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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 14(2), 134-143
Issue Date	1966-12
Doc URL	https://hdl.handle.net/2115/24812
Type	departmental bulletin paper
File Information	14(2)_P134-143.pdf

HYDROGENATION OF ETHYLENE ON
METALLIC CATALYSTS

Part 6—Dissociative Adsorption of Ethylene Concurrent
with the Catalyzed Hydrogenation of Ethylene
on Evaporated Nickel Film

By

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(Received August 3, 1966)

Abstract

Dissociative adsorption of ethylene concurrent with its hydrogenation on evaporated nickel film has been investigated A) by determining the adsorption of reactants in course of hydrogenation of light ethylene, B) by observing catalyzed hydrogen exchange between light and heavy ethylenes and C) by following the catalyzed deuteration of light ethylene with special reference to the deuterium distribution in hydrogen and ethylene in course of the reaction.

Experiment A) on fresh film revealed that the amount of hydrogen remaining plus that converted into costituent of ethane exceeded the original amount of hydrogen at temperatures above the optimum but not below; no such excess was observed above or below the optimum with a used film, *i. e.* that once used for the hydrogenation and subsequently evacuated at the same temperature.

Experiment B) showed that the exchange between light and heavy ethylenes on fresh film was, as observed both at −23°C and 120°C, about twice as rapid as that on used film and *ca.* tenfold rapider than on carbided film, *i. e.* a film preliminarily heated in ethylene at 200°C for *ca.* half an hour and then evacuated at the same temperature. In any case of the fresh, used or carbided film the rate of this exchange was *ca.* trebled by raising the temperature from −23°C to 120°C. A used film approximated the carbided film in its behaviour as concerns these catalyses by the repeated hydrogenation of ethylene at 200°C on it each followed by evacuation at the same temperature.

Experiment C) indicated that catalyzed deuteration of light ethylene on fresh film at temperatures notably below the optimum was accompanied by an appreciable evolution of protium, whereas used film caused deuteration but no protium to get into hydrogen below the optimum. Above the optimum deuterium gas was rapidly admixed with protium either in case of fresh or used film.

It was concluded from these results that the hydrogenation of ethylene catalyzed by fresh nickel film was accompanied with dissociative adsorption of ethylene but practically sup-

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pressed on used film. Used film thus appeared preferable for the analysis of the mechanism of the steady hydrogenation of ethylene on nickel catalyst.

Introduction

TURKEVICH, BONNER, SCHISSLER and IRSA[1] have found the predominant evolution of light ethane at the initial stage of deuteration of light ethylene on nickel catalyst at a temperature below the optimum. This phenomenon has been interpreted by ELEY[2] as due to the dissociative adsorption of ethylene liberating light hydrogen to form the light ethane. KEII[3] has alternatively explained the phenomenon on the basis of the rate-diagram theory of HORIUTI[4] as follows. According to the theory the rate is governed by the chemisorption of hydrogen below the optimum, steps $C_2H_4 \rightarrow C_2H_4(a)$ and $C_2H_4(a) + H(a) \rightarrow C_2H_5(a)$ occurring rapidly fore and back, where (a) signifies the adsorbed state. These steps give rise to a rapid exchange of hydrogen adatoms with abundant protium from ethylene, adatoms formed by the chemisorption of hydrogen being practically exclusively transferred into ethylene, and in consequence to $H(a)$'s consisting mainly of protium, which results in light ethane. Along this line the theory predicts the relative abundance of different deuterosubstituted ethane thus formed[3,5]. This prediction has been qualitatively verified[6]. Quantitatively, however, light ethane was evolved in excess over the theoretical amount at temperature above the optimum, which obliged to take the dissociative adsorption of ethylene into consideration[6].

The dissociative adsorption of ethylene has been shown to occur in course of hydrogenation in a previous work[7] as follows: hydrogen converted into ethane at 200°C plus residual hydrogen was found to be in excess over hydrogen initially introduced into the reaction vessel either on fresh or used film. The excess of hydrogen was, moreover, equimolar to the excess of initial amount of ethylene over the sum of the amount of residual ethylene plus that converted into ethane. It is inferred from the equivalence of the amounts that the amount of hydrogen was evolved by the dissociative adsorption of the latter amount of ethylene; the former process is termed the excess evolution of hydrogen.

