

# The Deactivation of Prussian Blue Heterogeneous Catalyst During the Decomposition of $H_2O_2$ in Aqueous Alkaline Solution

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The changes of surface and crystal structure of Prussian blue have been studied in neutral and alkaline solutions by electron microscopy and X-ray diffraction. The methods used in earlier work have been used to measure the performance of Prussian blue catalysts in  $H_2O_2$  decomposition.

## INTRODUCTION

Systematic studies in our laboratories (1-4) have shown that both Prussian and Turnbull's blue are highly active catalysts for the decomposition of hydrogen peroxide. Previous work (2) on the decomposition of hydrogen peroxide in alkaline solutions using Prussian blue showed that it was decomposed and partially deactivated. This was accompanied by a change of color of the catalyst from blue to dark-brown. In order to express these changes quantitatively some mathematical equations were derived, confirming the results of tests. It was also shown that the final activity of the catalyst was due to a mixture of ferrocyanide ions and ferric hydroxide. This was formed by decomposition of the Prussian blue. The new heterogeneous catalysts were a mixture of Prussian blue and ferric hydroxide.

In the present work, we have measured the pH of aqueous hydrogen peroxide solutions as 9.38 and the heterogeneous catalyst was periodically separated from the soluble compounds by filtration. The differences between the crystal structure of these new heterogeneous catalysts and the original

Prussian blue were investigated by X-ray diffraction methods. The catalytic activities of the new heterogeneous catalysts were also determined in buffered and unbuffered neutral, hydrogen peroxide solutions and some new equations for the deactivation of the catalyst surface were derived.

Investigations were made by electron microscopy (carbon replicas) to observe the changes of surface structure of the Prussian blue during the decomposition of aqueous hydrogen peroxide.

## METHODS AND RESULTS

### (a) Preparation of Original Catalyst

Pure Prussian blue from Hopkin and Williams Ltd. was sieved (DIN 4188 standard) and the particles between 200 and 100  $\mu$  were selected for use. The Prussian blue was then dried in an oven at 125°C, cooled in a desiccator, labeled as OPO catalyst, and stored in a stoppered brown bottle.

### (b) Preparation of Deactivated Catalysts

In each test, 1 ml of perhydrol and 1 g of OPO catalyst were poured into 500 ml

buffer solutions prepared with boric acid and sodium hydroxide according to Clark and Lubs (5). The pH of the buffer solution was measured by a pH meter (accuracy of  $\pm 0.01$ ). The mixture was stirred well for 10 min at the temperature of 44°C and filtered. The deactivated catalyst was collected on a Buchner funnel and well washed with distilled water under nitrogen. It was then dried in nitrogen at 75°C and subsequently powdered in an agate mortar and redried in a vacuum desiccator. This catalyst was labeled as OP10. The same procedure was repeated for 5, 15, 21, 28, 38, 50, 62, 75, 87, 100, 125, 150, and 175 min and labeled, respectively, OP5, OP15, OP21, OP28, OP38, OP50, OP62, OP75, OP87, OP100, OP125, OP150, and OP175.

(c) *Study of the Crystal Structure of the Catalysts by X-ray Diffraction (XRD)*

Besides OP0 catalyst, the catalysts OP10, OP28, and OP150 were considered as main catalysts and they were analyzed by X-ray diffraction. They were chosen on the strength of earlier determinations of the activity of the original catalysts at 10, 28, and 150 min (2). X-ray diffraction patterns, values of the angle  $2\theta$  and calculated  $d$ -spacings of these samples are shown in Fig. 1 and Table 1. All patterns of the samples were made in Crobaugh Laboratories Cleveland, Ohio.

The first pattern in Fig. 1 shows a well-known pattern for Prussian blue. Others refer to OP10, OP28, and OP150 catalysts.

The intensity of the peaks decrease gradually. The strongest peaks in the last pattern, which belongs to the OP150 catalysts, are only slightly stronger than the background noise level. In all the catalyst samples, no pattern ascribable to iron oxide or oxide hydrate can be seen. However, from the chemical analyses of the deactivated catalysts, ferric hydroxide is present. According to the X-rays the ferric hydroxide must be present in the amorphous form in the deactivated catalyst.

