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Author(s)	SATO, Shinri; MIYAHARA, Koshiro
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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 4—Pressure Dependence of Optimum Temperature on Evaporated Nickel Film

By

Shinri SATO and Koshiro MIYAHARA

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Abstract

Pressure dependence of the optimum temperature of hydrogenation of ethylene on evaporated nickel film was investigated.

A reproducible condition of reaction was secured by using highly purified hydrogen and ethylene, mass spectrometrically free from oxygen and nitrogen, and nickel films coated with freshly evaporated nickel in vacuum higher than 3×10^{-6} mmHg for every run of rate measurement. Initial rates of hydrogenation were observed at different temperatures to determine the optimum temperature at fixed initial partial pressures of ethylene and hydrogen, and the similar series of runs were conducted at different fixed initial partial pressures.

Results showed that the optimum temperature increased with increase of ethylene partial pressure and was apparently independent of hydrogen partial pressure; the optimum temperature shifted to higher temperature by repeating the reaction with the same nickel film without fresh coating or oxidizing and reducing it, which was attributed to poisoning of catalyst. There was a linear relation between reciprocal of the absolute temperature of the optimum and logarithm of ethylene partial pressure, which was in good agreement with theoretical equation derived from the structure theory of HORIUTI[1]. The heat of activation at temperatures below the opitmum with equimolar mixture of ethylene and hydrogen increased from 3.3 Kcal to 4.8 Kcal/mole with increase of the total pressure.

Introduction

It is well-known that the catalyzed hydrogenation of ethylene on nickel catalyst reveals an optimum temperature, where the reaction rate attains maximum. As so far reported[3~8], the optimum temperature depends on ethylene partial pressure but not hydrogen partial pressure.

The associative mechanism of catalyzed hydrogenation of ethylene in the presence of metallic catalysts follows the scheme[2]

$$\begin{array}{l} C_2H_4 \xrightarrow{I_a} C_2H_4(a) \\ H_2 \xrightarrow{I_b} \begin{cases} H(a) \\ H(a) \end{cases} \end{array} \Bigg\} \xrightarrow{II} C_2H_5(a) \Bigg\} \xrightarrow{III} C_2H_6 , \qquad (1)$$

where (a) denotes the adsorbed state of atoms or atom groups. The optimum temperature occurs according to the structure theory of HORIUTI[1] as the rate-determining step switches over from I_b to III with rise of temperature and depends on ethylene partial pressure but not hydrogen partial pressure.

The present work is devoted to verify the theoretical conclusion experimentally under the reproducible condition secured by using evaporated nickel film freshly coated by nickel evaporated in high vacuum for every run and highly purified materials.[7]

Experimental

Figs. 1, (a) and 1, (b) show diagramatic sketches of the apparatus and the reaction vessels made of all "Hario" glass.

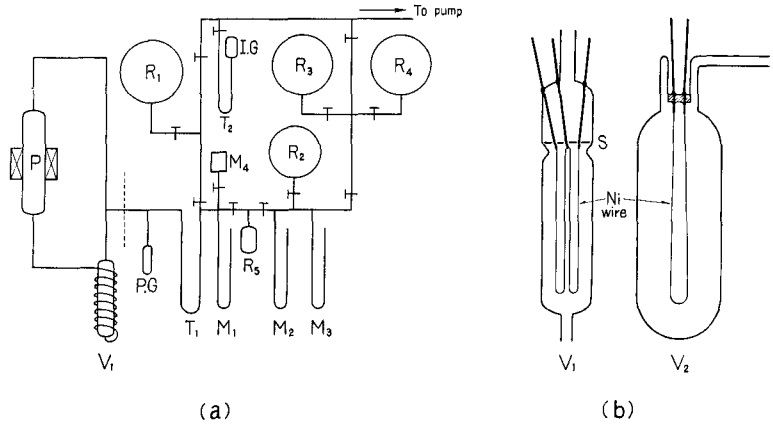

Fig. 1. Diagramatic sketches of the apparatus (a) and the reaction vessels (b).

