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KINETICS OF THE NICKEL-CATALYZED HYDROGENATION OF ETHYLENE AND ITS VARIATION WITH CATALYST POISONING

By

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Abstract

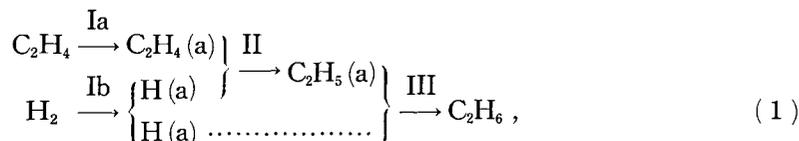
The reaction of the title has been investigated both theoretically and experimentally to inspect the validity of the experimental result, obtained by MASUDA,³⁾ that the order of reaction is 0.7 in hydrogen and 0 in ethylene below optimum temperatures, and that of the inference, drawn by MATSUZAKI *et al.*⁶⁾ on the premise of the HORIUTI-POLANYI's associative mechanism being operative, that catalyst poisoning might inhibit unevenly the constituent elementary steps.

Theoretical treatment, with preliminary approval of both the experimental result and premise mentioned above, has first been developed on the reaction at 50°C of ethylene and hydrogen each of 10 mmHg initial partial pressure for the correlation of the hydrogen partial pressure P_H , the dependence, n , of the reaction rate upon P_H and the degree of catalyst poisoning, and then followed by an experimental check.

The theoretical results have been found to be in semi-quantitative agreement with the experimental ones (i) that on clean catalyst n increases approximately from 0.8 to 1.0 as P_H decreases from 10 to 2 mmHg, and (ii) that increasing degree of catalyst poisoning causes n to increase by about 0.3, hence the validities under study having been augmented.

Introduction

In 1934 HORIUTI and POLANYI¹⁾ put forward the associative mechanism, as represented by Scheme (1), for the catalyzed hydrogenation of ethylene on metallic catalysts :



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where (a) denotes the adsorbed state and Ia, *etc.* signify each elementary step. In 1959 HORIUTI²⁾ developed the statistical mechanical theory of the associative mechanism for the nickel-catalyzed hydrogenation of ethylene, designating, with the aid of experimental data then available, the characteristic rate functions \mathfrak{R} (Ia), *etc.* to each constituent step as follows :

$$\mathfrak{R}(\text{Ia}) \gg \mathfrak{R}(\text{Ib}), \mathfrak{R}(\text{II}), \mathfrak{R}(\text{III}); \mathfrak{R}(\text{Ia}) \gg V \quad (2.1)$$

$$\mathfrak{R}(\text{Ib}) = 2.0573 \times 10^{-18} \times 10^{\frac{-1356.6}{T}} \times P_{\text{H}} (P_{\text{E}})^{0.525} \rho \quad (2.2)$$

$$\mathfrak{R}(\text{II}) = 2.4687 \times 10^{-20} \times 10^{\frac{-220.12}{T}} \times (P_{\text{H}})^{1/2} \rho \quad (2.3)$$

$$\mathfrak{R}(\text{III}) = 2.4012 \times 10^{-25} \times 10^{\frac{1032.3}{T}} \times P_{\text{H}} P_{\text{E}} \rho, \quad (2.4)$$

where \mathfrak{R} (Ia), *etc.* are the forward unidirectional rate of step Ia, *etc.*, respectively, which would be the case, if all steps of the associative mechanism but step Ia, *etc.* respectively were in equilibrium, V is the steady rate of the hydrogenation, *viz.* $-dP_{\text{H}}/dt$, P_{H} and P_{E} are the hydrogen and ethylene partial pressure respectively, and ρ is a common factor. The characteristic rate functions determine V and various associated reactions, *e.g.*, isotopic exchange reactions among C_2H_4 , H_2 and C_2H_6 , ortho-para conversion of hydrogen, H_2 - D_2 exchange, *etc.* The latter reactions, which reveal different aspects of the catalyzed hydrogenation, are constructed of \mathfrak{R} (Ib), *etc.* according to the mechanism (1). The mechanism incorporated with the specification, *e.g.*, (2) of \mathfrak{R} (Ib) *etc.*, will be called the structure of a steady reaction. This structure of the catalyzed reaction has been confirmed by a number of experimental results.^{7,11)} However there has recently been reported as follows an experimental result by MASUDA³⁾ which deviates from the above structure.