In order to understand the conversion of Prussian blue catalyst into the amorphous phase and other products, OP0 catalyst was mixed with buffer solution only and stirred for 28 min. Then following the hydrogen peroxide treatment in buffer solution explained above a new sample was prepared and labeled as PP28. In Fig. 2, the XRD pattern of this sample is compared with the OP28 pattern. The two samples possess essentially the same intensity, the same  $2\theta$  angles and calculated  $d$ -spacings.

(d) *Investigation of the Surface of Prussian Blue by Electron Microscopy*

Surfaces of OP0 catalyst and Prussian blue filtered from a neutral aqueous hydrogen peroxide solution after the oxygen evaluation had ceased were investigated by electron microscopy. These experiments showed the effects of hydrogen peroxide on the surface of the catalyst.

Carbon replica techniques were used with

TABLE I  
ANGLES  $2\theta$  AND CALCULATED  $d$ -SPACING OF THE MAIN CATALYSTS DETERMINED BY XRD PATTERNS

OP0	$2\theta$	17.2	24.5	34.9	39.3	43.1	50.4	53.7	56.9	65.9	68.6
	$d$	5.15	3.63	2.57	2.29	2.10	1.81	1.71	1.62	1.42	1.37
OP10	$2\theta$	17.5	24.8	35.3	39.6	43.3	50.8	—	—	—	69.9
	$d$	5.06	3.59	2.54	2.27	2.09	1.80	—	—	—	1.34
OP28	$2\theta$	17.2	24.5	34.9	39.5	43.2	—	—	—	—	—
	$d$	5.15	3.63	2.57	2.28	2.09	—	—	—	—	—
PP28	$2\theta$	17.2	24.6	35.1	39.4	43.2	—	—	—	—	—
	$d$	5.15	3.62	2.55	2.28	2.09	—	—	—	—	—
OP150	$2\theta$	17.3	—	35.2	—	—	—	—	—	—	—
	$d$	5.12	—	2.55	—	—	—	—	—	—	—