P: Circulation pump, P.G: Pirani gauge, T_1, T_2: Dry ice-alcohol trap, M_1, M_2: Hg manometer, M_3: Oil manometer, M_4: McLeod gauge, I.G: Ionization gauge, R_1: Reservoir of hydrogen for reduction, R_2: Reservoir of the gas mixture of hydrogen and ethylene, R_3, R_4: Reservoir of hydrogen or ethylene respectively, R_5: Gas pipette, V_1: Reaction vessel of circulation system, S: Mica shield to confine the evaporation underneath, V_2: Reaction vessel of static system.

Apieson-N grease was used for stop cocks and Octoil-S for oil manometer M_3, the vapour pressures of both being stated to be the order of 10^{-8} mmHg at

room temperature. Either a circulation method or a static method was employed according as total pressure was above or below a few mmHg respectively. The circulation system consisted of pump P and reaction vessel V_1 of 1.5 cm diameter contained nickel wire of 20 cm length for evaporation and was provided with a Hg manometer M_1 by which the reaction was followed. Volume of the circulation system was varied so as to obtain a rate of pressure changes suitable for measurement. The reaction vessel V_2 for the static system was a cylinder of 4 cm diameter and about 100 cc volume, which contained nickel wire of 16 cm length, and was fused to the apparatus in place of the circulation system at the dotted line shown in Fig. 1, (a). The reaction in the static system was followed by a Pirani gauge connected with the apparatus.

The nickel wires used were of 0.4 mm diameter and 99.99% purity or of 0.5 mm diameter and 99.4% purity, no difference being found between them in the results obtained with freshly coated film.

The experimental procedure was similar to that of previous works[7)9)]; the reaction vessel was evacuated at 500°C for a few hours and then heated in hydrogen of *ca.* 10 mmHg at the same temperature to reduce oxides possibly contaminating the nickel wire. The hydrogen was now evacuated and the nickel wire electrically heated with a current of 3.0 or 5.0 A, depending on the thickness of wire, while the evacuation was continued until 3×10^{-6} mmHg or higher vacuum was attained. The reaction vessel was then immersed in a salt bath*) at 250°C and the nickel wire was evaporated by heating it with a current of 5.0 or 6.0 A for two minutes. The bath was changed to another one of reaction temperature. Three minutes after the end of evaporation the gas mixture of ethylene and hydrogen was admitted from a gas pipette R_5 into the circulation or the static system, and the reaction was followed respectively by means of Hg manometer M_1 or the Pirani gauge connected to a pen recorder. The Pirani gauge was calibrated by McLeod gauge using the gas mixture for the reaction. The gas mixture was circulated at a rate of about 100 cc/sec. After recorded time, the reaction vessel was evacuated, heated to 500°C and the nickel film was freshly coated by nickel evaporated similarly as above for the subsequent run.

The negative of the initial inclination of recorded pressure–time curve of each run was regarded as the rate at the specified initial partial pressures. A series of runs was similarly conducted at different temperatures at fixed initial partial pressures of ethylene and hydrogen, and similar series were carried out at different fixed initial partial pressures. A value of optimum

*) The salt bath is a melt of 10 : 8 mixture of potassium nitrate and sodium nitrite.

temperature at fixed initial partial pressures was determined from each series.

Hydrogen was prepared by electrolysis and filtered through a palladium thimble. Ethylene from cylinder was purified by repeated distillation in vacuo between two traps reciprocatively from *ca.* −100°C to liquid nitrogen temperature. Hydrogen and ethylene thus purified were found mass spectrometrically free from oxygen and nitrogen.

Results

One of the present authors (K. M.) found[7] that the rate of hydrogenation was reproducibly observed without fresh coating, if the product of a run was not evacuated but the gas mixture was just replenished to conduct the subsequent run. This result was confirmed in the present experiment which secures the soundness of the initial rates or that they are free from poisoning except at temperatures higher than 170°C.

