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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 8—Effect of Reactivation of Nickel Catalyst by Hydrogen-Treatment on the Deuteration of Light Ethylene

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Abstract

Nickel film reduced by hydrogen at 200°C or 300°C for an hour or longer was compared with those freshly evaporated or once used for deuteration of light ethylene, as regards deuteration rate, deuterium distribution in reacted hydrogen and ethylene in the early stage of deuteration, activation heat, hydrogen isotopic effect on hydrogenation rate of light ethylene and the optimum temperature. It was found that the results obtained by reduced film was quite similar to those of film once used. It was hence concluded with reference to the previous discussion[1] that the dehydrogenated adsorption of ethylene in course of its hydrogenation was practically suppressed at temperatures below the optimum on reduced film similarly as in the case of film once used. A number of existing data on ethylene hydrogenations over reduced nickel catalysts thus proved to be competent for the analysis of the mechanism.

Introduction

The catalyzed hydrogenation of ethylene in the presence of metallic catalysts, especially of nickel, has been a subject of intensive investigations as a type of olefine hydrogenations. Rather poor reproducibility of the observed reaction rate, however, make them unsound basis for discussion of the mechanism; its rate as well as those of associated reactions, *e.g.*, parahydrogen conversion and deuterium exchange *etc.*, markedly decay on repetition of the runs of reaction over the same charge of catalyst. It has been found that the decay is caused not only by impurities in the reactants, *e.g.*, mercury,[2] greeze vapors

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and oxygen[3,4] *etc.*, but also by side reactions to form irreversibly adsorbed products *e.g.*, dehydrogenated adsorption and polymerization of ethylene, and that the latter is pronounced on metallic catalysts of less catalytic activity for the hydrogenation.[5,6]

Various pretreaments of metallic catalysts have been tried to exploring the reproducible condition; nickel catalyst, for instance, was preliminarily brought into contact with[7] or heated in[8] ethylene, or preliminarily oxidized at *ca.* 600°C and then reduced by hydrogen[9] at *ca.* 300°C or simply reduced by hydrogen.[4,10] The last-mentioned treatment of catalyst has been adopted by many investigators as a simple and effective method for securing the reproducibility.

Recently we have found[11,12,13] that the catalyzed hydrogenation on freshly evaporated nickel surface was accompanied with dehydrogenated adsorption of ethylene in the initial stage of hydrogenation even in case of pure reactants were used at a temperature as low as −45°C; the dehydrogenated adsorption of ethylene was practically suppressed at low temperatures over nickel film once used for the hydrogenation and evacuated at the same temperature.[1] On the basis of the results obtained with film once used, the mechanism of steady hydrogenation and associated reactions were quantitatively analyzed[6,13] according to the generalized statistical mechanical theory of heterogeneous reactions.[14,15]

JENKINS and RIDEAL[8] have, on the one hand, found that the hydrogenation rate was quite reproducible over nickel film preliminarily carbided by heating it at 200°C in ethylene, however, its kinetics was found quite different form that on the once used nickel film.[13] FOSS and EYRING[4] has, on the other hand, observed that the hydrogenation rate was reproducibly observed over a carbided nickel film with half a rate over a freshly evaporated nickel film in the case when it was preliminarily treated by 5 cmHg hydrogen at 250°C for 30 min. They gave, however, no account of the associated reactions, especially of the dehydrogented adsorption of ethylene.

The present work is devoted to investigate the catalyzed hydrogenation of ethylene over evaporated nickel film reduced by hydrogen after uses for several runs of reaction, with special regards to the associated dehydrogenated adsorption of ethylene.

Three states of evaporated nickel film, *i.e.*, freshly evaporated, once used or reduced by hydrogen after once use or more, are compared with each other with regards to the decreasing rate of total pressure and the relative amounts of deuterosubstitution products of hydrogen and ethylene in the initial stage of reaction of one to one mixture of light ethylene and deuterium.