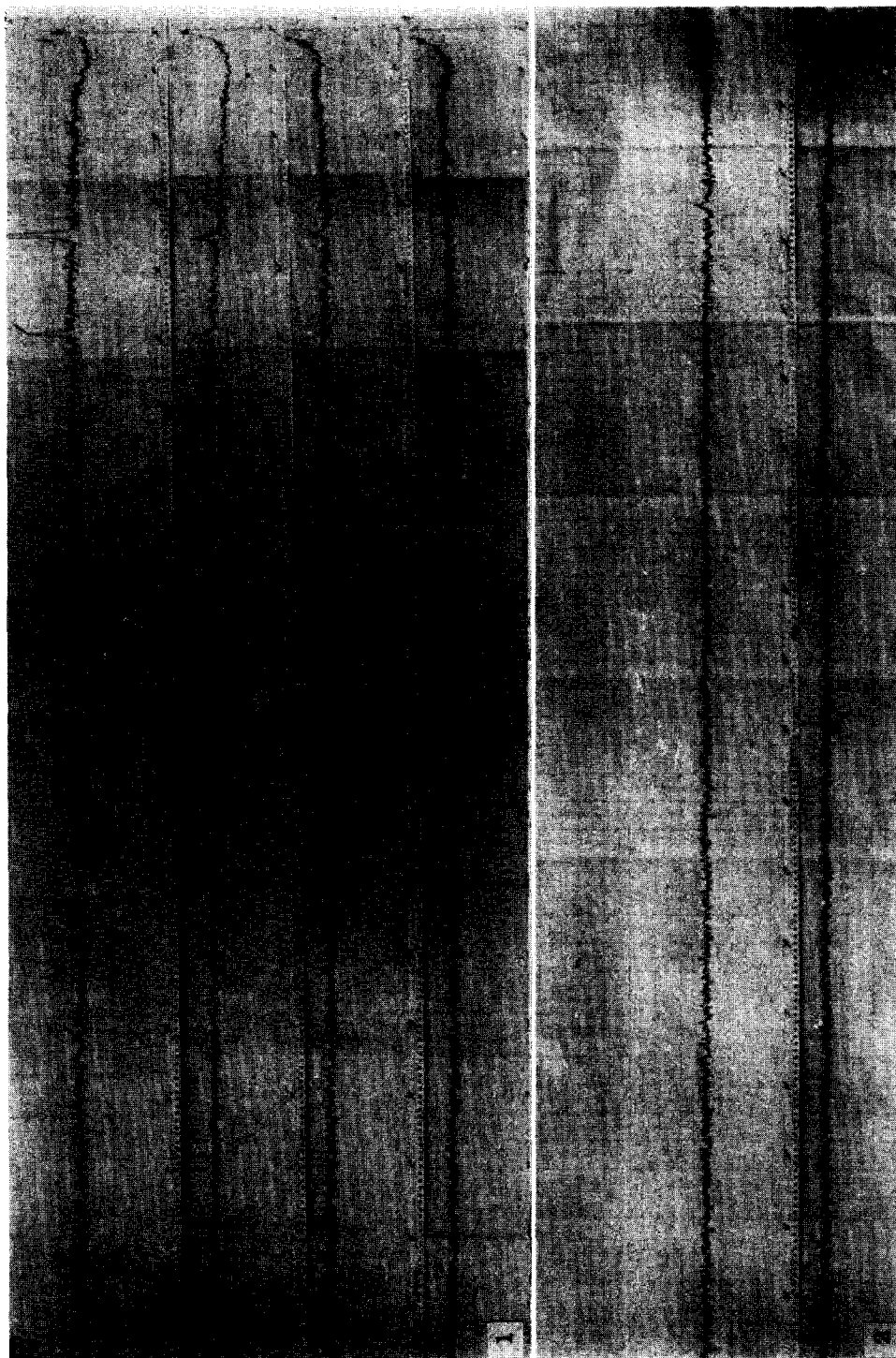


Fig. 1. XRD patterns of OP0, OP10, OP28, OP150 catalysts from the top to bottom.

Fig. 2. XRD patterns of OP28 (top) and PP28 (bottom) catalysts.

the electron microscope to investigate the surfaces. We have prepared carbon replicas following the method of vacuum evaporation developed by Bradley. Their shadowing with tungsten was carried out in Jena's High Vacuum Coating Plant HBA.120 and we have taken their photographs

(Fig. 3a,b) using a Zeiss EM-9 Electron Microscope.

(e) *Kinetics of the Catalyzed Reaction*

In this part of our studies we have measured the catalytic activity of the catalysts in buffered and unbuffered solu-