MASUDA³⁾ found with particular precaution against catalyst poisoning that the order of reaction of the nickel-catalyzed hydrogenation of ethylene is 0.7 or zero with respect to hydrogen or ethylene partial pressure below the optimum temperature; this result fits in with a revised \mathfrak{R} (Ib) expression $\mathfrak{R}(\text{Ib}) = k \times 10^{-1356.6/T} \times (P_{\text{H}})^{0.7}$ (k : constant). This conclusion is qualitatively supported by recent results.^{4,5)}

It is practically inevitable that heterogeneous catalysts are more or less subject to the effect of poison; hence it is of significance to elucidate the effect of catalyst poisoning. With this end in view, the present authors investigated in the preceding paper⁶⁾ the effect of catalyst poisoning in the nickel-catalyzed deuteration of ethylene on the basis of the premise that the catalyzed hydrogenation of ethylene proceeds via the associative mechanism irrespective of the extent of poisoning: the conclusion was that catalyst poisoning exerts

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greater inhibiting effect upon step III than upon step Ib. This conclusion suggests the possibility that increasing degree of catalyst poisoning will shift the kinetics from that with step Ib controlling the rate to that with step III operating as the rate-determining step.

The present research was attempted to make an experimental check on the suitability of the above-mentioned revision of the \mathfrak{R} (Ib) expression and on the validity of the inference mentioned above concerning the shift of the rate-determining step due to catalyst poisoning. It was advanced in the following order. First, with preliminary approval of both the above-mentioned MASUDA's experimental result and MATSUZAKI *et al.*'s premise, the reaction at 50°C of ethylene and hydrogen each of 10 mmHg initial partial pressure was treated theoretically, with the aid of the experimental result,⁷⁾ for the correlation of P_H , the dependence n of V on P_H and the degree of catalyst poisoning. This theoretical correlation was then experimentally tested.

Theoretical

1. Variation of n with P_H

The tentatively revised \mathfrak{R} (Ib) expression is :

$$\mathfrak{R}(\text{Ib}) = 1.375 \times 10^{-17} \times 10^{\frac{-1356.6}{T}} \times (P_H^{0.7}) \rho . \quad (3)$$

The simultaneous change of the value of the coefficient was made so that the optimum temperature, at which $\mathfrak{R}(\text{Ib}) = \mathfrak{R}(\text{III})$ holds, for the reaction of ethylene and hydrogen each of 10 mmHg partial pressure remained unaffected by the revision of the exponents of P_H and P_E .

The set of Eqs. (2. 1), (2. 3), (2. 4) and (3) enables us to derive, as a function of P_H , the values of V in the course of the reaction at 50°C of ethylene and hydrogen each of 10 mmHg initial partial pressure, the procedure of derivation having been described elsewhere.⁸⁾ Table 1 shows the values of V together with those of other characteristic quantities of the above-mentioned reaction thus obtained.

The value of n is now determined graphically using the data of Table 1 as follows ; according to the definition of n we have :

$$V = k(P_H)^n . \quad (k : \text{constant})$$

Differentiating the logarithms of both sides of the above equation with respect to $\log P_H$:

$$n = d \log V / d \log P_H , \quad (4)$$

which indicates that the value of n is identical with the slope of the plot of

TABLE 1. Theoretical data on the nickel-catalyzed hydrogenation $C_2H_4 + H_2 = C_2H_6$ at $50^\circ C$.
(Initial condition: $P_H = P_E = 10$, $P_A = 0$ mmHg)

