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UNEVEN INHIBITING EFFECTS OF CATALYST POISONING UPON ELEMENTARY STEPS CONSTITUTING THE NICKEL-CATALYZED HYDROGENATION OF ETHYLENE

By

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Abstract

Previous experimental data ^{2,3)} on the nickel-catalyzed deuteration of light ethylene have been analyzed for the effect of poisoning on the individual constituent steps of the reaction. The constituent steps were taken to be those of the associative mechanism⁵⁾ which has hitherto been established by a number of evidences. The catalyst was not intentionally poisoned but taken increasingly poisoned by repetition of the catalyzed deuteration followed by evacuation at the same temperature.

Effect of poisoning on the rates of individual constituent steps was thus determined from the changes of partial pressure, deuterium atomic fraction and non-equilibrium fraction of hydrogen.

The result shows that the poisoning exerted uneven inhibiting effects upon different steps.

Introduction

In heterogeneous catalysis on metallic catalysts the catalyst poisoning is of very frequent occurrence, usually acting as nuisance for the measurement of important characteristic quantities of reaction such as the order of reaction, activation energy, *etc.* It is hence of significance to investigate mechanistically the effect of catalyst poisoning upon the reaction.

The latest mechanistic research on the catalyst poisoning was made by HERINGTON and RIDEAL¹⁾ in 1944, who derived a rule on the basis of the model of homogeneous surface, that the inhibiting effect on an adsorption process became more pronounced with increasing number of sites participating in the act of adsorption, which was verified by a variety of experimental results then available.

In 1959 one of the present authors, studying^{2,3)} the nickel-catalyzed

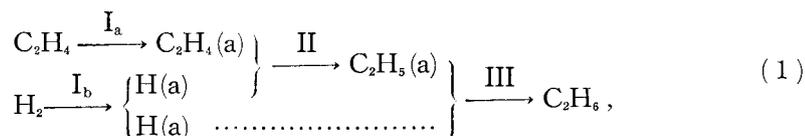
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deuteration*) of ethylene, observed a phenomenon, which might appear to be a sort of selective poisoning, that the catalyzed hydrogenation was poisoned more than the concurrent hydrogen exchange between deuterium and ethylene; a recent work⁴⁾ by two of the present authors has revealed that the hydrogen exchange is caused between hydrogen and ethylene only and not between ethane and other species.

The purpose of the present paper is to deduce the effect of poisoning upon different steps constituting the reaction in question from the above-mentioned experimental result^{2,3)}.

The set of steps underlying the present analysis is those of the associative mechanism, which was originally put forward by HORIUTI and POLANYI⁵⁾ and has gathered a number of experimental evidences^{2-4, 6-12)}. The set of steps is schematically represented as



where (a) denotes the adsorbed state and I_a , *etc.* signify each elementary step. The poisoning was taken to advance with the repetition of the experiment of the catalyzed deuteration followed by evacuation, no particular poisoning treatment being performed intentionally.

The conclusion is that the inhibition of step III by the catalyst poisoning is greater than that of step I_b . With a view to verifying this conclusion, the kinetics of the nickel-catalyzed hydrogenation of ethylene has been observed by repeating the run on the same catalyst to advance the poisoning stepwise, which will be reported in the subsequent paper.

Relative magnitudes of rates of elementary steps

For the sake of analyses in view, the rates of increase of P_2 and PD in course of the catalyzed deuteration of ethylene are derived as functions of the rates of the elementary steps of the scheme (1), ignoring the isotopic difference in reactivity between P and D. Below are summarized the notations to be used:

$v_+(\text{I}_b)$, $v_+(\text{III})$: forward unidirectional rates of step I_b , III.
 $v_-(\text{I}_b)$, $v_-(\text{III})$: backward unidirectional rates of step I_b , III.

*) In the present paper protium or deuterium is denoted by P or D, respectively; hydrogen is used as a generic term for protium and deuterium and H as a generic notation for P and D.

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- P_{H_2}, P_{PD}, P_{P_2} : partial pressures of H_2 , PD, P_2 .
 x^D : deuterium atomic fraction of the adsorbed hydrogen atoms H(a).
 V : steady rate of reaction $C_2H_4 + H_2 = C_2H_6$ as expressed by, e.g., $V \equiv -dP_{H_2}/dt$ in the absence of side reactions.

