Kinetics of Decomposition of Hydrogen Peroxide Over Different Electrodeposited Nickel Powder Catalysts

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ABSTRACT.The kinetics of decomposition of hydrogen peroxide have been studied over different electrodeposited nickel powders catalysts characterized by different particle sizes and morphological structure. The reaction was confirmed to be first-order and the decomposition rate constant was found to be dependent on the surface morphology of the catalyst. The thermodynamic parameters of activation were calculated. The energy of activation showed little variation with different samples. The entropies of activation have moderate negative values. The change in $\Delta S^{\ddagger}$ is of the same order as that of $\Delta H^{\ddagger}$. The compensation relationship between T $\Delta S^{\ddagger}$ against $\Delta H^{\ddagger}$ showed that there is small change in $\Delta G^{\ddagger}$ with catalyst samples. The mechanism of the reaction was discussed in the light of previous results. This mechanism involves an electron transfer from the metal to the H_2O_2 adsorbed at the interface.

Introduction

The catalytic decomposition of hydrogen peroxide by solid metals has gained considerable attention. The reaction has been treated by many authors from the point of view of the radical mechanism[1-5]. On the basis of the electron theory, the metal could be considered as a source and as a sink of electrons. Although, the high activity of solid metals towards the decomposition of H_2O_2 has been well-known for some time[1-5], very little work has been reported on the catalytic decomposition of that reaction using electrodeposited nickel powder catalysts[6-8].

Our previous studies[6-8] on electrodeposited nickel powders catalysts proved that these deposited powders are good catalysts for the decomposition of H_2O_2. Such catalysts showed different activities towards the decomposition reaction owing to the difference in their particle size and morphological structure. However, the kinetics

and/or the mechanism of decomposition using electrodeposited nickel powder catalysts were not investigated.

Thus, the present investigation deals with studies of the kinetics and an attempt has been made to discuss the mechanism for the decomposition of H_2O_2 using electrodeposited nickel powder catalysts. The dependence of the kinetics and thermodynamic parameters of activation on the catalyst microstructure are also considered.

Experimental

Different nickel powder catalysts sample 1-13 were prepared as reported earlier[6-8]. The differences in samples were due to the conditions of deposition. The relative catalytic activities of such catalysts were measured by a flow system at different reaction temperatures using a specially designed reactor cell[6]. In each experiment, 0.15 g of the catalyst powder was used with 50 ml of 0.4% H_2O_2 solution. The entire set was kept at the desired temperature for 20 min. before each run. The peristatic pump (LKB, Bromma model 2132) was adjusted to achieve the required flow rate, switched on to allow the H_2O_2 to pass over the catalyst. A Pye-Unicam Sp 500 spectrophotometer was used to identify the exact concentration of H_2O_2 before and after their passage over the catalyst. The percentage decomposition (D%) was then calculated at various flow rates and temperatures.

Results and Discussion

The effect of flow rate on the decomposition of H_2O_2 solution was investigated using different nickel powder catalysts (samples 1-13) at different reaction temperatures. It was found that the rate of decomposition at a fixed H_2O_2 is dependent on the flow rate up to $\simeq 400$ ml hr^{-1}. Above this higher flow rate limit, the fraction of peroxide decomposed was almost abundant. Morever, in all cases, at the range of temperature used, the percentage decomposition increases gradually with the corresponding decrease in the flow rate. This could be due to the corresponding increase in the contact time between the H_2O_2 molecules and catalyst surface. Figure 1 shows a typical results of the relation between the contact time and D% for samples 1-3 at 40°C.

Most researches had found that the decomposition of H_2O_2 proceeds in accordance, with first-order kinetics[3,11,13]. Accordingly, and in order to investigate the kinetics and the mechanism of decomposition, the present data were analyzed in the same manner as those earlier works. Two equations were used to verify the above requirements:

(1) First-order Basset-Habgood equation[9] as follows :

$$kK = \frac{F^o}{273\ R\overline{W}}\ \ln\frac{1}{1-x}$$

where κ is the adsorption equilibrium constant, W is the total weight of the catalyst and X is the fractional conversion.
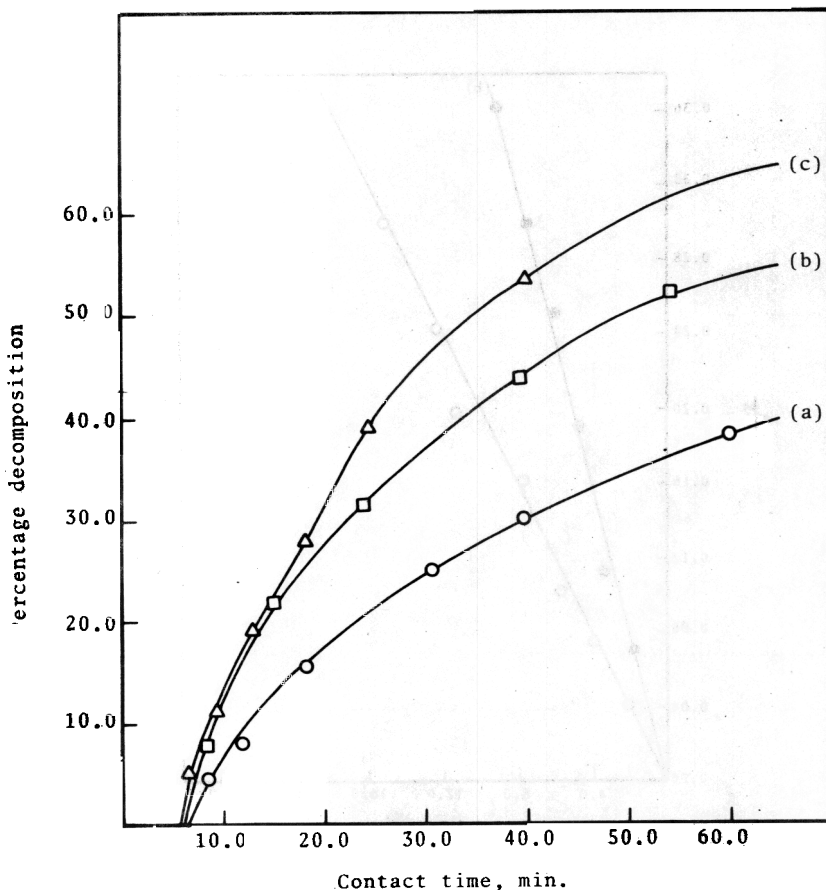
FIG. 1. Decomposition % of H_2O_2 (D%) vs. contact time for samples: (a) 3, (b) 4 and (c) 5.

(2) The simple first-order equation

$\ln (a - x) = \ln a - k\,t.$

Plotting $\ln \dfrac{1}{1 - x}$ against $\dfrac{1}{F^0}$ for the Bassett-Habgood equation gives a straight line passing through the origin in all cases. Accordingly, the decomposition of H_2O_2 with these catalysts can be considered to be a first-order reaction within the flow rates and temperatures range used over 95% of the total reaction time. Figure 2 shows a typical behaviour for this plotting. Morever, data of the relation between $\ln (a - x)$ against t reveal that the kinetics of this reaction also follows first-order behaviour. The good agreement between the results of the two equations proved that the reaction is strictly first-order.
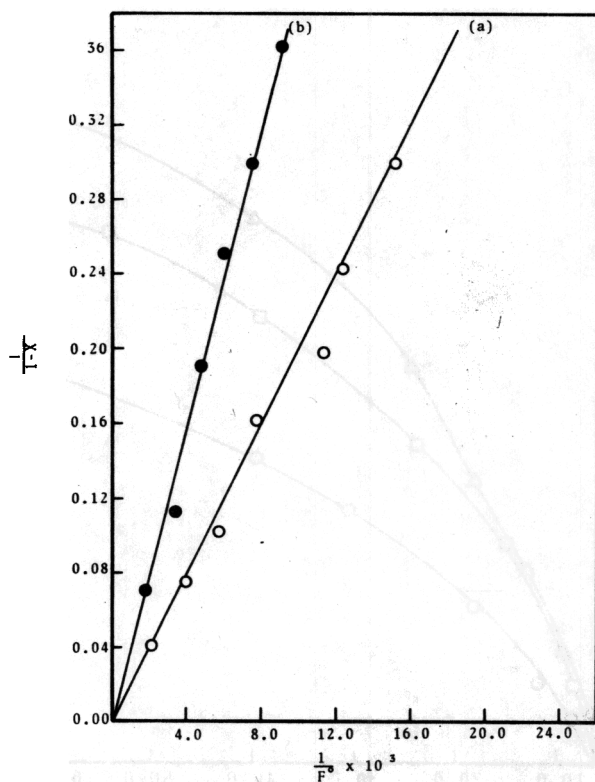
FIG. 2. Basset-Habgood plots for H_2O_2 decomposition over nickel powder catalysts: (a) 6 and (b) 7.

