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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 3—Adsorption in Course of Hydrogenation of Ethylene on Evaporated Nickel Film.

By

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Abstract

Adsorption of ethylene and hydrogen in course of hydrogenation of ethylene on evaporated nickel film was measured simultaneously with the rate of hydrogenation at temperatures from −45°C to 200°C. It was found that the adsorbed amounts both of ethylene and hydrogen were nearly constant independent of temperature and their sum amounted to less than 30% of the full coverage of the film.

It was concluded on these bases that the so-called optimum temperature was not due to the desorption of adsorbed ethylene as ever proposed.

Introduction

It is well-known that the hydrogenation rate of ethylene on nickel catalyst has an optimum temperature. SCHWAB[1] has attributed this phenomenon to the desorption of ethylene with rise of temperature through the optimum, whereas HORIUTI[2] has concluded this as due to switch over there of the rate-determining step from that of positive activation energy to another of negative activation energy. HORIUTI, MIYAHARA and TOYOSHIMA[3] have deduced from experimental results of the hydrogenation on evaporated nickel film[4][5] the number G_1^* of seats for the critical complex of the rate-determining step to be of the order of magnitude of $10^{15}\,cm^{-2}$. It follows from this result that ethylene should be desorbed at least by this amount with rise of tempetature through the optimum, provided that the former mechanism is operative, inasmuch as ethylene may be desorbed from somewhere else as well.

This conclusion is put to the experimental test in the present work by measuring the adsorbed amounts of hydrogen and ethylene on evaporated nickel film in course of hydrogenation at different temperatures through the optimum.

*) S. T., a Yukawa Fellow from Faculty of Science, Osaka University.

The result shows that no desorption of the magnitude occurs through the optimum but the amount of adsorption less than $0.3 \cdot 10^{15}$ cm^{-2} is kept constant throughout the temperature ranges of observation, which contradicts the former mechanism but is in conformity with the latter.

Experimental

Materials: The material for the nickel film was the same nickel wire of 0.5 mm diameter as that in the previous work[4]; its impurities were determined by chemical analysis*) as

Impurities	Co	Mn	Si	Fe	Cu	Mg
Weight %	0.25	0.23	0.04	0.011	0.003	0.002

Electrolyzed hydrogen was passed through a heated Pd thimble and chemically pure ethylene distilled repeatedly in vacuo from a trap at -94°C to another at -195°C until its vapour pressure at -195°C was reduced to $3 \cdot 10^{-3}$ mmHg; the 1 : 1 mixture of hydrogen and ethylene thus prepared, as called the reactant mixture in what follows, was stored in a reservoir. The reactant mixture was found mass spectrometrically free from water, oxygen, nitrogen, methane, ethane and propylene that each impurity was less than *ca.* 10^{-4} part of ethylene.

Apparatus and Measurements: Apparatus all made of Hario glass**) as used in the previous work[4] was utilized in the present experiment as shown in Fig. 1. The reaction vessel V of *ca.* 110 cc capacity was fused to the rest of the apparatus though an U-shaped trap T_1 of *ca.* 5 mm diameter and 30 cm length. G_1 is a Pirani gauge of *ca.* 3 cc dead space and G_2 a Mcleod gauge, both connected to V through a capillary tube of *ca.* 1 mm diameter. R_H or R_M is a reservoir containing hydrogen or the reactant mixture, M_1 an oil-manometer of sensitivity $5.78 \cdot 10^{-2}$ mmHg/mm Oil at 20°C, P_1 or P_2 a gas pipette of 3.48 cc or 55.0 cc capacity respectively and S_0, S_1 *etc.* sampling vessels each of *ca.* 500 cc voloum for mass spectrometric analyses of the reactant mixture and reacted gases. I.G. is an ionization gauge. Traps T_1 and T_2 were cooled by dry ice-alcohol mixture and T_3 by liquid nitrogen throughout the present observations.

Prior to evaporating nickel onto the wall of vessel V, Pirani gauge G_1 was calibrated by Mcleod gauge G_2 by using the reactant mixture; the absence of

*) This analysis has been conducted by Dr. KIRINUKI, a member of Tokyo Institute of Sumitomo Metal Mining Co. Ltd., to whom best thanks of the present authors are due.

**) This glass is supplied by Shibata Glass Co. Ltd., Japan, the composition and the properties being close to those of Pyrex glass.