Figs. 2 and 3 show the ARRHENIUS plots of the initial rates v_0 of hydrogenation of different series observed respectively by the circulation or the static method. In the series by the circulation method, the initial partial pressure of hydrogen was commonly 10 mmHg except for series 3, while the initial

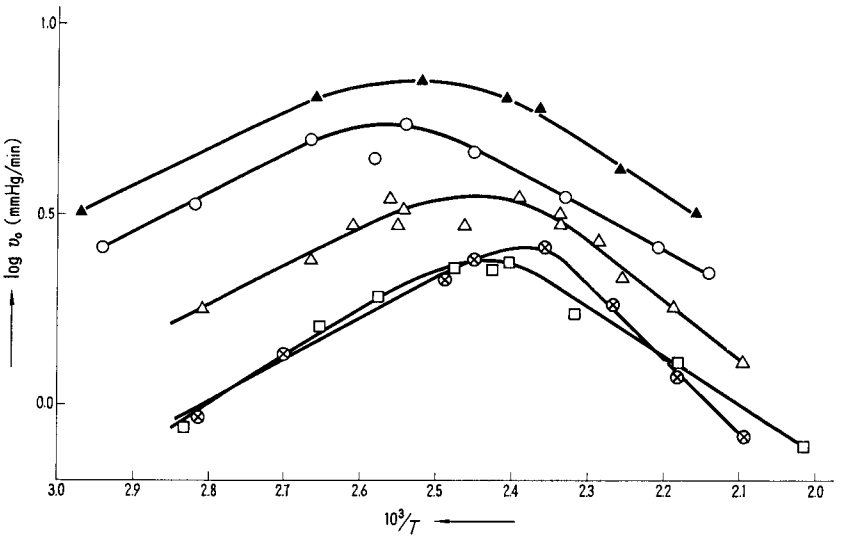

Fig. 2. ARRHENIUS plots of initial rates of the circulation series.

○ : Series 1, $P^E = 10$ mmHg, $P^H = 10$ mmHg, △: Series 2, $P^E = 20$ mmHg, $P^H = 10$ mmHg, ▲: Series 3, $P^E = 20$ mmHg, $P^H = 20$ mmHg, □: Series 4, $P^E = 50$ mmHg, $P^H = 10$ mmHg, ⊗: Series 5, $P^E = 100$ mmHg, $P^H = 10$mmHg.

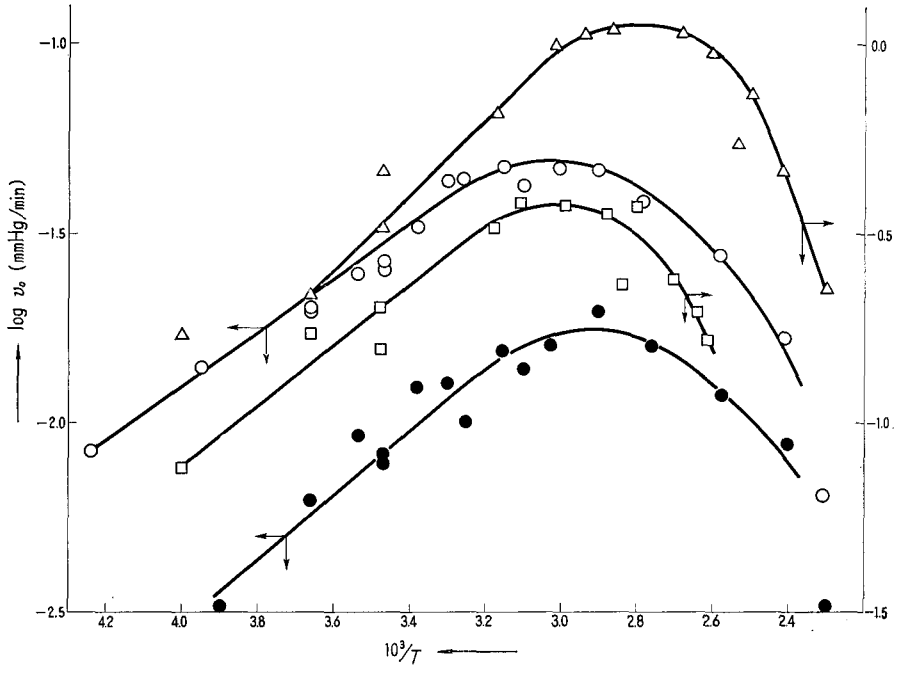

Fig. 3. ARRHENIUS plots of initial rates of the static series.
○ : Series 6-a, $P^E = 0.03$ mmHg, $P^H = 0.03$ mmHg, ● : Series 6-b, each run conducted without fresh coating after evacuation of the product of preceding run, $P^E = 0.03$ mmHg, $P^H = 0.03$ mmHg, △ : Series 7, $P^E = 0.3$ mmHg, $P^H = 0.3$ mmHg, □ : Series 8, $P^E = 0.03$ mmHg, $P^H = 0.075$ mmHg.

partial pressure of ethylene was varied from 10 mmHg to 100 mmHg.