The determined kinetics and activation parameters determined at 40°C are listed in Table 1. It shows that there is a marked change in both κ and $t_{1/2}$ from one catalyst to another. The lowest value of κ is observed for sample 4, and the highest value is that corresponding to sample 12. This change could be correlated with the methods and conditions of preparation which affected, to a great extent, the particle size as well as the surface morphology of the catalyst samples[7,8].

The influence of temperature on this decomposition reaction was studied at 10, 20, 30 and 40°C. It was found that the rate of decomposition of H_2O_2 increases with the increase in temperature, and obeyed a first order rate equation at these temperatures. It also appears that the rate constants increase with the increase in temperature in accordance with Arrhenius equation.

One possible approach to ascertain the intrinsic activity is to make use of a kinetic parameter, which is effectively independent of the catalyst microstructure. A suita-

TABLE 1. Kinetics and activation parameters for the decomposition of H_2O_2 over different electrodeposited nickel powder catalysts at 40°C.

Catalyst	k, min.$^{-1} \times 10^{-2}$	$t_{1/2}$, min.	E_a Kcal mol^{-1}	$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1}	$\Delta G^{\ddagger}$ Kcal mol^{-1}
1	1.08	64.00	16.50	15.88	−16.89	21.17
2	1.31	52.90	16.20	15.58	−17.46	21.05
3	2.15	32.28	15.90	15.28	−17.43	20.74
4	0.70	99.01	17.81	17.19	−13.56	21.43
5	1.24	55.89	16.45	15.83	−16.77	21.08
6	1.28	54.15	16.25	15.63	−17.35	21.06
7	1.03	67.96	16.62	16.00	−16.60	21.19
8	0.80	86.64	17.20	16.58	−15.25	21.35
9	0.73	94.55	17.53	16.91	−14.38	21.41
10	1.25	55.50	16.31	15.69	−17.20	21.08
11	1.95	35.54	16.10	15.48	−16.99	20.80
12	5.10	13.59	15.46	14.84	−17.13	20.20
13	0.72	96.80	17.66	17.04	−13.99	21.42

ble choice for this parameter is the activation energy for the decomposition reaction, which is independent of the catalyst type rather than the surface morphology[10]. The energy of activation of H_2O_2 decomposition on these catalysts were determined using Arrhenius equation and are cited in Table 1. Figure 3 shows typical plots for the Ar-
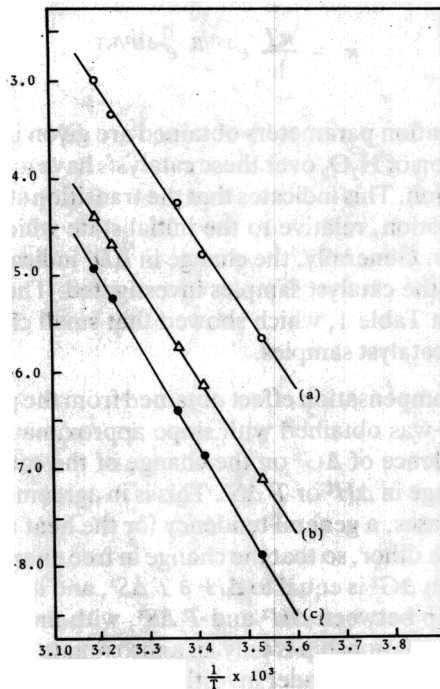

FIG. 3. Arrhenius plot for the decomposition of H_2O_2 over samples: (a) 12, (b) 10 and (c) 9.

rhenius equation. The values of activation energy obtained for catalyst samples shows little variation tending to be clustered in the range 15-17 kcal mol⁻¹. Similar results were obtained from the catalytic decomposition of H_2O_2 on cobalt aluminium oxides[11].

The values of activation energy obtained indicate that this reaction is characterized by chemisorption rather than physosorption[12]. The lowest and highest values of activation energy were observed for samples 12 and 4, respectively. This is in agreement with the observed catalytic activity of these catalysts, Table 1.