It is essential for the quantitative investigation of the rate-diagram theory on the hydogenation of ethylene catalyzed by nickel catalyst to locate the experimental conditions, under which the catalyzed hydrogenation is isolated from any concurrent reactions, especially the dissociative adsorption of ethylene.

The dissociative adsorption of ethylene on nickel catalyst has been investigated by BEECK[8] and JENKINS and RIDEAL[9], dosing ethylene stepwise onto evaporated nickel film at 20°C; they found that an amount of ethylene equi-

valent to *ca.* one-third of the full coverage was adsorbed leaving no gaseous components, whereas further doses resulted in the formation of ethane.

Several observations have been made on the rate of hydrogen exchange between heavy and light ethylenes with a view to probing the mechanism of the hydrogenation of ethylene; the results seem to have led to a general view that the exchange is effected by adsorbed hydrogen atoms created by the dissociative adsorption of ethylene which combine with undissociatively adsorbed ethylene to form adsorbed ethyl groups. If then, the rate of this exchange should increase with enhanced dissociative adsorption of ethylene.

The deuterium distribution in ethane deviated, in case of the catalyzed deuteration of light ethylene, from the theoretical conclusion, which was attributed to the dissociative adsorption of ethylene as mentioned above. Similar deviation of the deuterium distribution from the theoretical one may be observed in ethylene and hydrogen which may verify the dissociative adsorption.

Three kinds of experiments have been conducted in the present work in the presence of fresh, used and carbided nickel films with special reference to the dissociative adorption of ethylene; these experiments are on A) the adsorption of reactants in course of hydrogenation of light ethylene, B) the hydrogen exchange between light and heavy ethylenes and C) the deuterium distribution in hydrogen and ethylene in course of deuteration of light ethylene.

Experimental

Apparatus and the method of preparation of evaporated nickel film were the same as in the previous work[7] and the trap T_1 adjacent to the reaction vessel was cooled by dry-ice throughout the observation in order to prevent the contamination of films with mercury or grease vapour. The reactants were beforehand mixed at a specified mixing ratio and stored in a reservoir to ensure a complete mixture in every run of the present work. The mixtures have been individually verified mass spectrometrically as free from water, oxygen or nitrogen. The mixture was introduced into the reaction vessel by a pipette of 6.2 cc capacity up to *ca.* 0.1 mmHg total pressure for every run of reaction; the total pressure was registered by means of Pirani gauge and a pen recorder. After an elapse of specified time about half the reacted gas was diffused from the reaction vessel into a sampling vessel of *ca.* 300 cc capacity and mass spectrometrically analysed. The reaction vessel was *ca.* 120 cc capacity and the geometrical area of the evaported nickel film *ca.* 120 cm², which is *ca.* one-third of its BET area as determined in the previous work[7].

The adsorbed amounts Q_H and Q_E of hydrogen and ethylene in course of

the hydrogenation were individually determined at 0°, 101° and 145°C, notably apart from the optimum temperature, *i.e. ca.* 35°C[7], similarly to the previous work[7] by subjecting the gas sampled soon after introduction of the equimolar mixture of hydrogen and ethylene into the reaction vessel to the mass spectrometric analysis. The Q_E or Q_H is the excess of amount of hydrogen or ethylene respectively initially introduced over the sum of the amounts of residual hydrogen or ethylene and that converted into ethane.

Heavy ethylene was prepared by catalyzed deuteration on Pt-asbestos of heavy acetylene, which was generated by allowing 99.7 D % heavy water to react with calcium carbide preliminarily heated in a few mmHg deuterim gas and evacuated at *ca.* 300°C; heavy ethylene thus prepared was now purified by more than ten times of fractional distillation, mixed with a 2.70-fold amount of light ethylene and stored in a reservoir. The exchange reaction has been conducted in the presence of fresh, used or carbided film at −23°C and 120°C.

The catalyzed deuteration of light ethylene has been performed with equimolar mixture of light ethylene and deuterium gas. Deuteration was followed for *ca.* half a minute by the total pressure registered by means of Pirani gauge and a pen recorder.

Deuterium distribution in deuteration products was determined by mass spectrometric analysis as follows. The mass spectrum of deuterium-shifted hydrogen consisting of peaks M_2, M_3 and M_4 of mass number 2, 3 and 4 respectively was recorded by fixing the electron accelerating voltage V_e at 70 volt immediately after the introduction of gas from the sampling vessel into mass spectrometer, and then the mass spectrum ranged from M_{28} to M_{32} of parent ions of ethylenes C_2P_4, C_2P_3D, $C_2P_2D_2$, C_2PD_3 and C_2D_4 respectively was observed at V_e of 12.5 volt, where P or D signifies protium or deuterium respectively. The relative amounts of deuterated ethanes were not determined on account of their too small amounts available under the present experimental condition of low pressure.