The static series were conducted with equal hydrogen and ethylene partial pressures except for series 8 and the initial total pressure was varied from 0.06 mmHg to 0.6 mmHg instead of varying the initial partial pressure of ethylene alone; runs of series 6-b were conducted without fresh coating each after evacuation of the product of the preceding run. Series 8 was carried out statically to examine the pressure dependence of optimum temperature on hydrogen partial pressure. The calibration curve of the Pirani gauge indicated that the reaction could hardly be followed accurately by the Pirani gauge neither at the ratio of the initial partial pressure of hydrogen to that of ethylene higher than that in series 8 nor at the ratio lower than its reciprocal.

The total pressure did not decreased at temperature above 170°C in case of the static method, whereas it decreased in the subsequent run conducted at the same temperature after evacuation without fresh coating. This appears

to be due to decomposition of ethylene on the freshly evaporated film forming hydrogen.

The optimum temperatures were determined from smoothed curves through the ARRHENIUS plots at their maxima as shown in Figs. 2 and 3. Results are summarized in Table 1.

TABLE 1. Optimum temperature and heat of activation at different initial partial pressures.

No. of series	P^E mmHg	P^H mmHg	t_{opt} °C	t_{opt} (wire) °C	E_l Kcal	E_h Kcal
1	10	10	117	150	4.8	~ -5
2	20	10	135	160	5.0	~ -7
3	20	20	125	—	4.6	~ -6
4	50	10	140	—	—	~ -6
5	100	10	150	190	5.5	~ -14
6-a	0.03	0.03	56	—	3.3	—
7	0.3	0.3	84	—	4.6	—
8	0.03	0.075	60	—	~3.7	—

Cols. 2 and 3 in Table 1 give the initial partial pressures of ethylene P^E and hydrogen P^H respectively. The optimum temperatures observed on fresh nickel film are shown in Col. 4 in comparison with t_{opt} (wire) in Col. 5, *i.e.* the optimum temperatures on nickel wire previously observed[10]. Cols. 6 and 7 show the heat of activation at temperatures below and above the optimum respectively. The heat of activation above the optimum is hardly reliable because of the possible decomposition of ethylene mentioned above.

The optimum temperature rises definitely with increase of the initial partial pressure of ethylene but is apparently independent of that of hydrogen, and it shifts to higher temperature in series 6-b as shown in Fig. 3 where each run was conducted after evacuation of the product of the preceding run without fresh coating. The optimum temperatures observed on nickel wire are about 30°C higher than those on fresh nickel film. This indicates that the optimum temperature rises as the catalyst is poisoned by oxygen, nitrogen or so-called acetylenic residues. The heat of activation below the optimum temperature in case of the equimolar mixture increases with increase of the total pressure and that above the optimum temperature appears to increase in its absolute value as well, although it is not at all observable above the optimum temperature at the initial total pressures below a few mmHg because of the reason mentioned above.

Discussion

It follows from the structure theory of HORIUTI[1] that the absolute temperature T_{opt} of the optimum, where the rate-determining step switches over from I_b to III in scheme (1), is given by the equation

$$T_{opt} = \left(\Delta^*\varepsilon(I_b) - \Delta^*\varepsilon(III)\right) \Big/ R \ln(Q_P^E/P^E); \qquad (2)$$