Since all these catalysts are in a powdery form, and their individual particles are porous possessing irregular and discontinuous surface structure[7,8], the greatest contribution to the surface area arises from the pore walls of the internal structure developed. Thus the utilization of a catalysts internal surface leads H_2O_2 to diffuse into and along the catalyst internal pores. However, the decomposition reaction is a turbulent process, continuously releasing bubbles of oxygen gas. Such a process, occurring in subsurface pores would inevitably force out reactant solution curtailing further decomposition. According to this, liquid phase H_2O_2 decomposition is greatly restricted in a catalyst's internal pores and occur predominantly on the outer surface[13]. Similar results have been observed for decomposition of H_2O_2 on some metal oxide catalysts[11].

The enthalpy of activation $\Delta H^{\ddagger}$ were calculated using the following equation[13] :

$$\kappa = \frac{\kappa T}{h} \, e^{\Delta S^{\ddagger}/R} \, e^{-\Delta H^{\ddagger}/RT}$$

The results of the activation parameters obtained are given in Table 1. These results show that decomposition of H_2O_2 over these catalysts have moderate negative values for entropies of activation. This indicates that the transition state has an intermediate degree of restricted motion, relative to the initial state which is characterized by a high degree of disorder. Generally, the change in $\Delta D^{\ddagger}$ indicates that the decomposition is independent of the catalyst samples investigated. These results are also supported by the results in Table 1, which showed that small changes in $\Delta G^{\ddagger}$ were observed using different catalyst samples.

Figure 4 shows the compensation effect obtained from the present data at 40°C. As is clear, a straight line was obtained with slope approximate one. This means that there is a small dependence of $\Delta G^{\ddagger}$ on the change of the catalyst sample compared with the observed change in $\Delta H^{\ddagger}$ or $T \Delta S^{\ddagger}$. This is in agreement with the known fact that there is, in some cases, a general tendency for the heat and entropies of activation to compensate each other, so that the change in free energy is much smaller. The free energy of activation $\Delta G^{\ddagger}$ is equal to $\Delta H^{\ddagger} \partial T \Delta S^{\ddagger}$, and it follows that if there is an exact linear relationship between $\Delta H^{\ddagger}$ and $T \Delta S^{\ddagger}$, with unit slope, there will be no variation of $\Delta G^{\ddagger}$. If the relationship is only an approximate one, it means that the dependence of $\Delta G^{\ddagger}$ on the variable under investigation is much smaller than that of $\Delta H^{\ddagger}$ or $T \Delta S^{\ddagger}$[12].
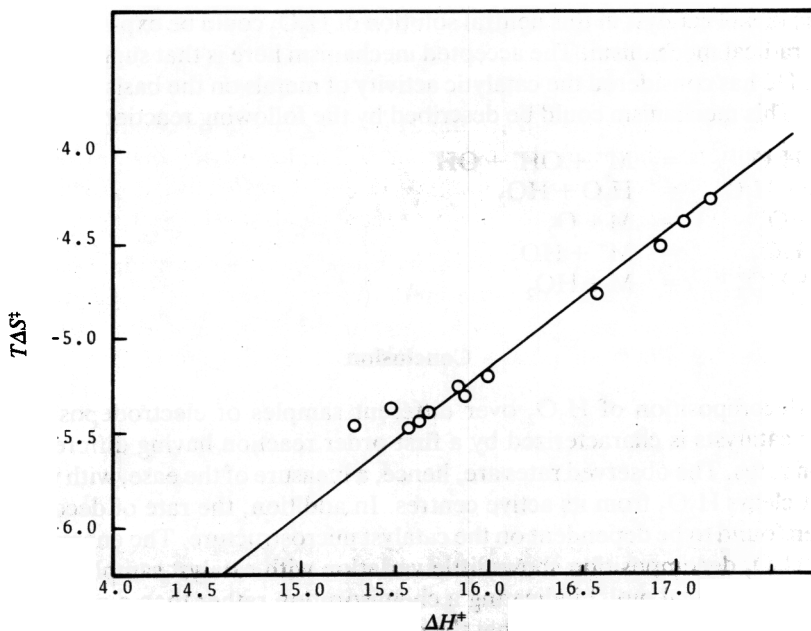
FIG. 4. The compensation effect = a plot of $T\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$ for H_2O_2 decomposition over different electrodeposited nickel powders.

