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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 11-Activity of Reduced Tungsten Surface

By

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Abstract

An evaporated tungsten film was heated in hydrogen gas and evacuated both at 300°C as usually done for activation of metallic catalysts and the reactivity of hydrogen persistently remained on this film was examined by the reaction with gaseous deuterium and ethylene. It was found that the hydrogen preadsorbed as such participated actively in these reactions and was used preferentially for ethane formation.

RYE's theory that the optimum temperature, T_X , of ethylene hydrogenation catalyzed by metals is caused by the complete decomposition of adsorbed ethylene into carbon deposit on catalyst surface, was found to be agreeable exceptionally in the case of tungsten catalyst, on reference to the following experimental results. The initial rate of ethylene hydrogenation on tungsten reduced at 300°C prior to each run of hydrogenation was reproducible when the reaction temperature was not raised above T_X , whereas it decreased remarkably by a run of hydrogenation conducted at a temperature above T_X . Thus, T_X was not observed in a case of that the reaction temperature was lowered successively from one above T_X .

Hydrogen exchange between deuterium and ethylene was scarce throughout deuteration of light ethylene conducted on a tungsten film preliminarily reduced by deuterium at 300°C. The relative amounts of d_0 - and d_2 -ethane formed at an early stage of deuteration exceeded remarkably those expected for the random distribution of D atoms in ethane, whereas the latter was agreeable with ethanes formed at the later stage. These experimental results were discussed on reference to RYE and HANSEN's results of flash desorption spectra of hydrogen and ethylene preadsorbed on tungsten and concluded that tungsten surface is divided into two parts with respect to its catalytic activity. The one is active for the self-hydrogenation of ethylene and not responsible for the steady hydrogenation on account of it being covered by acetylenic complexes. On the other part the steady hydrogenation by strongly adsorbed hydrogen proceeds *via* a set of steps similar to that proposed for the case of nickel catalyst, however, the steps of adsorption of ethylene and hydrogen are nearly irreversible in this case.

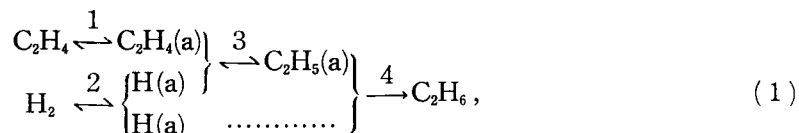
The rapid equilibration of a mixture of light and heavy hydrogen during ethylene hydrogenation over tungsten catalyst was finally concluded to be caused by ELEY mechanism proceeding on the latter part of the surface.

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Introduction

In the study of the present series, ethylene hydrogenation was detailedly examined by the use of evaporated nickel films as catalyst and deuterium as tracer^{1,2)}. It was found that dissociative adsorption of ethylene evolving hydrogen gas took place at a very early stage of the hydrogenation and it was practically eliminated in the run of hydrogenation conducted on a nickel film once used for the reaction or further reactivated by treating it with hydrogen at 300°C and evacuated at the same temperature. By this treatment of nickel catalyst kinetics of the hydrogenation, inclusive of the deuterium distribution in products of deuteration of light ethylene, became reproducible.

On the basis of results of these reproducible observations it was concluded²⁾ that ethylene hydrogenation catalyzed by nickel is caused steadily by a set of steps,



and it is rate-determined by step 2 or 4 at temperatures below or above the optimum, T_x . The experimental results ever obtained with respect to ethylene hydrogenation and its associated reactions, *e.g.*, hydrogen exchange between deuterium and ethylene, catalyzed by Pd, Pt and Ni were consistently interpreted²⁾ on the basis of above mechanism. An optimum catalyst for ethylene hydrogenation was then predicted in connection with the initial heat of hydrogen adsorption on metals, Rh, Pd, Pt, Ni, Fe and W, on the basis of above mechanism and the observed activities⁴⁾ of these metals for ethylene hydrogenation. Tungsten was found exceedingly poor in its hydrogenation activity, deviating remarkably from a general rule concluded for all of transition metals mentioned above. In connection with this peculiarity of tungsten it was found in the previous work⁵⁾ that equilibration of a mixture of P_2 (P denotes light hydrogen, *i.e.*, protium in what follows) and D_2 was completed at a very early stage of ethylene hydrogenation exceptionally over tungsten catalyst even at a temperature as low as -45°C , and, furthermore, the relative amounts of deuterio-ethylenes were wide of those of the random distribution of D atoms among them throughout the course of hydrogenation. This fact suggests that the mechanism of ethylene hydrogenation catalyzed by tungsten differs far from the case of nickel and

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other metallic catalysts.