The rate of increase of P_2 is given by

$$dP_{P_2}/dt = v_-(I_b)(1-x^D)^2 - v_+(I_b)P_{P_2}/P_{H_2}; \quad (2)$$

the first and second terms on the right-hand side correspond to the rate of increment of P_2 by the backward and forward act of I_b , respectively. Similarly, the rate of increase of PD is given by

$$dP_{PD}/dt = 2v_-(I_b)x^D(1-x^D) - v_+(I_b)P_{PD}/P_{H_2}. \quad (3)$$

We have on the other hand the steady state condition, *i.e.*

$$V \equiv -dP_{H_2}/dt = v_+(I_b) - v_-(I_b) = v_+(III) - v_-(III),$$

which is reduced on the basis of the experimental information⁴⁾ $v_-(III) \approx 0$, as

$$-dP_{H_2}/dt = v_+(I_b) - v_-(I_b) = v_+(III). \quad (4)$$

Eqs. (2) and (3) are now transformed with reference to Eq. (4) as

$$-dP_{P_2}/dP_{H_2} = \left\{ v_+(I_b)/v_+(III) \right\} \left\{ (1-x^D)^2 - P_{P_2}/P_{H_2} \right\} - (1-x^D)^2 \quad (5)$$

and

$$-dP_{PD}/dP_{H_2} = \left\{ v_+(I_b)/v_+(III) \right\} \left\{ 2x^D(1-x^D) - P_{PD}/P_{H_2} \right\} - 2x^D(1-x^D). \quad (6)$$

The $v_+(I_b)/v_+(III)$ is determined by eliminating x^D from Eqs. (5) and (6) on the base of the values of $-dP_{P_2}/dP_{H_2}$, $-dP_{PD}/dP_{H_2}$, P_{P_2}/P_{H_2} and P_{PD}/P_{H_2} which are calculated from the experimental data^{2,3)} as shown in the subsequent section.

Evaluation of $v_+(I_b)/v_+(III)$ from experimental data

It is readily seen from the experimental results^{2,3),*)} that the $P_{H_2} \sim Y$ and $Y \sim 1-u$ curves (Y : deuterium atomic fraction of hydrogen; u : equilibrium fraction of hydrogen with respect to reaction $P_2 + D_2 = 2PD$) vary similarly with increasing degree of the catalyst poisoning at every temperature of observation, the typical cases referred to in Table 1 being analyzed in the present research.

*) These experimental results were obtained statically, which have recently been checked with a carefully constructed circulation system. The previous result was thus reproduced, the possibility of diffusion more or less controlling being thus excluded.

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TABLE 1. Materials of the present analyses^{2,3)}.Initial partial pressure of H₂ and
C₂H₄: 10 mmHg

Run no. ^{a)}	React. Temp. (°C)	Catalyst used (g)	Degree of ^{b)} poisoning
5-1	50	0.045	0
5-3			0.96
6-1	100	0.045	0
6-2			0.84
6-3			0.95
8-1	150	0.045	0
8-2			0.67

a) A set of nos. such as $m-n$ denotes the n -th run of m -th series; every series was initiated with a new catalyst and consisted of successive runs of catalyzed deuteration each followed by evacuation with the same catalyst at a certain constant temperature shown in the second column of the Table.

b) 1. The degree of poisoning is defined^{2,3)} for the n -th run of a series as

$$1 - \left(-\frac{dP_{H_2}}{dt} \right)_{0,n\text{-th}} / \left(-\frac{dP_{H_2}}{dt} \right)_{0,1st},$$

where $(-dP_{H_2}/dt)_{0,n\text{-th}}$ is the initial rate of hydrogenation of the n -th run.

2. It has recently been experimentally confirmed that the rates were reproducibly observed at the same partial pressures of reactants in course of a run unless intervened by evacuation.

The $P_{H_2} \sim P_{PD}$ and $P_{H_2} \sim P_{P_2}$ relations were first derived from the observed $P_{H_2} \sim Y$ and $Y \sim 1-u$ curves as follows. We have

$$1 - Y = (P_{PD,e} + 2P_{P_2,e}) / 2P_{H_2}$$

and

$$4 = (P_{PD,e})^2 / P_{P_2,e} (P_{H_2} - P_{PD,e} - P_{P_2,e}),$$

where $P_{PD,e}$ and $P_{P_2,e}$ are the values of P_{PD} and P_{P_2} in the equilibrium of $P_2 + D_2 = 2PD$, respectively. The above two relations determine the value of $P_{PD,e}$ as $P_{PD,e} = 2P_{H_2} Y(1-Y)$, which is related with P_{PD} as $u \equiv P_{PD} / P_{PD,e}$; hence