It was found that the rate of total pressure decrease at $-45°$ or 0°C on reduced film was tolerably reproducible from run to run and *ca.* 1.5 or *ca.* 0.75 times as large as that over once used or fresh film respectively. The relative amounts of deuterosubstitution products of hydrogen and ethylene produced by the reaction over reduced film were found quite similar to those over the film once used. It was hence concluded that reduced film is more active than film once used but similar to the latter in its kinetics and elimination of the dehydrogenated adsorption.

Exprimental

The reaction over nickel film was investigated, similarly to the previous work,[1,13] with regards to the three states of the film as follows; the nickel film, freshly evaporated directly upon the inner surface of reaction vessel of *ca.* 150 cc capacity or upon the nickel film previously evaporated and used, was heated in deuterium gas of *ca.* 1.5 cmHg for an hour at 500°C, evacuated at the same temperature to 1×10^{-6} mmHg or higher vacuum and then coated anew with freshly evaporated nickel, immersing the vessel into a salt bath at 300°C. Within 5 min after the end of evaporation the salt bath was replaced by another one of the scheduled reaction temperature, when a known amount of the reactant gas, *i.e.*, one to one mixture of light ethylene and deuterium gas, was introduced into the vessel at *ca.* 0.1 mmHg total pressure; the initial decrease of total pressure was followed by a Pirani gauge and a pen-recorder and then a part of the reacted gas was diffused into a sampling vessel for mass spectrometric analysis. After a run over the freshly evaporated film thus conducted, the vessel was evacuated, constantly immersing it in the same bath, to a vacuum higher than 1×10^{-6} mmHg and then the reactant mixture was introduced into it to conduct a run on the "film once used." After a run on the film once used the reaction vessel was evacuated and the (twice) used film was heated at 200 or 300°C in deuterium gas of *ca.* 1.5 cmHg for a period indicated in Table 1 and then evacuated again to a vacuum higher than 1×10^{-6} mmHg at the same temperature. The reactant gas mixture was now introduced to conduct another run for the third time. "Reduced film" refers now in what follows to a film used twice, thrice or more times each followed by the reduction mentioned above.

Mass spectra of sampled gases were obtained by fixing the electron accelerating voltage at 70 volt for hydrogen and at 13 volt for ethylene similarly as in the previous works[1,13]; at the latter voltage we have a mass spectrum of ethylene consisting exclusively of peaks of parent ions of respective deuteroethylenes.