RYE and HANSEN⁶⁾ have recently observed a flash desorption spectrum of ethylene preliminarily adsorbed on tungsten and, on the basis of its results, one of the authors⁷⁾ proposed a theory that the optimum temperature of ethylene hydrogenation catalyzed by metals is the one, above which the complete decomposition of adsorbed ethylene to carbon on catalyst surface and, accordingly, retardation of ethylene hydrogenation is predominantly accelerated. This theory was, however, denied⁸⁾ in the case of iridium catalyst where T_x was *ca.* 50°C, far below the one, $T_x > 400^\circ\text{K}$, presumed by RYE⁷⁾. The result was interpreted by the same mechanism as in the case of nickel.

In the present work hydrogen irreversibly adsorbed on tungsten film at 300°C was first investigated with respect to its amount and reactivity for hydrogen exchange and ethylene hydrogenation. The optimum temperature of ethylene hydrogenation was next examined with special reference to RYE's theory and finally the mechanism of ethylene hydrogenation was reexamined by observation of deuterium distribution in gaseous hydrogen, ethylene and ethane in course of deuteration of light ethylene. In the previous analysis⁵⁾ of the deuterium distribution, ethane was not observed on account of its low sensitivity in analysis with a mass spectrometer alone. It was now improved by the use of gaschromato-mass spectrometer.

Experimental

Apparatus: It is a static system quite similar to those used in the previous works^{1,5,8)} and sketched in Fig. 1. The capacity of reaction vessel, R, was

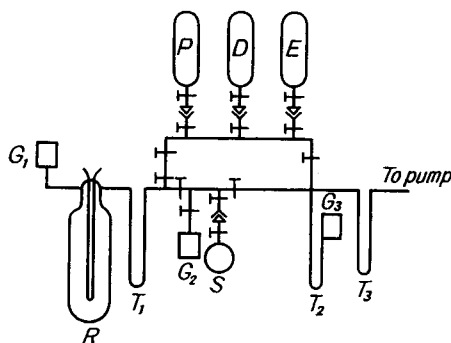


Fig. 1. Diagram of the reaction apparatus.

G_1 : PILANYI gauge, R: reaction vessel, T_1 : dry ice traps, G_2 : McLEOD gauge, S: sampling vessel, T_2 , T_3 : liquid nitrogen trap, G_3 : vacuum gauge, P, D, E: reservoir of protium, deuterium and ethylene, respectively, M: manometer.

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usually *ca.* 150cc and the geometric area of the film was *ca.* 100cm². PILANYI gauge, G₁, was calibrated by the use of McLEOD gauge, G₂.

Materials: Cylinder hydrogen and deuterium gas were purified by passing them through Pd-Ag thimble and liquid nitrogen trap. Cylinder ethylene was repeatedly distilled in *vacuo* until its vapour pressure at liquid nitrogen temperature decreased as low as 10⁻² mmHg. Tungsten wire of 0.2 mm diameter was preliminarily reduced by hydrogen and evacuated both at 500°C and evaporated onto the inner surface of reaction vessel at 300°C as thick as a complete mirror was formed.

Analysis: Silica gel column of one meter length at a room temperature was connected with HITACHI RMU-6 mass spectrometer through a helium separator made of porous quartz tube. Sampled gas of deuteration of light ethylene was first introduced directly into mass spectrometer through a liquid nitrogen trap and a by-pass for the analysis of relative amounts of P₂, PD and D₂. The relative heights of peaks of *m/e*=2, 3 and 4 were calibrated for the relative amounts on reference to a standard mixture of these isotopic hydrogen. The gas condensed in the trap was then sent by helium flow into the silica gel column and gaschromatographic peaks and mass spectra of individual hydrocarbons were registered. The peaks of gaschromatograph were calibrated by the use of standard mixtures of ethylene and ethane. The electron accelerating voltage of mass analysis was 70 volt. Isotopic effects on fragmentation of a hydrocarbon in mass analysis was neglected in calculation of mass spectra of each deuterio-isomers of hydrocarbons. Error in evaluation of relative amounts of deuterio-isomers of hydrocarbons may, thus, be as large as few percents.