$$P_{PD} = 2P_{H_2} Y(1-Y) u. \quad (7)$$

The value of P_{P_2} is now given on substituting P_{PD} from Eq. (7) into the relation $1 - Y = (P_{PD} + 2P_{P_2}) / 2P_{H_2}$ as

$$P_{P_2} = P_{H_2} (1-Y) (1-Yu). \quad (8)$$

Eqs. (7) and (8) enable us to calculate the $P_{H_2} \sim P_{PD}$ and $P_{H_2} \sim P_{P_2}$ relations from

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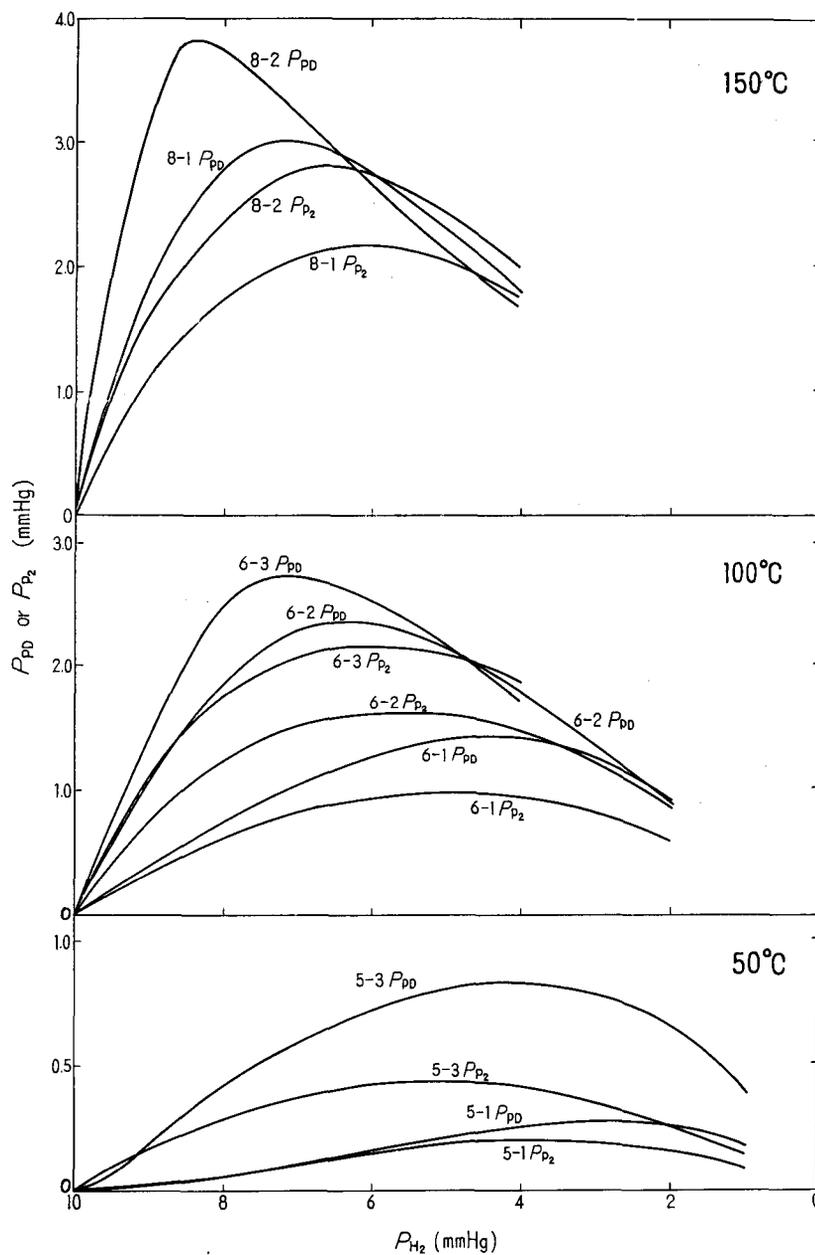


Fig. 1. The change of the partial pressures P_{PD} and P_{P_2} respectively of PD and P_2 in course of deuteration of 10 mmHg ethylene with 10 mmHg D_2 on nickel. The nos. correspond to those of the runs listed in Table 1.

the $P_{H_2} \sim Y$ and $Y \sim 1 - u$ curves as shown in Fig. 1.

