less heterogeneous distribution. In oxidation catalysis, however, such heterogeneity has not been introduced explicitly into quantitative analysis of catalytic activity except for a few studies.[9] The distribution of oxidation power represents the amount[7] of surface excess oxygen as a function of its oxidation power, which can be determined on the basis of oxidation-reduction equilibrium with a certain reducing reagent in an aqueous phase. It is interesting to examine whether catalytic activity can be accounted for by this oxidation power distribution, and if so to what extent.

As shown in Fig. 2, the catalytic activity of nickel oxide catalysts for the decomposition of hydrogen peroxide shows a complex curve against calcination temperature, and a monotonously decreasing curve against lithium oxide content. Since these relations are very similar to the behaviors in the surface excess oxygen of relatively higher oxidation power, the distribution of oxidation power is closely related to the catalytic activity for the decomposition of hydrogen peroxide. The regional analysis method[8] was applied assuming that the surface excess oxygen of oxides represents their active site for catalysis and a specific regional activity corresponds to each regional oxygen. The catalytic activity of the *i*-th catalyst, v_i (mol/min·g), can be represented by

$$v_i = \sum_j v_{0j} \times \delta_{ij} \tag{1}$$

where v_{0j} (mol/min·meq) denotes the specific activity characteristic of surface excess oxygen of the *j*-th region (suffix 0 indicates its independency of the type of catalyst) and δ_{ij} (meq/g) the amount of surface excess oxygen of the *j*-th region of the *i*-th catalyst. Surface excess oxygen over these catalysts has been classified experimentally into six regions.[7] Each region is defined by the free energy change of adsorption of oxygen (ΔG) as follows.

Region 1; $-\Delta G$=141.5—29.9 kcal/mol.
Region 2; $-\Delta G$= 29.9—19.8 〃
Region 3; $-\Delta G$= 19.8—14.6 〃
Region 4; $-\Delta G$= 14.6—12.6 〃
Region 5; $-\Delta G$= 12.6—11.1 〃
Region 6; $-\Delta G$ <11.1 〃

For the lithium-doped nickel oxides, the fifth and sixth regions could not be determined separately and had to be excluded. Since Eq. (1) holds, consequently, over nine kinds of the pure nickel oxide catalysts, a set of probable values of v_{0j} corresponding to six regions can be estimated by means of the method of least squares. However, the degree of freedom for analysis is too small and the treatment provides too erroneous results. Thus, regional analysis is applied to all the possible combinations from two to five regions combining some

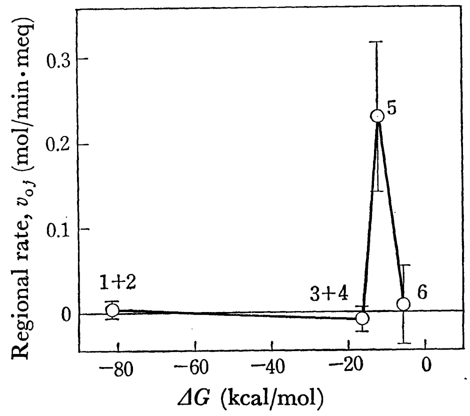

Fig. 3. Correlation between the regional rate calculated by Eq. (1) and the mean free energy change of the respective region.
Numerals in the Figure mean the numbers of regions. The range of errors is also shown.

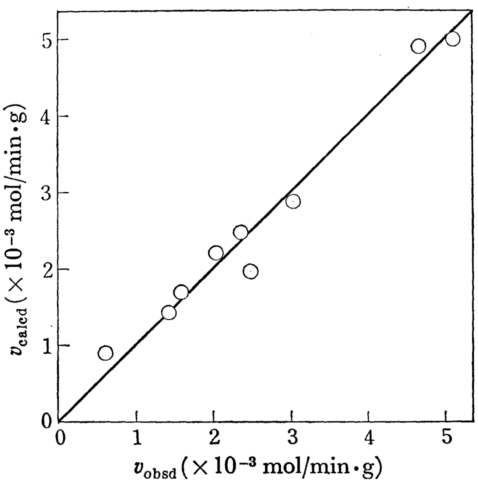

Fig. 4. Comparison of the rates calculated by Eq. (1), v_{calcd}, with the observed ones, v_{obsd}.

neighboring regions. From these the most acceptable one is picked to provide a solution having tolerable errors as well as reasonable physical meaning. In Fig. 3, the regional rates are plotted against the free energy changes of adsorption of oxygen. The result corresponds to such combination of regions as 1+2, 3+4, 5 and 6, and shows that the fifth region ($-\Delta G=$ 11.1—12.6) has a marked contribution to the reaction rate. The overall rates calculated with the above results by means of Eq. (1) are plotted against the observed ones in Fig. 4. A good agreement is observed.