Results

A. Amount and reactivity of hydrogen irreversibly adsorbed on tungsten.

Amount and reactivity of hydrogen persistently remained on a reduced tungsten surface was examined according to ELEY's method⁹⁾ of hydrogen exchange. Tungsten film was treated by 10 mmHg protium gas at a specified temperature for 30 min and evacuated at the same temperature. Deuterium gas of *ca.* 0.15 mmHg was then introduced onto the film at 0°C and its isotopic composition was analyzed time to time of contact. The results are given in Table 1. The values of *n_p* in the last column of the Table are the number of protium atoms turned into gas phase and it depends on the time and temperature of preliminar evacuation of the film as given in Fig. 2 and Table 2.

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TABLE 1 Exchange reaction at 0°C between D₂ gas and protium preadsorbed on a tungsten film at 300°C*.

Time of contact, sec	Amount of D ₂ introduced, 10 ¹⁷ molecules	Composition of gas, %			Number, n_p , of exchanged P atoms, 10 ¹⁷ atoms
		P ₂	PD	D ₂	
15	8.11	0.5	12	87.5	1.02
30	8.14	1	14	85	1.20
45	6.90	1	16	83	1.28
60	0.18	1	17	82	1.70
180	8.36	1	17	82	1.70
180	8.45	1	17	82	1.84
300	8.46	1	18	81	1.86

* Before each run of exchange tungsten film was heated in 10 mmHg protium gas at 300°C for 30 min and evacuated at the same temperature for 3 hrs.

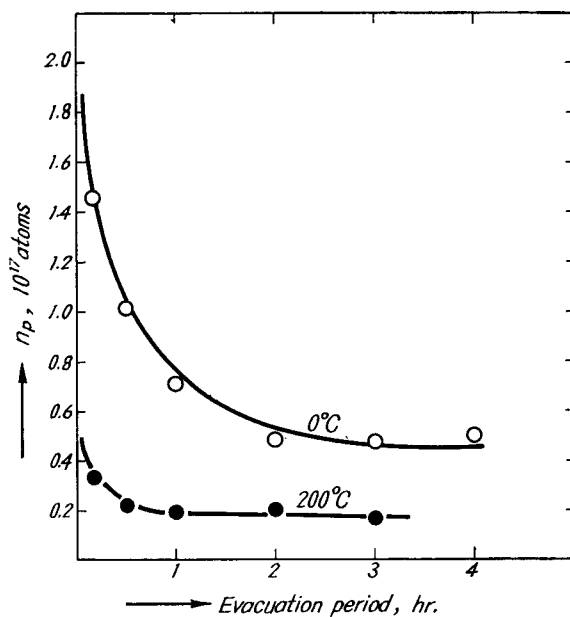


Fig. 2. Dependence of amount, n_p , of protium atoms turned out from tungsten surface into gas phase by exchange with D₂ on the period and temperature of preliminar evacuation of adsorbed protium.

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TABLE 2. Maximum amount of exchanged protium preadsorbed on a tungsten film*.

Temp. of evacuation, °C	0	100	200	300
n_p , 10^{17} atoms	5.14	3.14	2.00	1.88

* Before each run of exchange tungsten film was reduced by hydrogen and evacuated both at 300°C similarly to runs of Table 1. It was then brought into contact with 10 mmHg protium for 30 min and evacuated for 3 hrs both at a temperature specified in this Table. Deuterium was introduced at 0°C.

TABLE 3. Distribution of D atoms persistently remained on a tungsten film reduced by D_2 at 300°C in the products of reaction of an equimolar mixture of C_2P_4 and P_2 conducted on the film at -45°C. Initial total pressure of the mixture was *ca.* 0.7 mmHg.

Conversion, %	Hydrogen, %			Ethylene, %					Ethane, %						
	d_0	d_1	d_2	d_0	d_1	d_2	d_3	d_4	d_0	d_1	d_2	d_3	d_4	d_5	d_6
42.3	98	1	1	96	4	0	0	0	88	6	4	2	0	0	0
D atomic fraction	0.017			0.009					0.034						

The reactivity of irreversibly adsorbed hydrogen for ethylene hydrogenation was examined by introduction of a mixture of C_2P_4 and P_2 onto a tungsten film preliminarily heated in 10 mmHg D_2 gas at 300°C and evacuated for 3 hrs at the same temperature. An example of the results are given in Table 3, where the reaction time was 18 seconds. A tungsten film preliminarily heated in protium or deuterium gas of *ca.* 10 mmHg at 300°C for 30 minutes and then evacuated at the same temperature for 3 hours will be called in what follows simply as one reduced by P_2 or D_2 , respectively.