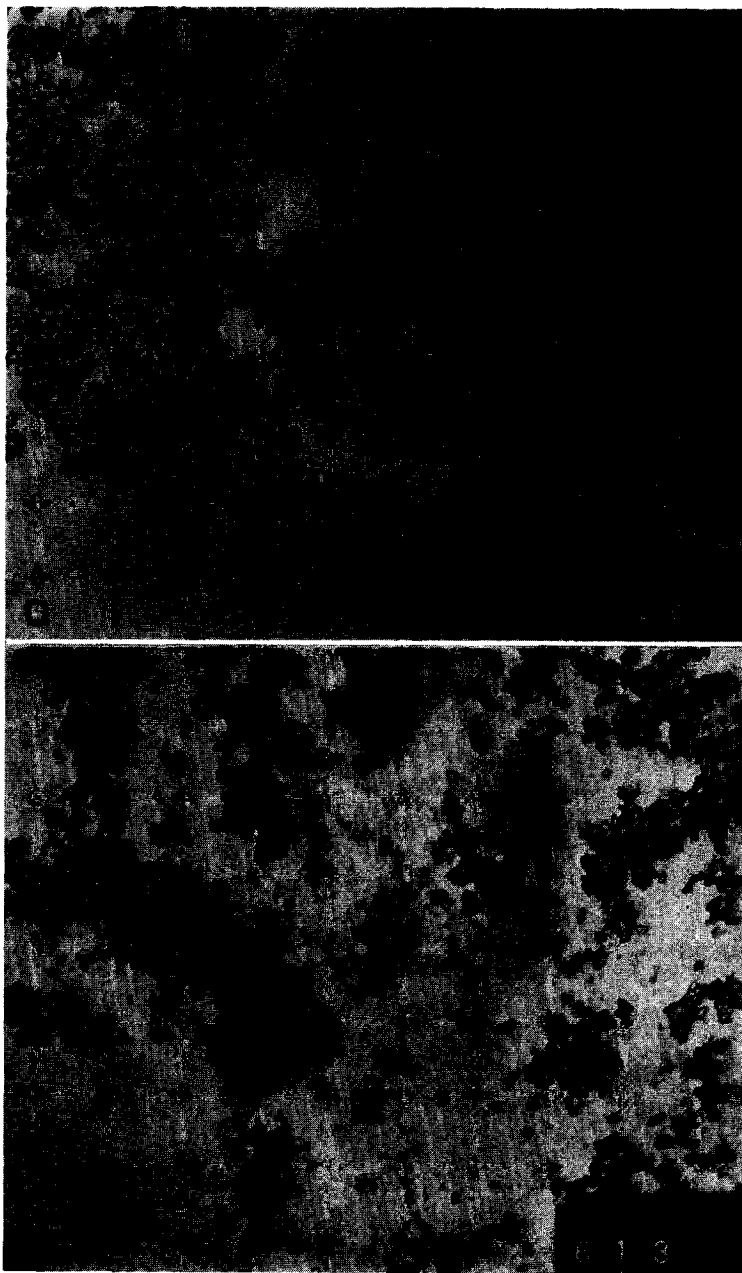


FIG. 3a. Electron micrographs of shadowed carbon replicas of OPO catalyst; (b) electron micrographs of shadowed carbon replicas of OPO catalyst which was treated by hydrogen peroxide.

tions and derived mathematical formulas for deactivation of heterogeneous catalysts. All experiments were performed at the temperatures of 30, 40, and 50°C ( $\pm 0.05^\circ\text{C}$ ) using a constant temperature bath. The reaction was followed by titrimetric techniques. During the catalytic decomposition of  $0.040 \pm 0.005 M$  hydrogen peroxide, samples of 10 ml of reaction mixture were taken off with a pipet and after acidification with  $\text{H}_2\text{SO}_4$ , titrated with 0.1 *N* permanganate solution. Plotting logarithms of the volume of permanganate used ( $\text{Log } V$ ) versus time ( $t$ ) produced straight lines, and rate constants were calculated from the slope of those lines. No decomposition was detected in the absence of catalyst.

The catalytic activities of the catalysts were studied in buffered and unbuffered solutions with 0.025, 0.050, and 0.100 g of catalysts in 100 ml solution at 30, 40, and 50°C. Let us take the results in buffered neutral media (pH 7.77) first. The experiments were performed in the neutral, buffered 0.040 *M* hydrogen peroxide solutions at 30, 40, and 50°C with an amount varying between 0.025–0.100 g of catalyst. The rate constants of the reactions were determined by a graphical method. The variation of the rate constants, using 0.100

g of catalyst at 50°C, with the decomposition time of catalyst is shown in Fig. 4. The rate constants which are found from the 50°C experiments by changing the amount of the four main catalysts are shown in Table 2. With 0.100 g of main

TABLE 2  
RATE CONSTANTS AS A FUNCTION OF CATALYST AMOUNT

Amount of catalyst (g)	OP0	OP10	OP28	OP150
$k_{(k)} 0.100$	0.197	0.151	0.104	0.080
$k_{(k)} 0.050$	0.099	0.075	0.053	0.041
$k_{(k)} 0.025$	0.050	0.038	0.026	0.020

catalysts the rate constants were determined at three different temperatures and these are shown in Table 3. The rate con-

TABLE 3  
RATE CONSTANTS AT 3 DIFFERENT TEMPERATURES

Catalyst temp ( $^\circ\text{C}$ )	OP0	OP10	OP28	OP150
$k_{(k)} 30$	0.176	0.130	0.085	0.054
$k_{(k)} 40$	0.188	0.144	0.092	0.066
$k_{(k)} 50$	0.197	0.151	0.104	0.080

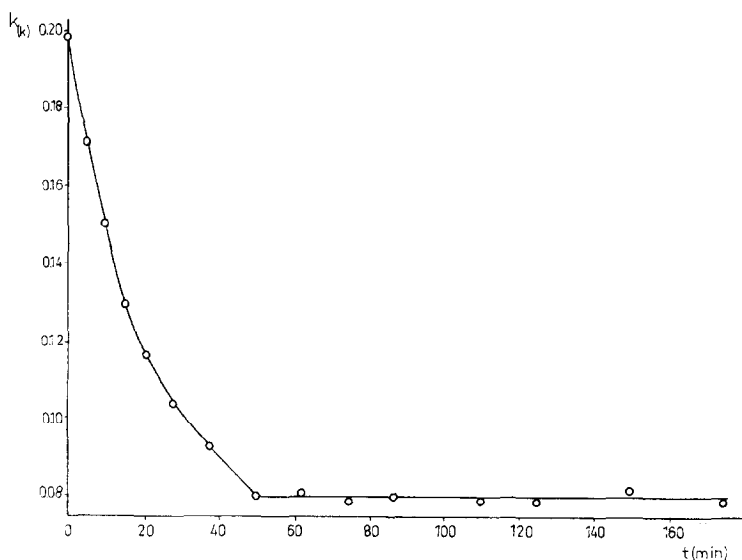


Fig. 4. Variation of the rate constants with the decomposition times of catalysts.