Since oxidation power distribution implies the energy distribution of surface oxygen over the fully oxidized catalysts, the distribution should be caused by the difference of the energy states of adsorption sites for oxygen, *i.e.*, probably bare metal ion, which will be caused by the removal of surface oxygen. Oxidation power distribution corresponds also to discrimination of the energy states of bare metal ion sites. The fifth region provides the largest contribution to catalytic activity, but it is not clear whether the actual active site during catalysis is the surface oxygen or the bare metal ion.

The reaction mechanism of the decomposition of hydrogen peroxide over the oxide catalysts is not known, but information on the homogeneous system catalyzed by ferrous or ferric ion can be referred to.[2] The decomposition of hydrogen peroxide is initiated by the formation of HO_2 or OH radical by oxidation or reduction with ferric or ferrous ion, and proceeds through radical chain mechanism. Ferrous ion catalyzes the decomposition much more effectively than ferric ion, and the same final steady state having a particular ferrous/ferric ratio is obtained, regardless of whether the initial feed is ferrous or ferric ion. As shown in Fig. 1, the catalytic activity of nickel oxide increases markedly by prior evacuation at high temperature, and decreases gradually towards the final constant value with repetition of reaction. Contrarily, the fully oxidized catalyst shows about the same catalytic activity as in the catalyst which underwent no pretreatment. The nickel oxide shows a much higher catalytic activity in the reduced state than in the oxidized state.

Dependency of catalytic activity of these nickel oxides on calcination temperature is not altered by any pretreatment. Therefore, in the light of regional analysis, it will be assumed that both the bare nickel ion and the surface excess oxygen catalyzes the decomposition of hydrogen peroxide more effectively as long as they belong to the fifth region, the former being much more active than the latter. Since the mode of catalytic activity in the pretreatment is similar to that of the ferrous/ferric ion catalyzed system, the catalytic reaction and deterioration of the active sites over the nickel oxide follow a similar mechanism to that in the homogeneous system.

The catalytic activity of lithium-doped nickel oxide decreases monotonously with the amount of lithium added. We might suggest that this tendency is in parallel to the summed surface excess oxygen of the fifth and sixth regions, and the activation energy does not differ from that of the other pure nickel oxides. These facts also give evidence to the usefulness of oxidation power distribution for understanding the catalytic activity of oxide catalysts.

The authors wish to express their sincere thanks to Dr. Y. Saito for his helpful discussions and to Mr. N. Nojiri for his kind help in the course of this experiment. The reagent was supplied by the Mitsubishi-Edogawa Co., Ltd. The work was partly defrayed by a Grant in Aid of The Kawakami Foundation.

References

1) Part XI of this series: T. Uchijima, Y. Ishida, N. Uemitsu, and Y. Yoneda, *J. Catal.*, **29**, 60 (1973).

2) J. Weiss, *Advan. Catal.*, **4**, 343 (1952); J. H. Baxendale, *ibid.*, **4**, 31 (1952).

3) I. Matsuura, Y. Kubokawa, and O. Toyama, *Nippon Kagaku Zasshi*, **81**, 1209 (1960).

4) A. B. Hart and R. A. Ross, *J. Catal.*, **2**, 251 (1963).

5) J. Deren, J. Haber, A. Podgorecka, and J. Burzyk, *ibid.*, **2**, 161 (1963); J. Deren and J. Haber, *ibid.*, **4**, 22 (1965); M. Nachman, I. Maxim, and T. Braun, *J. Phys. Chem. Solids*, **20**, 307 (1961).

6) I. Maxim and T. Braun, *ibid.*, **24**, 537 (1963); T. Yamashina and M. Sano, This Bulletin, **38**, 1801 (1965).

7) T. Uchijima, M. Takahashi, and Y. Yoneda, *J. Catal.*, **9**, 403 (1967).

8) Y. Yoneda, *ibid.*, **9**, 51 (1967).

9) G. K. Boreskov, V. V. Popovsky, and V. A. Sazonov, Proc. Intern. Cong. on Catalysis, 4th Moscow, 33 (1968); W. M. H. Sachtler, G. J. H. Dorgelo, J. Fahrenfort, and R. J. H. Voorhoeve, *ibid.*, 4th Moscow, 34 (1968).

10) Y. Morooka and A. Ozaki, *J. Catal.*, **5**, 116 (1967); Y. Morooka and A. Ozaki, *ibid.*, **7**, 23 (1967).

11) G. K. Boreskov, *Advan. Catal.*, **15**, 285 (1964).

12) W. M. H. Sachtler and N. H. DeBoer, Proc. Intern. Cong. on Catalysis, 3rd Amsterdam, **1**, 252 (1964).