B. Reproducibility of the rate of ethylene hydrogenation catalyzed by a reduced tungsten film.

With respect to RYB's theory⁷⁾ of the optimum temperature of ethylene hydrogenation, temperature dependence of the rate of ethylene hydrogenation was studied by the use of tungsten film reduced by P_2 . Equimolar mixture of C_2P_4 and P_2 was introduced over the film at *ca.* 0.8 mmHg of the initial total pressure and the hydrogenation rate, V_0 , was followed by the initial inclination of the total pressure registered by PILANYI gauge with a crude approximation of constant composition of the reacting gas.

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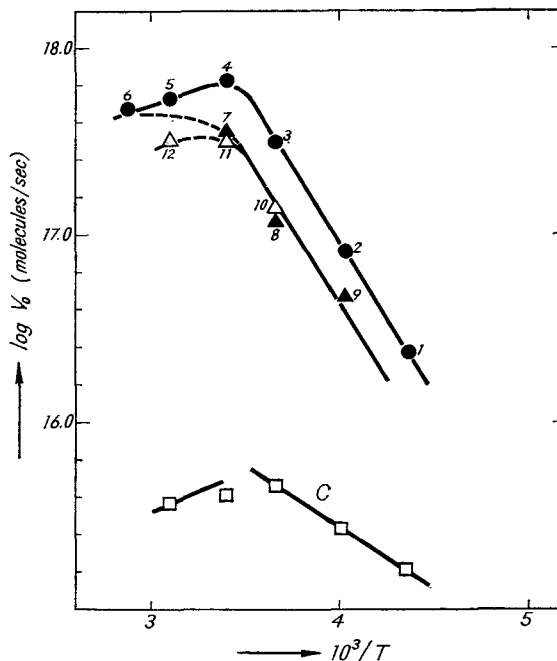


Fig. 3. Temperature dependence of the initial rate of ethylene hydrogenation on reduced tungsten film with an equimolar mixture of C_2P_4 and P_2 at *ca.* 0.8 mmHg of the initial total pressure. Curve C is a result on a carbided tungsten film.

The results are given in Fig. 3. Numerals annexed to each plots in the Figure indicates the sequence of runs of reaction. We see that T_x is observed at *ca.* 300°K in a case where reaction temperature was raised run to run, but absent when temperature was lowered from one above T_x . The rate, V_0 , is sufficiently reproducible so far as reaction temperature was never raised above T_x as seen from the results of runs 7 to 11. The rate was reproducible too by simple evacuation of film, irrespective of the reaction temperature, in a case of a carbided tungsten film, which was made by preliminarily heating a film in ethylene and evacuated both at 200°C.^{2,10} In this case T_x was again observed at *ca.* 300°K as shown by curve C in Fig. 3.

C. Deuteration of light ethylene.

Equimolar mixture of C_2P_4 and D_2 was introduced at *ca.* 0.7 mmHg over a tungsten film reduced by D_2 and its product was analyzed time to

TABLE 4. Deuteration of light ethylene catalyzed by a tungsten film reduced by D₂*.

Temp. °C	Time of reaction, sec	Conver- sion, %	D-atomic fraction			Relative amounts of deuterio-isomers, %																		
			H ₂	C ₂ H ₄	C ₂ H ₆	Hydrogen			Ethylene					Ethane										
						d ₀	d ₁	d ₂	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₁				
-45	19	52.7	0.959	0.014	0.202	1	7	92	94	6	0	0	0	0	31	23	40	6	0	0	0	(0 8 92)	(95.5 4.5 0 0 0)	(26 39 24 8 3 0 0)
-25	10	35.1	0.954	0.024	0.209	1	8	91	90	10	0	0	0	31	24	35	10	0	0	0	(0 9 91)	(90 10 0 0 0)	(25 38 24 9 3 0 0)	
0	4.6	50.5	0.948	0.031	0.195	1	8	91	89	10	1	0	0	34	26	30	10	0	0	0	(0 10 90)	(89 10.5 0.5 0 0)	(27 39 23 8 3 0 0)	
20	3.0	53.2	0.933	0.023	0.214	2	10	88	91	8.5	0.5	0	0	25	31	35	8	1	0	0	(0 13 87)	(91.5 8 0.5 0 0)	(24 38 25 9 4 0 0)	
50	4.0	60.3	0.889	0.040	0.276	4	17	79	86	12	2	0	0	16	28	37	13	6	0	0	(1.5 21 77.5)	(85.5 13.5 1 0 0)	(15 33 29 15 7 0 0)	
75	4.6	51.7	0.884	0.047	0.305	3	18	79	83	15	2	0	0	11	28	36	18	7	0	0	(1.5 20.5 78)	(82.5 16 1.5 0 0)	(10 29 30 18 12 0 0)	

* An equimolar mixture of C₂P₄ and D₂ was used at ca. 0.7 mmHg of the initial total pressure. Parenthesized figures shows the relative amounts of deuterio-isomers expected for the case of random distribution of D atoms among them with the observed D atomic fraction.