Quantities dP_{PD}/dP_{H_2} , dP_{P_2}/dP_{H_2} , P_{P_2}/P_{H_2} and P_{PD}/P_{H_2} are determined from Fig. 1, hence $v_+(I_b)/v_+(III)$ for each series of runs by Eqs. (5) and (6) by eliminating x^D from them, as shown in Fig. 2.

Effect of catalyst poisoning upon steps I_b and III

As seen from Fig. 2 and Table 1, the values of $v_+(I_b)/v_+(III)$ increase with increase of the degree of catalyst poisoning in each series at the same P_{H_2} . It can hence be concluded that the catalyst poisoning exerts greater inhibiting effect upon step III than upon step I_b.

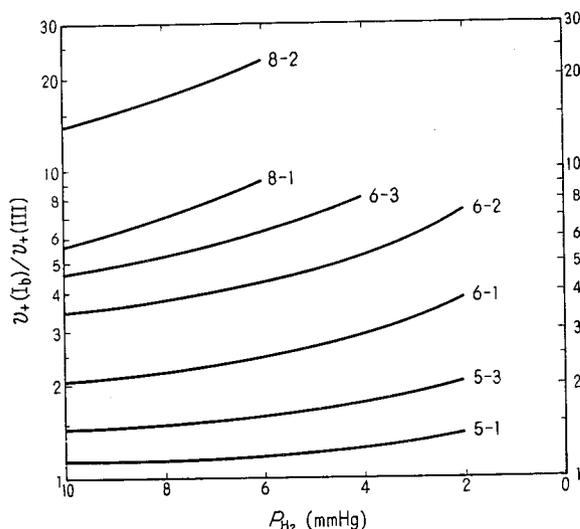


Fig. 2. $v_+(I_b)/v_+(III)$ vs. P_{H_2} calculated from the data in Fig. 1. The nos. correspond to those of the runs listed in Table 1.

The uneven inhibitions of steps I_b and III are now numerically expressed as below. Let $v_+(I_b)_{n-th,a}$ be the value of $v_+(I_b)$ at $P_{H_2}=a$ mmHg in the n -th run of a certain definite series. The ratio $v_+(I_b)_{n-th,a}/v_+(I_b)_{1st,a}$ or $v_+(III)_{n-th,a}/v_+(III)_{1st,a}$ ($n \neq 1$) is referred to, in what follows, as **the residual activity**, respectively, of step I_b or III for the n -th run at $P_{H_2}=a$ mmHg.

The residual activities are evaluated as follows for $P_{H_2}=10$ mmHg, where the initial rates of hydrogenation $(-dP_{H_2}/dt)_0$ are measured as shown in Table 1. Those $v_+(III)_{2nd,10}/v_+(III)_{1st,10}$ and $v_+(III)_{3rd,10}/v_+(III)_{1st,10}$ of step III are calculated from the data in Table 1 by Relation (4) as shown in Table 2. Those $v_+(I_b)_{2nd,10}/v_+(I_b)_{1st,10}$ and $v_+(I_b)_{3rd,10}/v_+(I_b)_{1st,10}$ of step I_b are calculated

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from the values of $v_+(\text{III})_{n\text{-th},10}/v_+(\text{III})_{1\text{st},10}$ thus determined and those of $v_+(\text{I}_b)_{n\text{-th},10}/v_+(\text{III})_{n\text{-th},10}$ shown in Fig. 2 according to the identity

$$\frac{v_+(\text{I}_b)_{n\text{-th},10}}{v_+(\text{I}_b)_{1\text{st},10}} = \frac{v_+(\text{I}_b)_{n\text{-th},10}/v_+(\text{III})_{n\text{-th},10}}{v_+(\text{I}_b)_{1\text{st},10}/v_+(\text{III})_{1\text{st},10}} \times \frac{v_+(\text{III})_{n\text{-th},10}}{v_+(\text{III})_{1\text{st},10}}$$

as shown in Table 3.

TABLE 2. Values of $v_+(\text{III})_{2\text{nd},10}/v_+(\text{III})_{1\text{st},10}$ or $v_+(\text{III})_{3\text{rd},10}/v_+(\text{III})_{1\text{st},10}$ for the 2nd or 3rd runs.