$\Delta^*\varepsilon(I_b)$ or $\Delta^*\varepsilon(III)$ is the heat of activation of the overall reaction with the rate respectively determined by step I_b or III, R the gas constant, P^E the partial pressure of ethylene in mmHg and Q_P^E the modified partition function[1] of a single ethylene molecule in unit volume, *i.e.*

$$Q_P^E = \frac{kT}{1333} \frac{(2\pi m^E kT)^{3/2}}{h^3} \frac{2\pi^2 (2\pi I^E kT)^{3/2}}{h^3} \prod_{i=1}^{12} \left(1-\exp(-h\nu_i/kT)\right)^{-1} e^4, \qquad (3)$$

where k, T and h are of usual meanings and other quantities m^E *etc.* are

m^E: mass of an ethylene molecule, *i.e.* $4.65 \times 10^{-23}\, g$,

I^E: the geometric mean of three principal moments of inertia of ethylene, *i.e.* $I^E = (I_A I_B I_C)^{1/3}$,

where $I_A = 33.2 \times 10^{-40}$, $I_B = 27.5 \times 10^{-40}$ and $I_C = 5.7 \times 10^{-40}$,

ν_i: i-th normal vibrational frequency of ethylene[11].

We have on the basis of the above values

$$\log Q_P^E = 14.7, \qquad (T = 373\,°K). \qquad (4)$$

It follows from (2) and (4) that

$$\frac{1}{T_{opt}} = \frac{2.303\,R}{\Delta^*\varepsilon(I_b) - \Delta^*\varepsilon(III)} (14.7 - \log P^E), \qquad (5)$$

which states that the reciprocal of T_{opt} varies linearly with the logarithm of P^E.

Fig. 4 shows the observed results of $1/T_{opt}$ plotted against $\log P^E$, from which we have

$$\frac{1}{T_{opt}} = \frac{1}{5300} (14.5 - \log P^E). \qquad (6)$$

The first term in the parenthesis of the above equation is in good agreement with the theoretical value of (4). We have on the other hand from the coefficient of $(14.5 - \log P^E)$ in the above equation $\Delta^*\varepsilon(I_b) - \Delta^*\varepsilon(III) = 24$ Kcal which is perfectly coincident with that determined[1] from the observation of ZUR STRASSEN[4].

Fig. 4 shows besides the linear relation between $1/T_{opt}$ and $\log P^E$ as observed on "carbided surface", *i.e.* the catalyst surface obtained by repeating

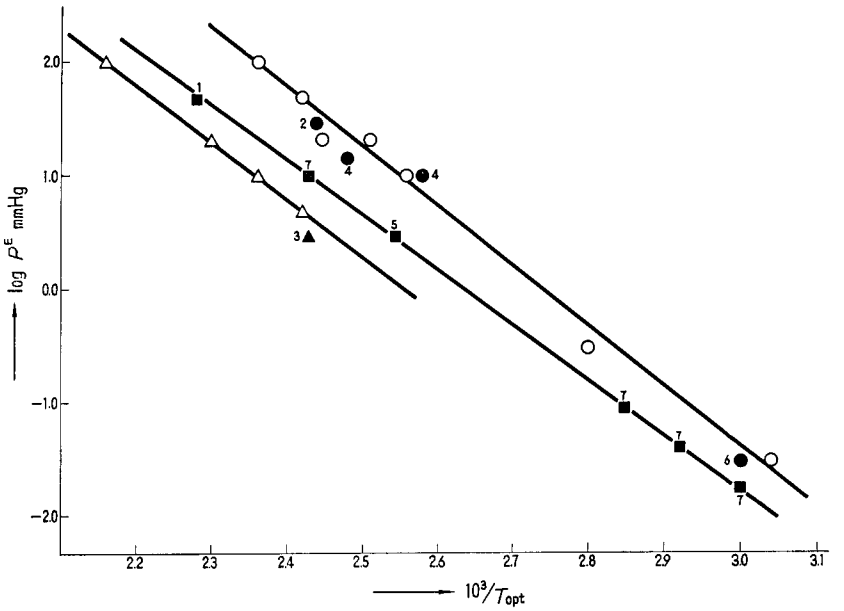

Fig. 4. Pressure dependence of optimum temperature on ethylene partial pressure.