$P_H = P_E$ (mmHg)	10	8	6	4	2	1	0.5
P_A (mmHg)	0	2	4	6	8	9	9.5
$\bar{\gamma}$ (H)	0.2762	0.3155	0.3730	0.4628	0.6342	0.7906	0.8916
$\bar{\gamma}$ (C_2H_5)	0.2514	0.2867	0.3383	0.4190	0.5761	0.7272	0.8312
V/V_0	1	0.8340	0.6519	0.4479	0.2097	0.0810	0.0273
$v_+(Ib)/V_0$	1.083	0.9261	0.7572	0.5700	0.3508	0.2160	0.1330
$v_-(Ib)/V_0$	0.083	0.0922	0.1053	0.1221	0.1411	0.1350	0.1057
$v_+(II)/V_0$	11.16	9.122	7.004	4.736	2.291	1.0101	0.4028
$v_-(II)/V_0$	10.16	8.288	6.352	4.282	2.081	0.9291	0.3755
$v_+(III)/V_0$	1	0.8340	0.6519	0.4479	0.2097	0.0810	0.0273
$(v_-(III)/V_0) \times 10^{13}$	0	1.85	3.69	5.52	7.37	8.31	8.78
$v_+(Ia)/V_0$	∞						
$v_-(Ia)/V_0$	∞						

- Note. 1) P_A stands for the partial pressure of ethane.
 2) V_0 is the value of V at $P_H = P_E = 10$ and $P_A = 0$ mmHg.
 3) $v_+(Ia)$, $v_+(Ib)$, $v_+(II)$, $v_+(III)$: forward rate of step Ia, Ib, II, III.
 $v_-(Ia)$, $v_-(Ib)$, $v_-(II)$, $v_-(III)$: backward rate of step Ia, Ib, II, III.
 4) cf. Ref. 2) or 8) for the definition of $\bar{\gamma}$ (H) and $\bar{\gamma}$ (C_2H_5).

$\log V$ against $\log P_H$. Fig. 1 shows the plot of $\log V$ against $\log P_H$ based on the data of Table 1 and the values of n obtained graphically according to Expression (4). As seen from Fig. 1, n increases approximately from 0.8 to 1.2 as P_H decreases from 10 to 2 mmHg.

2. Relation between n and $v_+(III)/v_+(Ib)$

As a preparatory step for deriving the relation between n and catalyst poisoning, we consider the relation between n and the ratio $v_+(III)/v_+(Ib)$. Since $v_-(III)$ is negligible as compared with $v_+(III)$ as seen from Table 1, the following relation holds:

$$V = v_+(III) . \quad (5)$$

The definition of $\mathfrak{K}(Ib)^2$ gives:

$$v_+(Ib) = \mathfrak{K}(Ib) . \quad (6)$$

From the above two relations we obtain:

$$V = \mathfrak{K}(Ib) \cdot v_+(III)/v_+(Ib) . \quad (7)$$

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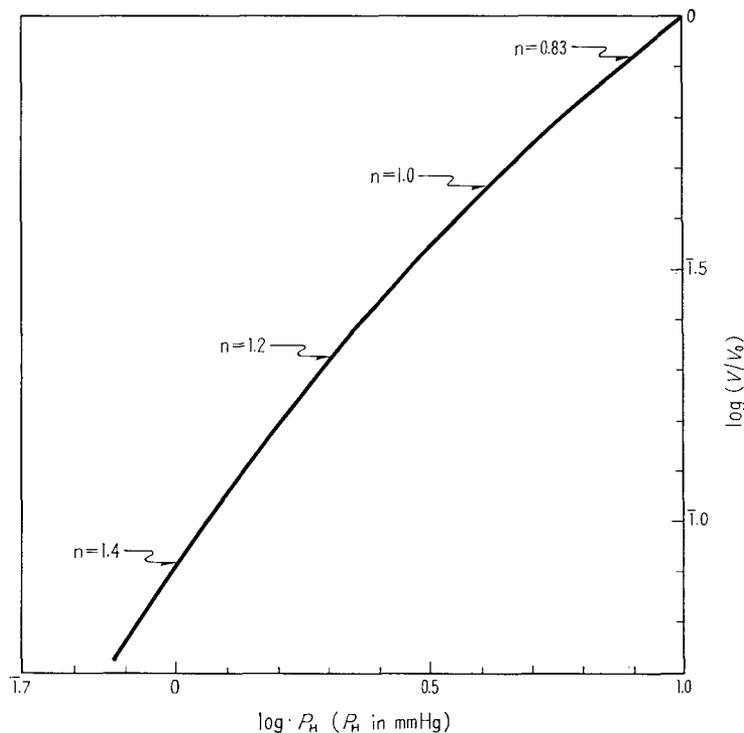


Fig. 1 $\log (V/V_0)$ vs. $\log P_H$ plotted with the data of Table 1 and the values of n evaluated graphically according to Expression (4).