TABLE 1

I Reaction temp. °C	II State of Ni film	III Reacted %	IV V_0 mmHg/min	V Relative amounts of deuterosubstituion products								VI D-atom fraction	
				M_2	M_3	M_4	M_{28}	M_{23}	M_{30}	M_{31}	M_{32}	y_H	y_E
−45	F	2.2	0.0130	4.5	16.4	79.2	65.0	30.0	5.0	0	0	0.874	0.100
				(1.6	22.0	76.4)	(65.6	29.2	4.9	0.3	0)		
	S	2.5	0.0064	0.8	1.6	97.7	92.3	7.7	0	0	0	0.985	0.019
				(0.0	3.0	97.0)	92.6	7.2	0.2	0	0)		
	R (300°C, 1 hr)	3.2	0.0097	2.3	3.1	94.7	80.0	17.2	2.9	0	0	0.963	0.058
				(0.1	7.1	92.8)	(78.7	19.4	1.8	0.1	0)		
	R (300°C, 3 hr)	3.1	0.0099	1.6	2.6	95.8	79.2	20.8	0	0	0	0.971	0.052
	R (300°C, 14 hr)	3.2	0.0096	1.4	2.0	96.7	90.6	9.4	0	0	0	0.977	0.024
−45	F	3.1	0.0123	3.7	14.1	82.2	71.4	25.0	3.6	0	0	0.893	0.081
	S	3.2	0.0069	3.2	3.3	94.5	66.7	29.6	3.7	0	0	0.962	0.093
	R (200°C, 1 hr)	3.1	0.0091	1.9	3.0	95.1	82.2	17.7	0	0	0	0.966	0.044
	R (200°C, 2 hr)	3.1	0.0091	1.0	2.4	96.6	—	—	—	—	—	0.979	—
	R (200°C, 14.5 hr)	3.2	0.0089	1.1	2.2	96.7	84.2	14.9	1.0	0	0	0.978	0.037
	R (200°C, 70 hr)	—	—	2.2	3.8	94.3	89.7	10.3	0	0	0	0.962	0.026
0	F	8.4	0.0339	4.6	16.3	79.1	47.4	36.9	13.2	2.5	0	0.879	0.175
	S	4.9	0.0176	2.8	3.8	93.9	66.7	26.7	6.6	0	0	0.956	0.105
	R (300°C, 1.5 hr)	5.8	0.0254	2.5	4.6	92.9	61.2	30.6	5.6	2.6	0	0.951	0.125
	R (300°C, 1.5 hr)	6.1	0.0249	3.3	5.7	91.0	58.8	32.4	5.9	2.9	0	0.939	0.122
				(0.4	11.5	88.1)	(59.4	33.0	6.9	0.6	0)		
75	F	1.7	0.0469	19.2	35.6	45.2	29.1	30.9	25.5	10.9	3.6	0.630	0.323
				(13.7	46.6	39.7)	(21.0	40.1	28.7	9.1	1.1)		
	S	6.0	0.0287	24.9	42.6	32.5	18.5	30.9	30.9	15.4	4.3	0.490	0.429
				(26.0	50.0	24.0)	(10.6	31.9	36.0	18.0	3.5)		
	R (200°C, 2 hr)	9.2	0.0427	30.1	48.1	21.8	15.1	30.3	33.3	18.2	3.1	0.459	0.409
				(29.3	49.7	21.1)	(12.2	33.8	35.1	16.1	2.8)		
	R (200°C, 14.5 hr)	9.2	0.0418	29.7	48.2	22.1	14.3	28.6	31.4	20.0	5.7	0.462	0.436
86	F	11.1	0.0485	25.5	56.8	17.7	13.0	30.4	34.9	17.4	4.3	0.461	0.424
	S	11.2	0.0217	22.4	57.0	20.6	13.2	30.2	34.0	17.0	5.6	0.490	0.429
	R (200°C, 1.5 hr)	11.9	0.0316	28.0	57.1	14.9	9.1	31.8	36.4	18.2	4.5	0.434	0.443
	R (200°C, 2.5 hr)	11.5	0.0344	25.0	59.8	15.2	13.0	30.4	34.8	17.4	4.4	0.441	0.424
	R (200°C, 13.5 hr)	8.7	0.0343	24.3	58.2	17.5	12.8	30.8	33.3	18.0	5.1	0.466	0.430

Results

Table 1 shows the results obtained by the use of film in fresh, once used or reduced state as signified in the second column of the Table by F, S or R respectively. The parenthesized figures there show the temperature and the period of reduction by deuterium gas. The "Reacted %" in the third column is the percentage ratio of total pressure decrease at the moment of sampling to the initial partial pressure of ethylene and V_0 in the fourth column the decreasing rate of the total prassure respectively. The M_3, M_3 and M_4 in the fifth column are the relative heights of peaks of mass numbers 2, 3 and 4 respectively in a mass spectrum of sampled hydrogen gas and M_{28}, M_{29}, M_{30}, M_{31} and M_{32} in the same column are those of mass numbers 28, 29, 30, 31 and 32 respectively of the sampled ethylene; the relative heights approximate the relative amounts of $^1H_2$, ^1HD and D_2 or of $C_2{}^1H_4$, $C_2{}^1H_3D$, $C_2{}^1H_2D_2$, $C_2{}^1HD_3$ and C_2D_4 respectively. The parenthesized figures in the fifth column show the relative amounts of respective deuterosubstitution products