The literature has offered several approaches to the study of heterogeneous H_2O_2 decomposition by metal systems. Several mechanisms, such as cyclic oxidation-reduction, formation of atomic oxygen, reciprocal depolarization of atomic hydrogen and hydroxyl radicals, and electron transfer have been suggested to account for the catalysis of hydrogen peroxide decomposition by metals. Rockstroch[14] reviewed this subject and concluded that the active form of metal is the metal itself, which provides a site for reaction rather than centering into an oxidation reduction scheme. Rockstroch[14] and Weiss[3] concluded also that the reaction of H_2O_2 with metals proceeds by donation of an electron from the metal to the hydrogen peroxide molecule, which causes the latter to split up and form an OH^- anion and OH radical as in the following equation :
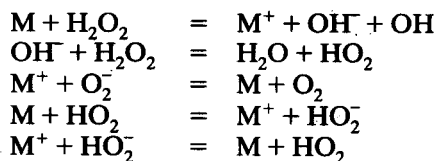
$$H_2O_2 + M = M^+ + OH + OH^-.$$
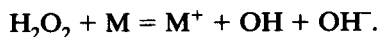
The generation of the OH^- anion is considered vital to the initiation of the decomposition, which then proceeds as follows:

$$OH^- + H_2O_2 = H_2O + HO_2.$$
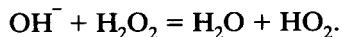
The first-order kinetics (generally observed) is taken to indicate that the rate limiting step is the diffusion of H_2O_2 molecules to the metal surface.

If the above explanation is accepted, the reaction between H_2O_2 molecules and a metallic nickel catalyst in this neutral solution of H_2O_2 could be explained according to free radical mechanism. The accepted mechanism here is that suggested by Dowden[15]. He has considered the catalytic activity of metals on the basis of the electron theory. This mechanism could be described by the following reactions :

$$
\begin{aligned}
M + H_2O_2 &= M^+ + OH^- + OH \\
OH^- + H_2O_2 &= H_2O + HO_2 \\
M^+ + O_2^- &= M + O_2 \\
M + HO_2 &= M^+ + HO_2^- \\
M^+ + HO_2^- &= M + HO_2
\end{aligned}
$$

Conclusion

The decomposition of H_2O_2 over different samples of electrodeposited nickel powder catalysts is characterized by a first-order reaction having different decomposition rates. The observed rates are, hence, a measure of the ease, with which each catalyst clears H_2O_2 from its active centres. In addition, the rate of decomposition has been found to be dependent on the catalyst microstructure. The energy of activation of H_2O_2 decomposition shows little variation with catalyst samples and having values of 15-17 kcal mol^{-1} indicating a chemisorption rather than a physosorption. The activation parameters show that the decomposition of H_2O_2 with these catalysts has moderate negative values for entropies of activation. The changes in $\Delta S^{\ddagger}$ are of the same order as that for $\Delta H^{\ddagger}$, indicating that the decomposition mechanism is independent of the structure of the investigated catalysts.

This conclusion is also supported by the results of the compensation relationship which showed that there is a small change in $\Delta G^{\ddagger}$ with the change in the catalyst samples.

The initial process of the catalytic decomposition of H_2O_2 by nickel powder catalysts involves an electron transfer from the metal to the H_2O_2 adsorbed on the surface. The hydrogen peroxide is thereby attacked monovalently, i.e., one electron is transferred, resulting in the formation of the radicals OH or HO_2. Therefore, the transition of one electron to form a OH$^-$ ion and a OH radical from a H_2O_2 molecule is far more likely than the simultaneous formation of two OH$^-$ ions.

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كيناتية تحلل فوق أكسيد الهيدروجين فوق مساحيق نيكل مترسبة كهروكيميائيًا

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يتناول هذا البحث بالدراسة كيناتية تحلل فوق أكسيد الهيدروجين باستخدام عدة محفزات من مساحيق النيكل المتباينة الخواص والمحضرة بتقنية الترسيب الكهروكيميائي . وقد وجد أن رتبة تفاعل التحلل من الدرجة الأولى ، وأن ثابت معدل التفاعل يعتمد على الشكل السطحي لحبيبات المسحوق المستخدم كعامل حفاز . وقد تم حساب بعض بارامترات التنشيط الديناميكية الحرارية ، واتضح أن قيم طاقة التنشيط تتغير تغيراً طفيفاً باختلاف عينة المحفز المستخدم . في حين كانت قيم الإنتروبيا متوسطة سالبة .

كما وجد أيضاً أن هناك ارتباطاً مباشراً بين قيم كل من الإنتروبيا والإنثالبي وفي ضوء النتائج السابقة تمت مناقشة ميكانيكية تفاعل التحلل واتضح أنها تتضمن انتقال إلكترون من سطح الفلز المستخدم كمحفز إلى جزيء فوق أكسيد الهيدروجين المدمص على سطح المحفز . .