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time by gaschromato-mass spectrometer. Table 4 shows the results obtained at ca. 50% of Conversion at various reaction temperature, from which the optimum temperature is estimated at ca. 300°K coinciding with that in the case of hydrogenation with P₂. Conversion % is the percents of the amount of ethane in the sum of those of ethylene and ethane in sampled gas. Figure 4 shows the time courses of partial pressures, P_i's, in unit of 0.35 mmHg, of individual d_i-ethanes formed by a run at -45°C given in

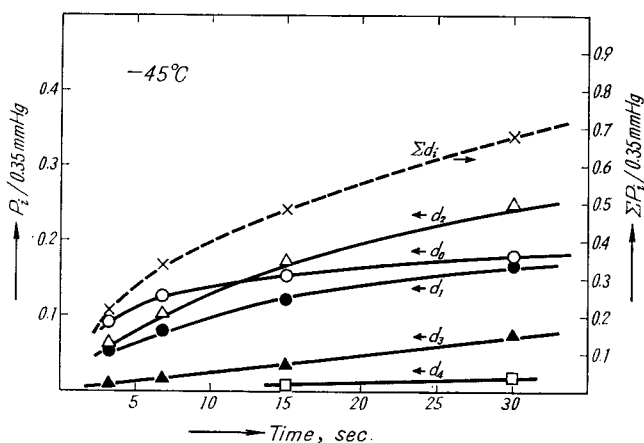


Fig. 4. Time courses of the partial pressures of d_i-ethanes in the products of deuteration at -45°C of light ethylene with equimolar D₂ catalyzed by a tungsten film preliminarily reduced by D₂. Initial total pressure is ca. 0.7 mmHg.

TABLE 5. Relative amounts of deuterio-isomers of ethane formed during 50~70% of conversion of the runs of deuteration given in Table 4.

Temp. °C	Relative amounts of d _n -ethanes, %							D atomic fraction
	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
-45	8	22	36	23	11	0	0	0.347
	(8	23	32	23	11	3	0)	
-25	8	25	32	29	6	0	0	0.336
	(9	25	32	25	7	2	0)	
0	7	23	31	27	12	0	0	0.349
	(8	23	32	23	11	3	0)	

TABLE 6. Deuteration of light ethylene catalyzed by a carbided tungsten film. Equimolar mixture of C_2P_4 and D_2 at *ca.* 0.7 mmHg of the initial total pressure.

Temp. °C	Time of reaction, sec	Conver- sion, %	D-atomic fraction			Relative amounts of deuterio-isomers, %														
			H ₂	C ₂ H ₄	C ₂ H ₆	Hydrogen			Ethylene					Ethane						
						d ₀	d ₁	d ₂	d ₀	d ₁	d ₂	d ₃	d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₅
-45	30	15.7	0.965	0.041	0.244	1	5	94	89	6	4	1	0	19	34	32	11	4	0	0
	120	50.0	0.866	0.173	0.269	4	18	78	62	18	11	7	2	16	33	30	14	6	1	0
	180	69.5	0.769	0.266	0.294	9	28	62	42	23	23	10	2	14	31	30	17	7	1	0
						(5.5	35.5	59)	(29	42	23	5	1)	(12.5	30.5	31.5	18	6.5	1	0)

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Table 4. These partial pressures were calculated according to the relation,

$$P_1 = (\text{Conversion } \%) \times (d_1\text{-ethane } \%) \times 10^{-4}.$$

Broken lines in the same Figure give the time course of $\sum P_1$.

Table 5 shows the relative amounts of d_1 -ethanes formed in the interval from 50 to 70 Conversion %. These values were calculated from those of P_1 's at 0.5 and 0.7 of $\sum P_1$ estimated on the basis of smoothed curves of Fig. 4. They are in accordance with the random distribution of D atoms in ethanes of observed D atomic fraction as given in parenthesis of the same Table. Table 6 gives the results obtained by a carbided tungsten film formed by the pretreatment similar to the case of curve C of Fig. 3.