stants which are found at the same temperature were plotted against the amount of catalysts. As shown in Fig. 5, all the

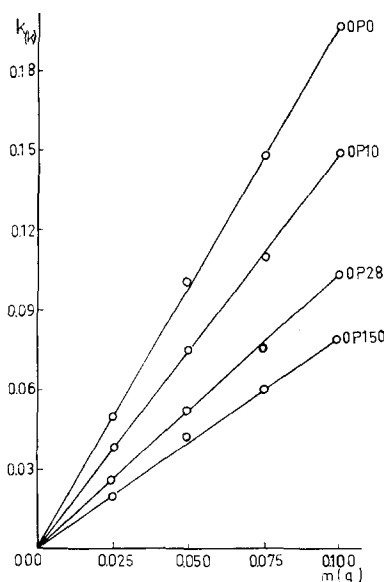


FIG. 5. The variation of reaction rate constants with the amount of catalysts.

values are on a straight line, which passes through the origin.

The relation between the mass of catalyst and apparent rate constant follows the relation,

$$k_{(k)} = km \text{ or } \log k_{(k)} = \log k + \log m$$

where  $m$  is the mass of catalyst in grams in 100 ml of buffered neutral aqueous solution containing  $\text{H}_2\text{O}_2$ . The activation energy may be formulated as

$$k_{(k)} = A m e^{-E_a/RT},$$

$$\log k_{(k)} = \log A + \log m - \frac{E_a}{4.57 T}$$

The values of  $\log k_{(k)}$  were plotted against  $1/T$  and the activation energies found for each catalyst (cal/g-mole) are shown in Table 4.

The experiments performed in unbuffered neutral solution give rise to surprising results, showing an anomaly in graph. In this case, experiments were repeated with the amounts 0.025, 0.050, and 0.100 g of catalysts for the 30, 40, and 50°C reaction temperatures. The reaction rate constants were calculated by the previous procedure. The variation of the logarithm of the rate constants with the deactivation periods of the catalysts are shown in Fig. 6, and the rate constants of the main catalysts are plotted versus their masses in Fig. 7. As shown in Fig. 7, the relation of reaction rate and the amount of catalyst is exponential, not linear. The relations between rate constants and mass of catalysts were calculated from Fig. 7; the observed and calculated rate constants are given in Table 5.

## DISCUSSION

### Deactivation of Catalyst

The deactivation kinetics of the catalysts were first derived and formulated by Pekin

TABLE 4  
ACTIVATION ENERGIES OF MAIN CATALYSTS AND DERIVED GENERAL FORMULAS

Catalyst	$E_a$ (cal/mole)	A	Log A	General formula	
				Logarithmic	Exponential
OP0	1156	12.05	1.0810	$\log k_{(k)} = 1.0810 - \log m - \frac{1156}{4.57T}$	$k_{(k)} = 12.05m e^{-1156/RT}$
OP10	1503	15.90	1.2016	$\log k_{(k)} = 1.2016 - \log m - \frac{1503}{4.57T}$	$k_{(k)} = 15.90m e^{-1503/RT}$
OP28	2081	26.70	1.4266	$\log k_{(k)} = 1.4266 - \log m - \frac{2081}{4.57T}$	$k_{(k)} = 26.70m e^{-2081/RT}$
OP150	3801	300.3	2.4776	$\log k_{(k)} = 2.4776 - \log m - \frac{3801}{4.57T}$	$k_{(k)} = 300.3m e^{-3801/RT}$