○ : Present results (evaporated film), △ : Previous results[10] (wire), ● ■ ▲ : Other results in literature; 1 : JENKINS and RIDEAL[6], 2 : RIDEAL[3], 3 : TUCHOLUSKI and RIDEAL[5], 4 : MIYAHARA[7)10], 5 : TUUL and FARNSWORTH[8], 6 : ZUR STRASSEN[4], 7 : MIYAHARA[10] ("carbided surface"). Catalyst classification; ○ ● : Evaporated film or foil, ■ : "Carbided surface", △ ▲ : Reduced wire.

the reaction followed by evacuation of the product without fresh coating until stable activity was observed as in the case of JENKINS and RIDEAL[6], or on nickel wire activated by oxidation followed by reduction for every run. The linear relation is satisfied both in the latter cases, although more or less shifted.

TUUL and FARNSWORTH[8] observed the hydrogenation of ethylene using a high vacuum system and cleaning the catalyst surface by argon ion bombardment prior to every run. They obtained the optimum temperature as 120°C at 3 mmHg partial pressure of ethylene. Their result belongs rather to the "carbided surface" group on Fig. 4. The argon ion bombardment in their experiment might have brought upon the "carbided surface", hence the above result.

According to SCHWAB[12], ethylene is desorbed at the optimum temperature with rise of temperature. His rate equation based on this assumption leads to the equation

$$\frac{1}{T_{opt}}=\frac{2.303R}{\lambda^{E}}\left(\log\frac{-q+\lambda^{E}+\lambda^{H}}{b_0^{E}(q-\lambda^{H})}-\log P^{E}\right), \tag{7}$$

where λ^{E} is heat of adsorption of ethylene, q "true" activation energy, λ^{H} heat of adsorption of hydrogen and b_0^{E} adsorption coefficient of ethylene. SCHWAB evaluated $q-\lambda^{H}$ and λ^{E} in (7) by fitting his rate equation to the experimental result of ZUR STRASSEN[4] as

$$q-\lambda^{H}=7.3\ \text{Kcal} \tag{8}$$

and

$$\lambda^{E}=17.3\ \text{Kcal}; \tag{9}$$

we have further

$$\log b_0^{E}=-9.1 \tag{10}$$

by fitting his rate equation to the same experimental result[3], hence

$$\frac{1}{T_{opt}}=\frac{1}{3760}(9.3-\log P^{E}), \tag{11}$$

which states the linear relation between $1/T_{opt}$ and $\log P^{E}$ as (5) or (6), but the constants implied are considerably different from observed ones in (6).

MIYAHARA, TERATANI and TSUMURA[9] have recently observed the adsorption of ethylene and hydrogen in course of hydrogenation. Their result shows that desorption of ethylene does not at all occur at the optimum temperature to each an extent as required to attribute the optimum to desorption[13]. The desorption mechanism is thus negatived by these results.

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References

1) J. HORIUTI, This Journal, **6**, 250 (1958).
2) J. HORIUTI and M. POLANYI, Trans. Faraday Soc., **30**, 1164 (1934).
3) E. K. RIDEAL, J. Chem. Soc. (London), **1922**, 309.
4) H. ZUR STRASSEN, Z. physik. Chem., **A 169**, 81 (1934).
5) T. TUCHOLUSKI and E. K. RIDEAL, J. Chem. Soc. (London), **1935**, 1701.
6) G. I. JENKINS and E. K. RIDEAL, *ibid.*, **1955**, 2490.
7) K. MIYAHARA, This Journal, **11**, 1 (1963).
8) J. TUUL and H. E. FARNSWORTH, J. Am. Chem. Soc., **83**, 2247 (1961).
9) K. MIYAHARA, S. TERATANI and A. TSUMURA, This Journal, **12**, 98 (1965).
10) Unpublished results.

11) R. L. ARNETT and B. L. CRAWFORD, J. Chem. Phys., **18**, 118 (1950).
12) G. M. SCHWAB, Z. physik. Chem., **A 171**, 421 (1934).
13) J. HORIUTI, K. MIYAHARA and I. TOYOSHIMA, a paper submitted to the Colloquim on *Physical Chemistry of Process on Superficies of Solids*, Madrid, 20–25th, October 1964.