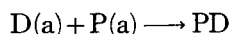
Discussion

With respect to irreversible adsorption of hydrogen on tungsten, ROBERTS¹¹⁾ has found that hydrogen occupies whole surface of tungsten at a room temperature and at a pressure as low as 10^{-4} mmHg and could not be evacuated at all up to *ca.* 700°K. ELEY⁹⁾ has found that whole amount of protium preadsorbed on tungsten at a room temperature was replaced by deuterium in gas phase at the same temperature within 3 min. With respect to the states of these adsorbed hydrogen, RYE and HANSEN⁶⁾ found three peaks, α , β_1 and β_2 with maxima at *ca.* 100, 390 and 570°K, respectively, in a flash desorption spectrum of hydrogen preadsorbed on tungsten wire at 95°K. The β_2 peak tailed up to temperatures as high as 1000°K. The adsorbed state of hydrogen on tungsten was classified, on the other hand, into four sorts by ROOTSEART *et al.*¹²⁾ on the basis of their field emission microscopic studies. This classification is based on the crystal planes of tungsten surface, which are not clear for the present evaporated film. The results of the present experiments will be discussed with reference to the above discrimination between adsorbed states, α , β_1 and β_2 , of hydrogen.

Table 1 shows that the exchanges at 0°C between *ca.* 0.15 mmHg deuterium and protium persistently remained on tungsten film preliminarily reduced by P_2 was so fast as to nearly complete within one minute. On reference to the result of flash desorption experiment mentioned above these protium atoms are responsible to a part of β_2 peak. Table 2 indicates, in agreement with ELEY's results, that hydrogen of β_1 peak exchanges so easily with gaseous hydrogen as that of β_2 .

As seen from Table 1, *ca.* 10^{17} protium atoms of β_2 appeared during initial 15 seconds. In this period the dilution of deuterium gas by protium

was a little. We see, thus, only 10^{-6} portion of D_2 molecules striking tungsten surface takes place exchange with adsorbed protium atoms. Tungsten surface in this experiment is initially occupied fully by preadsorbed P(a)'s of β_2 type and additional D(a)'s of β_1 and β_2 types. The adsorption of these hydrogen are irreversible at 0°C , as observed by ROBERTS¹¹, RYE and HANSEN⁶) and others, hence desorption of P(a)'s due to



is improbable.

Taking account of the small factor, 10^{-6} , of the exchange mentioned above, the exchange is plausibly caused by



which is the so-called ELEY's mechanism accompanied with reversible, molecular adsorption of hydrogen on sparsely distributed, vacant sites of adsorption.

Hydrogen atoms adsorbed on tungsten in β_2 type are found to participate actively in hydrogenation of ethylene as shown by Table 3. The results indicate that the number of D atoms transferred into gaseous hydrogen, ethylene and ethane are 4.0×10^{16} , 4.5×10^{16} and 1.63×10^{17} , respectively, and 2.5×10^{17} atoms as a whole. Taking into account the reaction vessel in this experiment being a little larger than that used in experiments of Tables 1 and 2, we see that whole of deuterium atoms participate in ethylene hydrogenation and preferentially transferred into ethane.

RYE's theory, mentioned in Introduction, on the optimum temperature of ethylene hydrogenation was now agreeable on reference to the results of Fig. 3. This figure shows that the initial rate of ethylene hydrogenation at temperatures below T_x was reproducible by reduction of tungsten by hydrogen and subsequent evacuation both at 300°C prior to each run of hydrogenation, whereas it decreased irreversibly by *ca.* 20% by one run or two conducted at a temperature above T_x . The optimum temperature was, thus, not observed by runs, 6 to 9 in Fig. 3, conducted successively by lowering the reaction temperature from one above T_x . In the previous work⁵) it was found that the initial rate of ethylene hydrogenation catalyzed by a freshly evaporated tungsten film at -45°C decreased in the second run by *ca.* 45% and further by repetition of runs, whereas the decrement was reproducibly *ca.* 30% when the film was reduced by hydrogen at 300°C prior to each run of hydrogenation. These facts are able to be understood by taking into account the dehydrogenated products, $C_2H_2(a)$ and (C_2) , of adsorbed ethylene, *i. e.*, acetylenic complex and carbon deposit, respectively, which have been