From Expressions (3), (4) and (7) the following is readily derived:

$$n = 0.7 + d \log \left\{ v_{-}(\text{III})/v_{+}(\text{Ib}) \right\} / d \log P_H, \quad (8)$$

which indicates that it is the change of $\log \{v_{-}(\text{III})/v_{+}(\text{Ib})\}$ with $\log P_H$ that is responsible for the change of n with P_H mentioned in the preceding section.

3. Effect of catalyst poisoning on n

Consideration here is advanced on the basis of the same premise that was adopted in the preceding paper,⁶⁾ *i. e.*, that on poisoned catalysts the ethylene hydrogenation also proceeds via the associative mechanism.

As is evident from the procedure of derivation described in the preceding section, Expression (8) can be applied also for the case with poisoned catalysts provided that the relation $v_{+}(\text{III}) \gg v_{-}(\text{III})$ holds. We have two separate experimental results, combination of which leads to the conclusion that $v_{+}(\text{III}) \gg v_{-}(\text{III})$ holds in the case in question: one is the result obtained by two of the

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present authors⁸⁾ that the deuterium atoms of deuterio-substituted ethane exchanged with neither hydrogen nor ethylene while nickel catalyst was kept, for about 27 hrs., in contact with a mixture of hydrogen, ethylene and deuterio-substituted ethane each of *ca.* 10 mmHg initial pressure, and the other is the result to be reported in this paper that such a contact gives rise to decrease in the catalytic activity by 60% of the initial value. It is therefore concluded that Expression (8) can be applied for the case with poisoned catalysts.

Let us now evaluate the second term of r.h.s. of Expression (8) for both a clean and a heavily poisoned catalyst; Fig. 2 shows two plots, constructed with the data of Fig. 2 of Ref. 6), of $\log \{v_+(III)/v_+(Ib)\}$ against $\log P_H$. The slopes of these plots give the values of the second term of r.h.s. of Expression (8) as a function of P_H , as represented by the figures in Fig. 2. From Fig. 2 and Expression (8) it is concluded that increasing degree of catalyst poisoning will cause the value of n to increase by about 0.15.

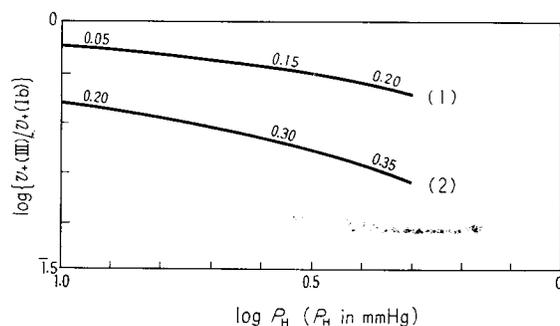


Fig. 2 Plots of $\log \{v_+(III)/v_+(Ib)\}$ vs. $\log P_H$, constructed with the data of Fig. 2 of Ref. 6).

(1) ... with clean catalyst, corresponding to Run no. 5-1.

(2) ... with poisoned one, corresponding to Run no. 5-3.

Experimental method

1. Materials and apparatus

The apparatus, the nickel catalyst and the sources of ethylene and hydrogen employed are all the same that were used in the preceding experiment.⁸⁾ Points to be supplemented here with particular reference to the present experiment are as follows. A great deal of care was taken lest there should appear appreciable concentration gradient throughout the reaction system; for this purpose the dead space of the reaction system was made as small as possible by employing capillary tubings for branching parts, and the circulation

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velocity of the reacting mixture was controlled so as to keep the conversion, caused during one circulation of the reacting mixture through the reaction system, less than 0.1% of the total amount of the conversion to be attained at the completion of the reaction.