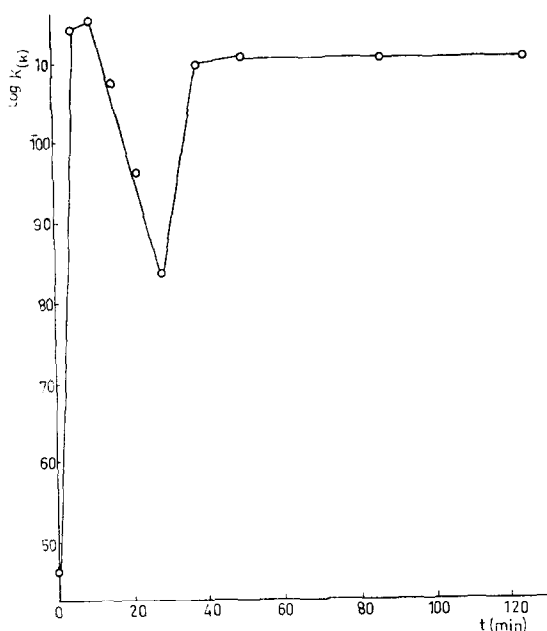


FIG. 6. The variation of  $\log k_{(k)}$  with the deactivation period of catalyst in unbuffered neutral solution at 50°C.

(2). To express the change of surface activity at pH 9.38, we have tried to apply these relationships to our present work. In this article, the theory will be explained very briefly. The catalytic decomposition of hydrogen peroxide may be expressed by means of the following equation,

$$-\frac{dc}{dt} = (a + be^{-k_d t})c, \quad (1)$$

where,

- $c$  = the concentration of hydrogen peroxide at any definite time,
- $a + b$  = catalytic activity of the surface of OP0 catalyst,

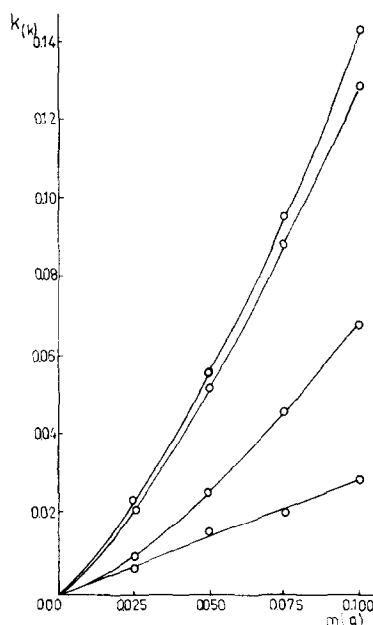


FIG. 7. The variation of reaction rate constants with the amount of catalyst.

- $a$  = catalytic activity of final surface, (this is accepted as the catalytic activity of OP150 catalyst),
- $b$  = the difference of the catalytic activity between original and final surfaces,
- $k_d$  = deactivation coefficient of the catalyst.

If we integrate Eq. (1), we obtain

$$-\ln c = at - \frac{b}{k_d} e^{-k_d t} + I. \quad (2)$$

When  $t = 0$ , the concentration of hydrogen peroxide is equal to  $c_0$ ; so Eq. (2) can be written as

TABLE 5  
MASS RELATIONS AND RATE CONSTANTS

Catalyst	Rate constant-mass equation	Rate constant with (g)							
		0.025		0.050		0.075		0.100	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
OP0	$k_{(k)} = 0.290 m^{1.0}$	0.0071	0.0073	0.0150	0.0145	0.0209	0.0218	0.0290	0.0290
OP10	$k_{(k)} = 2.79 m^{1.3}$	0.0234	0.0231	0.0561	0.0569	0.0956	0.0963	0.1428	0.1398
OP28	$k_{(k)} = 1.93 m^{1.45}$	0.0089	0.0092	0.0256	0.0251	0.0460	0.0451	0.0684	0.0685
OP150	$k_{(k)} = 2.24 m^{1.25}$	0.0223	0.0223	0.0525	0.0525	0.0881	0.0880	0.1278	0.1259

$$\ln \frac{c_0}{c} = at - \frac{b}{k_d} e^{-k_d t} + \frac{b}{k_d},$$

$$2.303 \log \frac{c_0}{c} = at + \frac{b'}{k_d} (1 - e^{-k_d t}), \quad (3)$$

or,

$$-2.303 \frac{d \log c}{dt} = a + b e^{-k_d t}. \quad (4)$$

When  $t = 0$

$$-2.303 \frac{d \log c}{dt} = a + b = k_{(k)}^0 \quad (5)$$

where  $k_{(k)}^0$  is the activity of OP0 catalyst, that is the rate constant for OP0 catalyst, and when  $t = \infty$

$$-2.303 \frac{d \log c}{dt} = a = k_{(k)}^\infty \quad (6)$$

where  $k_{(k)}$  is the activity of final surface, that is the rate constant of OP150 catalyst.