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concluded by RYE and HANSEN⁶⁾ on the basis of their results of flash desorption spectra of ethylene preadsorbed on tungsten. During ethylene hydrogenation on fresh tungsten surface, nearly a half of the surface is covered by $C_2H_2(a)$ and/or (C_2) even at temperatures as low as $-45^\circ C$, which retard adsorption of hydrogen and ethylene, hence ethylene hydrogenation, as observed in many works^{2,10)}. Acetylenic complex may be partly hydrogenated off from the surface and partly decomposed into (C_2) by the treatment of reactivation at $300^\circ C$, and consequently *ca.* 30% of the surface is constantly covered by (C_2) . Acetylenic complex decomposes further to (C_2) during ethylene hydrogenation at a temperature above T_x , *i. e.*, *ca.* $300^\circ K$ and even at a room temperature by simple evacuation¹³⁾. In consequence, a surface of tungsten preliminarily used for ethylene hydrogenation and subsequently reduced by hydrogen and evacuated at $300^\circ C$ is covered partly by carbon deposit as well as β_2 hydrogen atoms. RYE and HANSEN⁶⁾ found that ethane was evolved remarkably just after introduction of ethylene at $300^\circ K$ onto tungsten preliminarily treated by hydrogen at $95^\circ K$ and, further, that β_2 peak of hydrogen was not eliminated by ethylene introduced by an amount little but enough to cover tungsten surface. A part of tungsten surface responsible for β_1 peak of hydrogen desorption is, thus, considered to be covered by $C_2H_2(a)$ formed by the self-hydrogenation of ethylene and a steady hydrogenation may be caused principally on a part of surface responsible for β_2 hydrogen.

Above inferences on the activity of reduced tungsten surface was further confirmed by the results of reaction between D_2 and C_2P_4 , which are given in Table 4 and 5.

In the case of nickel catalyst, T_x of deuteration was found higher than that of hydrogenation with P_2 , by *ca.* 30° in agreement with our theory²⁾, which attributes¹⁴⁾ T_x to a change of a rate-determining step of hydrogenation from hydrogen chemisorption at $T < T_x$ to combination of adsorbed ethyl radical with adsorbed hydrogen atom at $T > T_x$. However, in the present case of tungsten catalyst, none of such an isotopic effect on T_x is expected, provided that T_x is caused by carbon deposition due to complete decomposition of adsorbed ethylene at temperatures above T_x and, further, that the process producing hydrogen adatoms on tungsten surface is not rate-determining at temperatures below T_x . In agreement with this expectation, we see from Table 4 that T_x is *ca.* $300^\circ K$ coinciding with that of the case of hydrogenation with P_2 , given in Fig. 3, and further with a temperature, above which RYE and HANSEN⁶⁾ found that decomposition of $C_2H_2(a)$ to (C_2) became perceptible.

With respect to the deuterium distribution in deuteration products of hydrocarbons, we may intuitively presume that the kinetic difference between fission or formation of C-P and C-D bonds may be large enough to affect the relative amounts of deuterio-substitution products of hydrocarbons. However, JONGEPIER and SACHTLER¹⁵⁾ calculated this effect on the relative amounts of deuterio-propanes formed by the hydrogen exchange between D₂ and propane catalyzed by metals and found that such an isotopic effect, although numerically large, can be eliminated with respect to the D distribution in products under the conditions used in many experiments. We discuss on this basis the observed results of Tables 4 and 5 in comparison with the random distribution of D atoms in products of deuteration.

Table 5 shows that evolution of d₀- and d₂-ethanes exceed their amounts expected in the case of random distribution of D atoms among deuterio-isomers of ethane. Such an evolution of d₀-ethane may be interpreted by dissociative adsorption of ethylene onto bare sites responsible to β₁ peak of hydrogen desorption spectrum. This results in self-hydrogenation of ethylene, $2C_2H_4 = C_2H_2(a) + C_2H_6$, hence in preferential evolution of d₀-ethane. Fast addition to ethylene of D atoms preliminarily adsorbed on sites of β₂ hydrogen results in the preferential evolution of d₂-ethane. In the experiment of Table 3, P(a)'s on β₂ sites and, accordingly, d₁-ethane was formed noticeably, however, the result shows again the formation of d₂-ethane exceeding its amount expected for the random distribution of D atoms.