The pressure change of the circulation system was followed by measuring the mercury level of manometer M_1 (the notations specifying the parts of the apparatus are the same as in Ref. 8)) by means of a travelling microscope. That the manometer M_1 functioned well without the sticking of the mercury was confirmed preliminarily by applying the manometer for measuring the pressure of hydrogen which was being evacuated slowly and steadily out of the circulation system.

2. Procedure

2.1. Activation of the catalyst

Reaction vessel RV had been left disconnected from trap T_1 , for about four months, since the end of the preceding experiment⁸⁾ lest the catalyst should be rendered irreversibly poisoned due to the contact with the vapor of mercury condensed at trap T_1 during the preceding experiment. The reaction vessel was first connected to trap T_1 , evacuated to 10^{-6} mmHg and inserted in an electric furnace regulated at 300°C. Trap T_1 was now immersed in methanol-dry ice mixture and hydrogen of about 20 mmHg introduced into the reaction system and circulated. Heating of the catalyst at 300°C in hydrogen lasted about 20 hrs. to complete recovery of the catalytic activity. Reactivation of used catalyst was effected by similar reduction.

2.2. Run of reaction

The reaction system was evacuated to 10^{-6} mmHg and the electric furnace replaced by a methanol-dry ice bath. Then the two 3-way taps connecting to trap T_1 were positioned so that the gas could be circulated in the reaction system except the reaction vessel. Ethylene was first introduced into the reaction system precisely to 16.00 mmHg, which had been found to amount to 10.30 mmHg when expanded into the reaction vessel and to 11.30 mmHg with the reaction vessel immersed in a 50°C-oil bath, and condensed at capillary C by immersing C in liquid nitrogen. Then hydrogen was introduced in the same way and mixed with the ethylene slowly by removing the liquid nitrogen from capillary C. The mixture was expanded into the reaction vessel and circulated through the reaction vessel by switching the 3-way taps; it had been preliminarily confirmed that under this condition the progress of reaction was practically negligible.

The methanol-dry ice bath was now replaced by an oil bath regulated at 50°C and measurements of both the pressure of the reaction system and the electric resistance of the catalyst were continued to deep conversion. Then evacuation of the reaction vessel was conducted with the reaction vessel immersed in the methanol-dry ice bath, followed by repetition of another run of reaction in the same way as above. In such a manner several runs were successively carried out.

Results and Discussion

1. Observed pressure-time curves and $V-P_H$ curves uncorrected for catalyst poisoning

As confirmed by a preliminary experiment using hydrogen, about five minutes were required for the reaction system to attain thermal equilibrium after immersing the vessel in the 50°C-oil bath; owing to this time lag the observed pressure-time curves in the initial stage of reaction took such forms

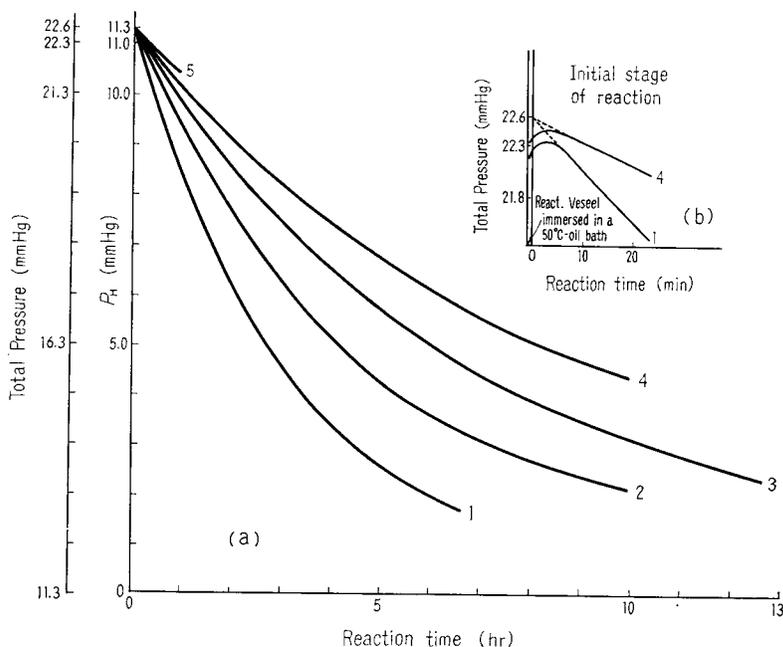


Fig. 3 Observed pressure-time curves for the nickel-catalyzed reaction at 50°C of ethylene and hydrogen each of 11.30 mmHg initial partial pressure. The nos. represent those runs successively conducted in the increasing order of nos. on the same catalyst with evacuation at -80°C between runs.