Run no.	$\frac{v_+(\text{III})_{2\text{nd},10}}{v_+(\text{III})_{1\text{st},10}}$	$\frac{v_+(\text{III})_{3\text{rd},10}}{v_+(\text{III})_{1\text{st},10}}$
5-3		0.04
6-2	0.16	
6-3		0.05
8-2	0.33	

TABLE 3. Values of $v_+(\text{I}_b)_{2\text{nd},10}/v_+(\text{I}_b)_{1\text{st},10}$ or $v_+(\text{I}_b)_{3\text{rd},10}/v_+(\text{I}_b)_{1\text{st},10}$ for the 2nd or 3rd run.

Run no.	$\frac{v_+(\text{I}_b)_{2\text{nd},10}}{v_+(\text{I}_b)_{1\text{st},10}}$	$\frac{v_+(\text{I}_b)_{3\text{rd},10}}{v_+(\text{I}_b)_{1\text{st},10}}$
5-3		0.056
6-2	0.294	
6-3		0.126
8-2	0.891	

Comparison of Tables 2 and 3 shows quantitatively that the catalyst poisoning inhibits step III more than step I_b , and that this tendency is amplified with increase of reaction temperature and the degree of catalyst poisoning.

The residual activities are not individually calculable at other P_{H_2} values, while the ratio of that of step I_b to that of III is determined by the identity

$$\begin{aligned} \frac{v_+(\text{I}_b)_{n\text{-th}}/v_+(\text{III})_{n\text{-th}}}{v_+(\text{I}_b)_{1\text{st}}/v_+(\text{III})_{1\text{st}}} &= \frac{v_+(\text{I}_b)_{n\text{-th}}/v_+(\text{I}_b)_{1\text{st}}}{v_+(\text{III})_{n\text{-th}}/v_+(\text{III})_{1\text{st}}} \\ &= \frac{\text{Residual activity of step } \text{I}_b}{\text{Residual activity of step III}} \end{aligned} \quad (9)$$

The first member of the above equation is evaluated from Fig. 2, hence the

values of the ratio in question given by the last member, which are plotted against P_{H_2} in Fig. 3. We see from Fig. 3 that the ratio representing the degree of the unevenness is approximately constant irrespective of P_{H_2} value, and that it becomes more pronounced with rise of reaction temperature and increase of the degree of catalyst poisoning, noting that the abscissa corresponds

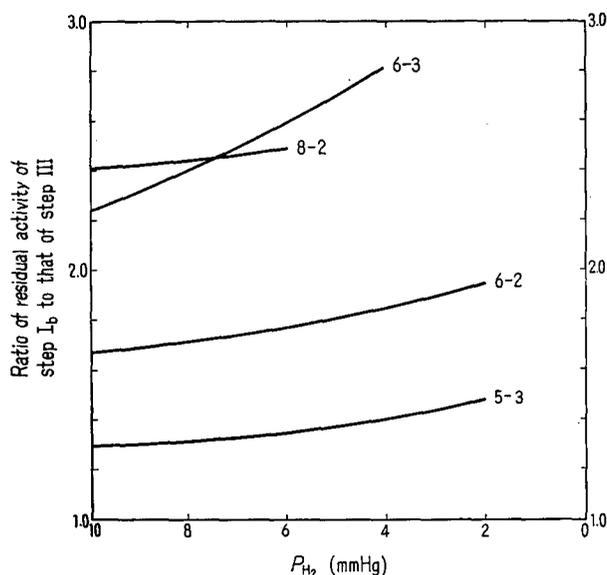


Fig. 3. The ratios of residual activity of step I_b to that of step III as calculated from the data of Fig. 2 by Eq. (9). The nos. correspond to those of the runs listed in Table 1.

to the line for the 1st run for every series; it follows from Fig. 3 and the values of the degree of catalyst poisoning of Table 1 that **on heavily poisoned catalyst** the ratios of the residual activity of step I_b to that of step III are 1.5 at 50°C, 2–2.5 at 100°C and 3–3.5 at 150°C.

Question arises now how the catalyst poisoning exerts uneven inhibiting effects upon step I_b and III, which might better be left open until more experimental results on the catalyst poisoning have been accumulated. In this connection the kinetics of the nickel-catalyzed hydrogenation of ethylene has been experimentally investigated with the result that the rate law shifted with increasing degree of catalyst poisoning toward that with step III determining the rate from that with the rate governed by I_b , which will be reported in the subsequent paper.

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