The relative amounts of deuteroethylenes in the product of the exchange reaction as well as those in the reactant mixture were determined by mass spectra recorded similarly at V_e of 12.5 volt, which consisted of parent peaks alone.

Results

A) Table 1 shows the results of adsorption measurements in course of hydrogenation of ethylene at 0°, 101° and 145°C respectively on fresh, used and carbided films, which are signified with I, II and C respectively. A change from film I to II makes little difference as in the previous work[7] in the

adsorbed amount Q_H of hydrogen and that Q_E of ethylene at 0°C and 101°C, apart from run 7–II conducted under extraneous condition; at 145°C Q_H was found negative and equal in the absolute amount to Q_E on film I, whereas small but positive on film II. The negative value of Q_H may be termed the amount of excess evolution of hydrogen with reverse sign. The resultant of run 7–II in the Table was sampled not at the initial stage of the reaction as in the other runs but at the final stage where the total pressure no more decreased, that is, ethylene was exhausted. This result implies that adsorbed ethylene was decomposed in the final stage into gaseous hydogen and surface residue in contrast with the result of run 8–II in the initial stage. Q_H on carbided film was almost imperceptible as seen from the results of runs 8–C, 8'–C and 9–C.

TABLE 1. Adsorbed amounts Q_H and Q_E of hydrogen and ethylene on evaporated nickel films I, II and C in course of hydrogenation of ethylene.
I : fresh, II : used and C : carbided film

React. temp. °C	No. of run	Adsorbed amount, 10^{16} molecules	
		Q_H	Q_E
0	5–I	3.3	10.3
	6–I	2.7	10.1
	5–II	3.9	9.3
	6–II	2.0	10.6
	8–C	1.0	7.9
101	7–I	0.8	9.4
	8–I	1.6	6.0
	7–II*	− 5.3	5.9
	8–II	1.3	7.0
	8–C	0.3	5.7
145	9–I	− 5.8	5.8
	9–II	0.5	6.9
	9–C	0.0	6.0

The previous result of the excess evolution of hydrogen at 200°C amounting to equivalent of Q_E has been reproduced in the present work and, furthermore, it was found that the total pressure of gas increased slowly in the presence of fresh or used film in spite of progress of hydrogenation.

*) *cf.* the comment on this run in the text.

B) Table 2 shows the results of hydrogen exchange between light and heavy ethylene. Values in line with '0' or '∞' of "Time" is the relative amounts of ethylenes in the initial mixture or calculated for the random distribution of deuterium atoms among them. Under Column "Rate const." shows the values of $k = 1/t \cdot \ln(x_t - x_\infty)/(x_0 - x_\infty)$ in terms of time t in sec. and mole fraction x_0, x_t or x_∞ of C_2P_4 in gaseous ethylenes at the initial stage, time t or the exchange equilibrium of deuterium atoms respectively. The total pressure of gas in the reaction vessel attained to a constant value immediately after introduction of reactant mixture into the reaction vessel, indicating that the adsorption of ethylene was so much fast. The amounts of ethylene introduced minus that remained in gas phase are given under the Column "Adsorbed amount" of the Table. We see from the results of Table 2 that the exchange was very rapid on fresh film even at $-23°C$ and its rate was reduced to *ca.* one half or less on used film and further to *ca.* one tenth on carbided film both at $-23°C$ and $120°C$; the rate of the exchange at $120°C$ was about thrice as large at $-23°C$ for every kind of the film.

TABLE 2. Hydrogen exchange between light ethylene C_2P_4 and heavy ethylene C_2D_4 on evaporated nickel films.

React. temp. °C	Film	Time sec.	Gaseous ethylenes, %					Exchange %	Rate const. k sec^{-1}	Adsorbed amount, 10^{17} molecules
			C_2P_4	C_2P_3D	$C_2P_2D_2$	C_2PD_3	C_2D_4			
		0	72	2	0	1	26	0		
		∞	29	42	23	5	1	100		
	I		38	35	20	6	1	74	0.052	1.40
-23	II	30	52	20	9	10	9	47	0.021	1.31
	C		68	6	1	4	21	9	0.003	1.02
	I		32	37	23	7	1	93	0.177	1.53
120	II	15	40	33	19	7	1	74	0.090	1.14
	C		65	9	2	6	18	16	0.012	1.09

Adsorption measurement in course of hydrogenation of ethylene and hydrogen exchange between light and heavy ethylenes were also conducted on a film which was used beforehand repeatedly for hydrogenation of ethylene at 200°C each followed by evacuation at the same temperature. The results were quite similar to those of the carbided film C in Tables 1 and 2.