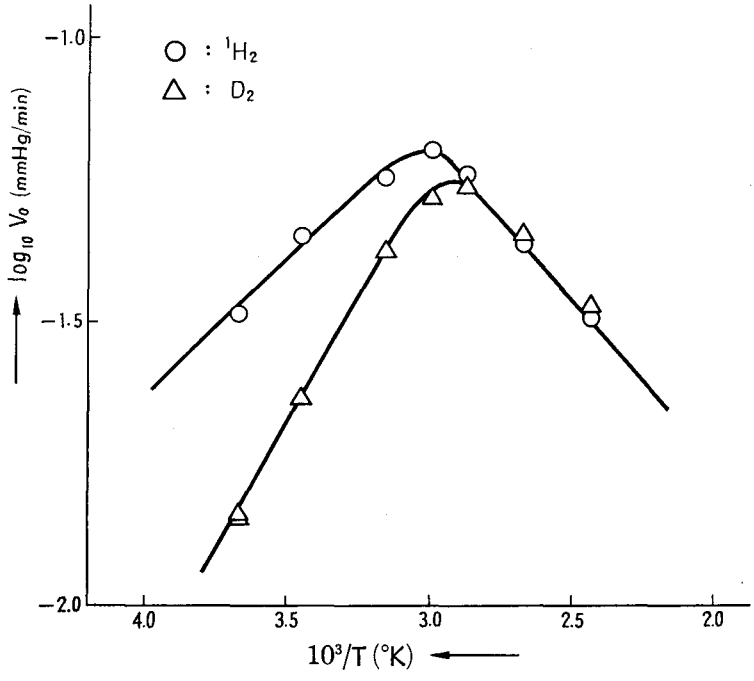

Fig. 1. Arrhenius plots of hydrogenation rate of light ethylene with equimolar light hydrogen ($^1H_2$) or deuterium (D_2) at *ca* 0.1 mmHg initial total pressure in the presence of a reduced nickel film.

of hydrogen and ethylene calculated, in the representative cases, assuming the random distribution of deuterium atoms in gaseous hydrogen or ethylene respectively of observed deuterium atom fraction y_H or y_E as given in the sixth column of the Table.

Fig. 1 is the Arrhenius plots of V_0's of hydrogenation by $^1H_2$ or D_2 over other samples of R than that of Table 1. In Fig. 1 the optimum temperature estimated at *ca.* 60 or 80°C and the activation heat at temperatures below the optimum is read as 52. kcal/mole or 5.5 kcal/mole for hydrogenation by $^1H_2$ or D_2 respectively. We have 2.8 kcal/mole for the latter from V_0-values at −45 and 0°C given in Table 1. The activation heat amounts, at temperatures above the optimum, nearly −5.3 kcal/mole both for hydrogenation by $^1H_2$ and D_2 as derived from date in Fig. 1. From Fig. 1 the ratio, α, of the rate of hydrogenation by $^1H_2$ to that of D_2 is evaluated as *ca.* 2.3 at −45°C and it decreases monotonously with rise of temperature down to 1.0 at the optimum.

Discussion

Table 1 shows that the hydrogenation rate, V_0, over R is tolerably reproducible from run to run at −45 or 0°C, *i.e.*, at temperatures sufficiently below the optimum, and *ca.* 0.75 or *ca.* 1.5 times as large as that over F or S respectively, while the amount of evolution of $^1H_2$ and ^1HD over R are much the same as that over S,[1,6,13] but far smaller than that over F. These behaviours of R remain the same irrespective of the reduction temperature being 200 or 300°C and of the reduction period ranged from one to 70 hr.