If we combine Eqs. (3), (5), and (6) we have

$$2.303 \log \frac{c_0}{c} = k_{(k)}^\infty t + \frac{k_{(k)}^0 - k_{(k)}^\infty}{k_d} (1 - e^{-k_d t}), \quad (7)$$

or

$$-2.303 \frac{d \log c}{dt} = k_{(k)}^\infty + (k_{(k)}^0 - k_{(k)}^\infty) e^{-k_d t}. \quad (8)$$

At any definite time ( $t$ ),  $-2.303(d \log c/dt)$  is proportional to the activity of catalyst which is deactivated during ( $t$ ) time. This is designated as  $k_{(k)}^t$ . Therefore Eq. (8) may be written as

$$k_{(k)}^t = k_{(k)}^\infty + (k_{(k)}^0 - k_{(k)}^\infty) e^{-k_d t}, \quad (9)$$

or, in a logarithmic form,

$$k_d = \frac{2.303}{t} \log \frac{k_{(k)}^0 - k_{(k)}^\infty}{k_{(k)}^t - k_{(k)}^\infty},$$

Plotting  $\log(k_{(k)}^t - k_{(k)}^\infty)$  versus ( $t$ ), it is possible to calculate  $k_d$ , the deactivation constant of catalyst.

From the experiments with the buffered solution (pH 7.77) at 50°C,  $\log(k_{(k)}^t - k_{(k)}^\infty)$  was calculated and then plotted against the deactivation times of the catalysts in Fig. 8. It is clearly shown that all

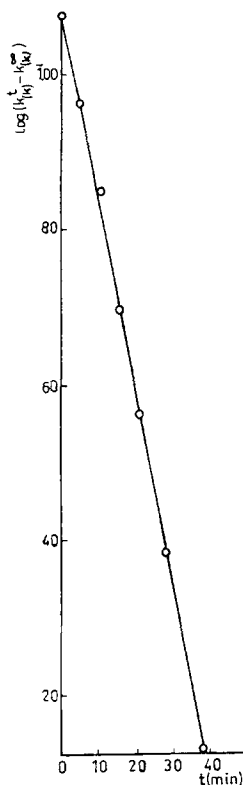


FIG. 8. The plot of  $\log(k_{(k)}^t - k_{(k)}^\infty)$  against ( $t$ ).

the values are on a straight line. The deactivation constant is calculated from the slope,

$$k_d = 0.055.$$

According to this result, the general deactivation formula for 50°C can be written as,

$$k_{(k)}^t = 0.080 + 0.119e^{-0.055t}$$

Applying the same procedure to the data of the catalysts between OP10 to OP28 obtained from the experiments in unbuffered neutral solution, the deactivation constant was similarly calculated. It is interesting that this range shows the same result of  $k_d$ , so in the unbuffered solution at 50°C the general deactivation formula was found as,

$$k_{(k)}^t = 0.068 + 0.074e^{-0.055t}$$

#### CONCLUSIONS

During the conversion of the OP0 catalyst in the buffered solution of 9.38 at 44°C, new amorphous heterogeneous cat-



alysts are formed (Fig. 1). This conversion is completed in 50 min, under our experimental conditions (Figs. 4 and 6).

Although some physical degradations are observed on the surface of OP0 catalyst after  $H_2O_2$  decomposition (Fig. 3a and b), these degradations do not change the catalytic activity of OP0 catalyst.

The deactivation of catalyst comes from the conversion of Prussian blue to ferric hydroxide, gradually.

The catalytic activity of OP0, and of its solid conversion products change with the media whether buffered or unbuffered (Figs. 4 and 6).

In the buffered solution (pH 7.77) the activity differences of the catalysts [one is prepared for ( $t$ ) minutes and other is the final product] change in a logarithmic way with the conversion period ( $t$ ) (Fig. 8).

In the unbuffered system, however, the same decrease of the activities are seen for the catalysts, between OP10-OP28. In this medium the activities of the converted catalysts are generally higher than those of OP0 catalyst.

In the buffered solution the variation of

the rate constant ( $k_{(k)}$ ) with the mass of catalyst is linear but in the unbuffered system this variation is exponential, for all but OP0 catalyst (Fig. 7).

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