C) Table 3 shows the observed relative amounts of different isotopic species of hydrogen and ethylene formed in course of deuteration of light ethylene on

TABLE 3. Deuterium distribution in hydrogen and ethylene formed by deuteration of light ethylene on fresh and used nickel films

React. temp. °C	Kind of film	Rate of deuteration $-\%\ C_2H_4/min.$	Deuteration, %	Hydrogen, %			Ethylene, %					Deuterium atomic fraction	
				P_2	PD	D_2	C_2P_4	C_2P_3D	$C_2P_2D_2$	C_2PD_3	C_2D_4	y_H	y_E
− 45	I	9.7	4	8.5	22.5	69	63	31	7	0	0	0.803	0.112
	II	3.5	2	0	1.6	98.4	93	7	0	0	0	0.992	0.017
− 23	I	31.8	15	10	25	65	57	34	9	0	0	0.775	0.130
	II	18.2	10	0	1.6	98.4	90	10	0	0	0	0.992	0.025
0	I	74.3	35	11	26	63	44	36	18	2	0	0.760	0.195
	II	56.9	20	0	6	94	64	30	6	0	0	0.970	0.105
28	I	110.3	40	11	30	59	45	38	14	2	0	0.740	0.180
	II	98.0	43	2	10	88	66	28	5	1	0	0.930	0.103
32	I	129.7	45	11	22	67	49	34	11	7	0	0.780	0.165
	II	107.1	41	10	19	71	40	36	20	4	0	0.805	0.220
75	I	102.1	40	30	42	28	21	35	28	13	3	0.440	0.355
	II	97.0	38	30	29	41	29	38	24	7	2	0.555	0.263
110	I	54.0	18	11	39	50	16	32	32	16	4	0.695	0.400
	II	50.2	21	14	39	47	21	29	37	10	2	0.665	0.340

fresh or used nickel film. The percentage decrease of the total pressure is given in the Column of "Deuteration, %" relative to the initial amount of ethylene. The negative of the initial rates of the total pressure decrease are shown in the Column of "Rate of deuteration", which show that the optimum temperature of deuteration lies between 32°C and 75°C. Values of y_H or y_E in the last two Columns give the observed atomic fraction of deuterium in gaseous hydrogen or ethylene rsepectively. Following remarks may be made upon the results of this Table as regards the difference between films I and II.

1. The values of y_H is considerably smaller in case of film I than in case of film II at low temperatures, while the reverse is case for y_E, the difference of y_H or y_E between films I and II decreasing with rise of temperature.

2. The "Rate of deutration" decreases from film I to II at temperatures below the optimum but not above.

Discussion

The excess evolution of hydrogen observed in the experiment A) indicates unequivocally the decomposition of ethylene, inasmuch as the unique other source of hydrogen, *i.e.* ethane, remains altogether unchanged[7] under the present condition as verified by MATSUZAKI and NAKAJIMA[10] under a somewhat different condition[*].

The amount of excess evolution of hydrogen was previously found to be equivalent to the amount Q_E of adsorbed ethylene in course of hydrogenation at 200°C both on fresh and used films[7], as mentioned in the introduction; such excess evolution has now been observed again, as seen in Table 1, on fresh film at 145°C at the initial stage of hydrogenation, but not on used or carbided film at the same temperature; such excess was not at all observed on any kinds of film at 0°C and 101°C. Ethylene is thus subject to the dissociative adsorption accompanied by the excess evolution of hydrogen appreciably on fresh films but only slightly or not at all on used and carbided films. Such dissociative adsorption of ethylene may be instantaneous as inferred by the result of experiment B) that the total pressure of gas in the reaction vessel attained to a constant value immediately after introduction of reactant mixture into the reaction vessel. In addition to the fast dissociative adsorption slow decomposition of ethylene is to be operative at high temperatures from the result of run 7–II in Table 1 at 101°C and the slow increase of total pressure

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*) MATSUZAKI and NAKAJIMA have shown that heavy ethane of 9 mmHg pressure mixed with the reactants of catalyzed hydrogenation, *i.e.* light hydrogen and ethylene both of 10 mmHg pressure, in the presence of nickel wire remained altogether unchanged in its quantity at 50°, 100° and 150°C.

of gas at 200°C in experiment A) as mentioned above. This accounts for now the fact that a used film approximates the carbided film in its catalytic behaviour by the repeated hydrogenation of ethylene at 200°C each followed by evacuation at the same temperature. The decomposition may be occurring at lower temperature as well, if slowed down to such an extent as insufficient to outweigh the consumption of hydrogen by hydrogenation.