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as shown by the solid lines in Fig. 3 (b), so that the pressure-time curves in the initial stage of reaction, expected to be observed in the absence of this time lag, were decided by extrapolation as shown by the dotted lines in Fig. 3 (b). In Fig. 3 (a) are shown the pressure-time curves, corrected for this time lag, for five successive runs conducted in the increasing order of nos. indicated.

From Fig. 3 (a) we can determine graphically the value of V as a function of P_H as shown by the solid lines in Fig. 4.

2. V - P_H curves corrected for catalyst poisoning

As is evident from Fig. 3 (a), the activity of catalyst decreased with use. Here arise the following questions concerning the nature of the poisonous matter: does the poisonous matter result from the formation of acetylenic complex⁹ due to contact of ethylene with nickel catalyst or from the evacuation treatment¹⁰ adopted in conducting successive runs? and is the poisonous

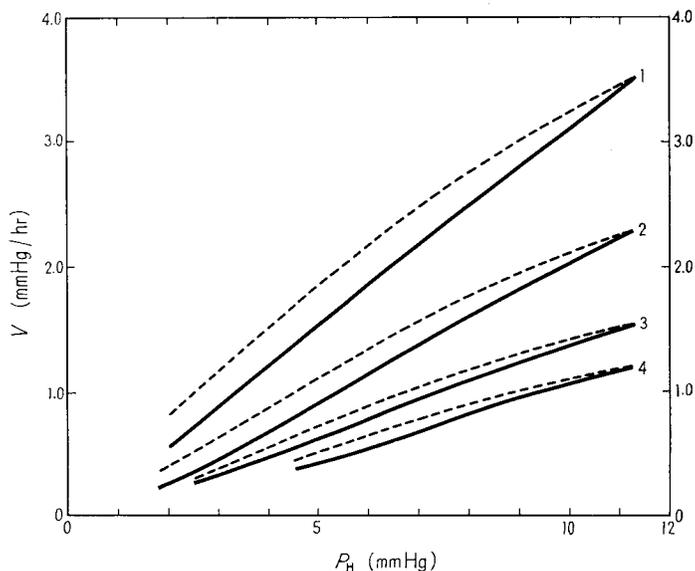


Fig. 4 Plot of V vs. P_H .

— obtained directly from Fig. 3 (a).
 obtained by correcting the above solid lines for the decrease of catalyst activity based on Figs. 2 and 5; catalytic activities corresponding to each curve are:

curve 1	...	specific activity	1.0
" 2	...	"	0.65
" 3	...	"	0.44
" 4	...	"	0.33

matter capable of being hydrogenated in the reaction atmosphere employed and removed from the surface of catalyst? These problems were investigated preliminarily with the result that the poisonous matter was neither formed by the evacuation treatment nor removed by hydrogen, hence we might take the poisonous matter to become accumulated on the catalyst surface according as the contact of the catalyst with reacting mixtures prolonged. On the basis of this information about the nature of the poisonous matter the activities of catalyst in use were estimated as shown in Fig. 5 by making use of the initial velocities of each run. From Fig. 5 the activity of catalyst may be considered to have varied from 1.0 to 0.65, 0.65 to 0.44, 0.44 to 0.33 to and 0.33 to 0.29 during the first, second, third and fourth run, respectively.

From Figs. 3 and 5 we can estimate the catalytic activity at arbitrary reaction times in each run, hence we can correct the solid lines in Fig. 4 for catalyst poisoning to obtain the $V-P_H$ curves expected when the catalyst activity had maintained constant at 1.0, 0.65, 0.44 and 0.33, respectively; these corrected $V-P_H$ curves are shown by the dotted lines in Fig. 4.