It has been concluded in the previous work[1] that the evolution of $^1H_2$ and ^1HD at temperatures below the optimum was due to the dehydrogenated adsorption of ethylene and practically suppressed over film S. It follows now from the previous and the present results that the pretreatment of film S to prepare R accelerates the deuteration of ethylene without stirring the dehydrogenated adsorption of ethylene. The optimum temperature and isotopic effect, α, were as well found over R quite similar to those over S. A good many date on nickel catalysts reduced similarly are thus competent for analysis of the mechanism[6,13] and presumably for investigation of the difference in the activity of various metallice catalysts for the hydrogenation ofethylene,[5,16] which is the main purpose of the present series of work.

The fresh, once used and reduced films result in, at temperatures near and above the optimum, similar relative values of M_2, M_3 and M_4, as seen from Table 1, which shows the dehydrogenated adsorption of ethylene proceeds to the same extent over them in course of hydrogenation as discussed in the previous papers.[1,13]

Table 1 shows that observed relative amounts of M_{28} *etc.* of ethylene are close to those calculated for the random distribution irrespective of the state of film and the reaction temperature, whereas the observed relative values of M_2 *etc.* of hydrogen over R are remarkably different from those calculated for random distribution at temperatures sufficiently below the optimum; observed M_2 *etc.* over R approach, however, those of random distribution and y_H approaches y_E as the temperature rises beyond the optimum. These results over R are in agreement with those over S in the previous work,[1,13] from which it was concluded,[6,13] in accordance with the HORIUTI's theory,[14] that the rate-determining step of the hydrogenation switches over, with rise of temperature, at the optimum temperature from the chemisorption of hydrogen to the combination of chem isorbed hydrogen atom and adsorbed ethyl radical to form ethane.

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References

1) K. MIYAHARA, This Journal **14**, 134 (1966).
2) K. C. CAMPBELL and S. J. THOMSON, Trans. Faraday Soc. **55**, 306, 985 (1951).
3) K. MIYAHARA, This Journal **11**, 1 (1963).
4) J. G. FOSS and H. EYRING, J. Phys. Chem. **62**, 103 (1958).
5) O. BEECK, Discuss. Faraday Soc. **8**, 118 (1950); G. C. BOND, *Catalysis by Metals*, Acad. Press. Inc. London & New York, 1962.
6) J. HORIUTI and K. MIYAHARA, *a Monograph 'NSRDS-NBS 13'* of the National Bureau of Standards, U.S.A., in press.
7) K. J. LAIDLER and R. E. TOWNSHEND, Trans. Faraday Soc. **57**, 1590 (1961); O. TOYAMA, Rev. Phys. Chem. Japan **11**, 353 (1935), **9**, 123 (1937).
8) G. I. JENKINS and E. K. RIDEAL, J. Chem. Soc. 2490, 2496 (1955).
9) *e.g.*, G. H. TWIGG and E. K. RIDEAL, Proc. Roy. Soc. **A 171**, 55 (1936).
10) *e.g.*, I. MATSUZAKI, A. TADA and T. NAKAJIMA, Shokubai (Catalyst) **8**, 5 (1966); T. TUCHOLSKI and E. K. RIDEAL, J. Chem. Soc. 1701 (1935); M. MASUDA, This Journal. **12**, 67 (1964); J. TURKEVICH *et al.*, J. Phys. Colloid. Chem. **55**, 1078 (1951).
11) K. MIYAHARA, This Journal **12**, 98 (1964).
12) K. MIYAHARA and H. NARUMI, *ibid.* **13**, 20 (1965).
13) K. MIYAHARA, *ibid.* **14**, 144 (1966).

14) J. HORIUTI, *ibid.* **2**, 1 (1947), **6**, 250 (1958), **7**, 163 (1959).
15) J. HORIUTI and T. NAKAMURA, *Advances in Catalysis* **17**, 1 (1967).
16) J. HORIUTI and K. MIYAHARA, a paper submitted to the IVth International Congress on Catalysis, Moscow, June, 1968.