On these bases the present results on the hydrogen exchange between light and heavy ethylene and deuteration of light ethylene are now discussed.

According to the rate-diagram theory[4] of the catalyzed hydrogenation of ethylene on nickel catalyst, the reaction proceeds through the four steps, i. e.
$$C_2H_4 \xrightarrow{\text{Ia}} C_2H_4(a), \quad H_2 \xrightarrow{\text{Ib}} 2H(a), \quad C_2H_4(a) + H(a) \xrightarrow{\text{II}} C_2H_5(a) \quad \text{and} \quad C_2H_5(a) + H(a) \xrightarrow{\text{III}}$$
C_2H_6, it having been concluded by comparison with experiments that the overall rate is determined by Ib or III at temperatures notably below or above the optimum respectively. The backward rate of the step III is neglected on the base of the theoretical conclusion[4] as well as the experimental results that ethane was not adsorbed under coexistence of ethylene[7] and that obtained by MATSUZAKI and NAKAJIMA[10] mentioned above. The hydrogen exchange between light and heavy ethylenes should then be caused by steps Ia, Ib and II in the presence of H(a), and should become faster with increase of the amount of H(a), provided that those of $C_2H_4(a)$ and $C_2H_5(a)$ remain approximately unchanged.

On the other hand, the adsorbed amount of ethylene on film I is much the same as that on film II as seen from Table 2 in agreement with the result of Table 1. The "Adsorbed amount" of ethylene should include that of $C_2H_5(a)$ as well as $C_2H_4(a)$ in accordance with the rate-diagram theory and moreover the product of the dissociative adsorption. It is hence probable the amonts of $C_2H_4(a)$ and of $C_2H_5(a)$ are respctively approximately the same on the fresh and used films. This accounts for the rapid exchange between light and heavy ethylenes on the fresh film as compared with that on used one on the ground of hydrogen evolved in excess on fresh film as concluded above. This argument is supported by the present result that the exchange occurs hardly on film C, on which ethylene is adsorbed approximately by the same amount as seen from Table 2, whereas hydrogen is scarcely as shown in Table 1; inasmuch as the carbided film is evacuated at 200°C.

The difference between films I and II in their catalytic behaviour as given in Table 3 is now interpreted similarly to above as follows.

Plenty of protium adatoms provided by fast dissociative adsorption of light ethylene may be converted into hydrogen to dilute the latter. The results on

y_H in Table 3 commented upon in Remark 1 of the foregoing section thus indicate that the dissociative adsorption of light ethylene is predominant on film I as compared with film II even at low temperatures and equally enhanced on both films at temperatures highly above the optimum. The initial value 0.992 of y_H was retained in course of the progress of deuteration at $-45°C$ and $-23°C$ on film II, from which it follows that the dissociative adsorption of ethylene is practically suppressed on film II at such low temperatures.

The result of the deuterium atomic fraction y_E of ethylene mentioned in Remark 1 is accounted for on the basis of the rate-diagram theory as follows ignoring provisionally the dissociative adsorption. The rate-diagram theory predicts that at temperature below the optimum the hydrogenation rate is governed by Ib and D(a) formed by the latter is practically exclusively transferred into ethylene as mentioned in the introduction. Since the deuteration rate is greater on film I than on film II, y_E should be greater on the former than on the latter. The intervention of the dissociative adsorption lowers deuterium content of hydrogen adatoms on the one hand and multiplies the balanced forward and backward rates of step II. It follows that the effect of the dissociative adsorption is ignorable provided that the mass action law holds at least approximately.

It is concluded that the used film is preferable to the fresh film as regards the examination of the catalyzed hydrogenation of ethylene on nickel catalyst at temperatures below the optimum. The result in Table 3 obtained with used film will be discussed in the next paper in comparison with those with carbided film.

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