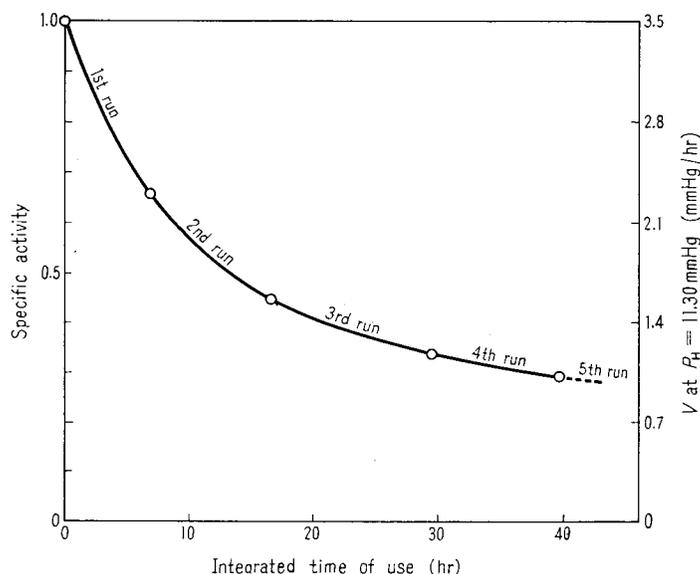


Fig. 5 Decrease of the catalytic activity with use. The values of the integrated time of use were obtained from Fig. 3, and those of V at $P_H = 11.30$ mmHg from Fig. 4. The value of the initial velocity in the first run was taken as standard of the specific activity determination.

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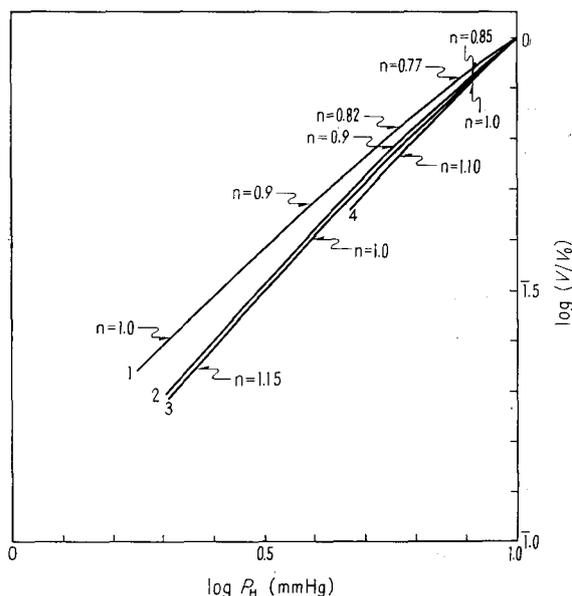


Fig. 6. Plot of $\log (V/V_0)$ vs. $\log P_H$ constructed from the dotted curves of Fig. 4. The values of n represented were obtained graphically according to Expression (8).

3. Values of n

The value of n , as a function of P_H , at specific activity = 1.0, 0.65, 0.44 and 0.33 is determined by plotting $\log (V/V_0)$ against $\log P_H$ and measuring the slope of the plot as shown in Fig. 6.

It is seen from curve 1 of Fig. 6 that the value of n for clean catalyst increases approximately from 0.8 to 1.0 as P_H decreases from 10 to 2 mmHg, which change is in approximate agreement with the theoretically deduced change of from about 0.8 to 1.2. It is thus concluded that the revised $\mathfrak{R}(Ib)$ expression (3) is semi-quantitatively suitable and accordingly the MASUDA's experimental result is reliable.

As for the change of n with catalyst poisoning we see from Fig. 6 that increasing degree of catalyst poisoning causes the value of n to increase by about 0.3, which is in approximate agreement with the theoretical value of 0.15. Thus we have had an experimental support for the validity of the MATSUZAKI *et al.*'s inference under study.

Points to be investigated in future are (i) to survey the revised $\mathfrak{R}(Ib)$ expression (3) from the standpoint of statistical mechanical theory of chemical kinetics and (ii) to consider the mechanism by which the catalyst poisoning

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exerts uneven inhibiting effects upon constituent elementary steps.

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