In the case of deuteration of light ethylene deuterio-ethylenes are formed far slower than ethane as seen from Table 4. This result is wide of the previous one⁵⁾ and such a difference is supposed to be due to that the catalytic activity for reversible dissociation of ethylene proposed previously⁵⁾ was decreased in the present experiment by many times repetition of reactivation of one and the same tungsten film. Table 4 shows that distribution of D atoms are nearly random in gaseous hydrogen and ethylene, however, their D atomic fractions are quite different from each other. This fact suggests that the hydrogen intermediates of these hydrogen exchanges would be discriminated from each other. Furthermore, the results of Table 5 that deuterium were randomly distributed among isomers of ethane formed at the later stage of deuteration, prove the view that the process preferentially forming d₀-ethane is not steady and limited at the early stage. The value, nearly 0.33, of D atomic fraction of ethane formed at the later stage indicates that they were formed steadily by addition of D₂ to C₂P₄, being accompanied with randomization of D atoms.

Summerizing above informations on the deuterium distribution in prod-

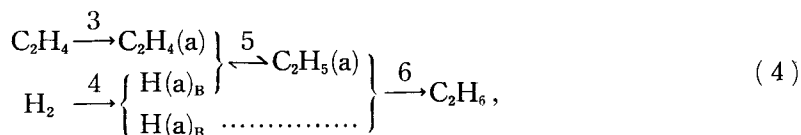
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ucts of deuteration, the following mechanism is concluded for ethylene hydrogenation on reduced tungsten catalyst.

Discriminating hydrogen atoms, $H(a)_A$, on sites A and responsible to β_1 peak of flash desorption spectrum from that, $H(a)_B$, on sites B and responsible to β_2 peak, we conclude that steps,



proceed preferentially on sites A of tungsten surface, and a set of steps similar to (1),



is caused preferentially on sites B. All of steps, but 5, are nearly irreversible and surface diffusion of adsorbed hydrogen atoms are so slow in the presence of ethylene that mixing of $H(a)_A$'s with $H(a)_B$'s is negligible. Otherwise, D atomic fractions of hydrogen, ethylene and ethane would be equally *ca.* 0.33 against the results of Tables 4 and 5. At an early stage of ethylene hydrogenation, ethylene is dissociatively adsorbed on bare A sites of tungsten surface and results in self-hydrogenation of ethylene and full occupation of these sites by $C_2H_2(a)$, which makes A sites inactive for further hydrogenation.

Rapid equilibration of a mixture of P_2 and D_2 as observed previously⁵⁾ in course of ethylene hydrogenation is plausibly attributed to ELEY's mechanism (2), which proceeds mainly on site B as most of sites A are occupied by $C_2H_2(a)$. Deuterium atomic fraction of $H(a)_B$ is, thus, equal to that of gaseous hydrogen, *i. e.*, nearly unity in the case of deuteration of light ethylene. However, those of gaseous hydrogen, ethylene and ethane are possible to be far different from each other so far as step 3 of scheme (4) is irreversible and mixing of $H(a)_A$'s with $H(a)_B$'s is retarded by ethylene. Formation of deuterio-ethylenes with randomly distributed D atoms given in Table 4 is then plausibly caused by hydrogen exchange *via* adsorbed species of lowest D atomic fraction, *i. e.*, $C_2H_2(a)$, through step 1 of (3), which may be something reversible as discussed previously⁵⁾.

Toya¹⁶⁾ has deduced from the variations of electrical resistance and work functions of evaporated metal films caused by chemisorption of hydrogen that two, r- and s-, types of adsorbed hydrogen atom are present on Ni, Pt

and Fe surface, whereas r-type alone on tungsten surface. The present discrimination between adsorbed hydrogen $H(a)_A$ and $H(a)_B$ may be attributed to some different crystal planes of tungsten surface as considered by ROOTSAERT *et al.*¹²⁾, however, the details are not clear for the present.

Table 6 shows that, at the later stage of deuteration catalyzed by a carbided tungsten film, deuterium distribution in ethane is nearly random, but not in hydrogen and ethylene. Furthermore, we see that the relative amounts of d_1 -, d_2 - and d_3 -ethylenes formed, *e.g.*, at -45°C during 180 sec are equal to those with randomly distributed D atoms at $y_D=0.4$, *i.e.*, 22.6, 22.8 and 10.1%, respectively. This fact indicates that randomization of D atoms among adsorbed, deuterio-substituted ethylenes is completed before their appearance into gas phase, and the step of ethylene adsorption is not in equilibrium. The value, 0.4, of y_D of adsorbed ethylene differs clearly from those of gaseous hydrogen and ethane. Thus, the surface of a carbided tungsten film would be apparently divided into two parts, at least; one contributes mainly to hydrogen exchange between hydrogen and ethylene and the other to the formation of ethane.

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