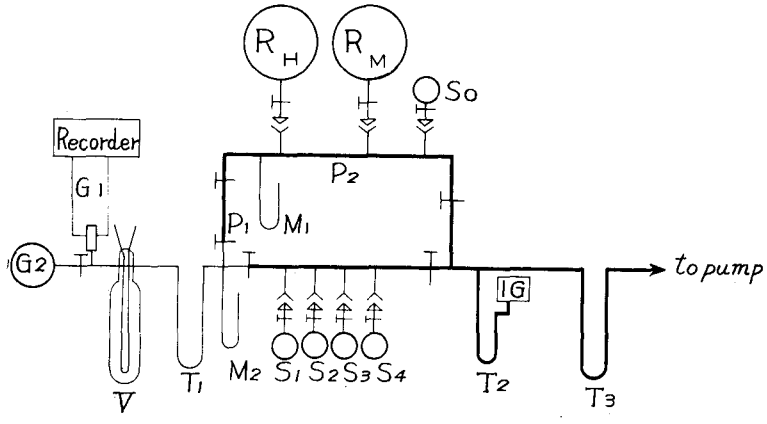

Fig. 1. Reaction apparatus.

adsorption of hydrogen or ethylene by glass wall was preliminarily confirmed.

The wall of the vessel kept at 200°C was now coated with evaporated nickel by the same procedure as described in the previous paper[4]; the bath around V was now changed to another at a reaction temperature and the reactant mixture of *ca.* $2.5 \cdot 10^{17}$ molecules was introduced from R_M into V to start the hydrogenation, which was followed by G_1 and a pen-recorder. At a recorded time a part of the reacted gas was sampled from V into S_1. The subsequent run was started by evacuating the reacted gas from V at the reaction temperature and by introducting the same amount of reactant mixture from R_M.

Fig. 2 illustrates a record of a run of reaction thus conducted, point a, b or c showing a reading of the pen-recorder against the time of reactant mixture introduction into V, that of sampling of reacted gas or that of evacuation of V respectively. After these two runs the nickel film was coated fresh with evaporated nickel keeping the wall of V at 200°C and new successive two runs of reaction at a difierent temperature were conducted similarly as the foregoing ones.

The pressure of gas mixture in V was determined from the record illustrated in Fig. 2, which was calibrated as mentioned above, ignoring the shift of composition of gas in G_1 due to the reaction in V on the ground of that G_1 was connected to V by a capillary tube and the pressure in V decreased monotonously.

The composition of the sampled gas was determined by means of a mass spectrometer as follows. Ion beams of mass number less than 12 being only poorly focussed by the mass spectrometer, the voltage of the focus grids was first adjusted to the maximum height at the peak M_2 of mass number 2 and then to that at peak M_{28} to record a spectrum of hydrogen and then that of

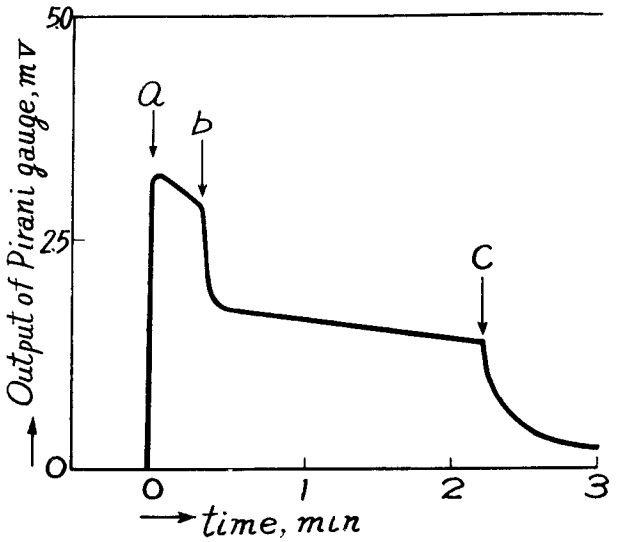

Fig. 2. A record of a run of reaction.
a: introduction of reactant mixture.
b: sampling. c: evacuation of reacted gas.

hydrocarbons, comprizing peaks from M_{26} to M_{30}, respctively. The sensitivity ratio of M_2 to M_{28} in the mass spectra was determined as the height ratio of M_2 to M_{28} in the mass spectrum of the reactant mixture, which was sampled from P_2 into S_0. The sensitivity ratio of ethylene to ethane was similarly determined on the bases of mass spectra of pure ethane and a standard mixture of 84.3% ethylene and 15.7% ethane by calculating contributions of ethylene and ethane to the height of peak M_{28} in the spectrum of the standard mixture, referring to the fact that peak M_{30} in this spectrum originates from ethane alone.

The relative amounts of hydrogen, ethylene and ethane in the reacted gas were then determined on the bases of heights of peaks M_2, M_{28} and M_{30} in the spectrum of the gas and the sensitivity ratios determined as above, and thus the absolute amounts of these components of gas in V were determined referring to the total pressure measured by Pirani gauge G_1 at the moment of sampling the gas from V (*i.e.* at the point b in Fig. 2). The adsorbed amount of hydrogen or ethylene was determined as the excess of the amount of the component introduced into V over the sum of its amount left in reacted gas and that converted into ethane, adsorption of ethane being neglected on account of the following result of a preliminary experiment. Pure ethane was found to be adsorbed by $3.98 \cdot 10^{16}$ molecules on fresh-coated nickel film at 0°C, but none

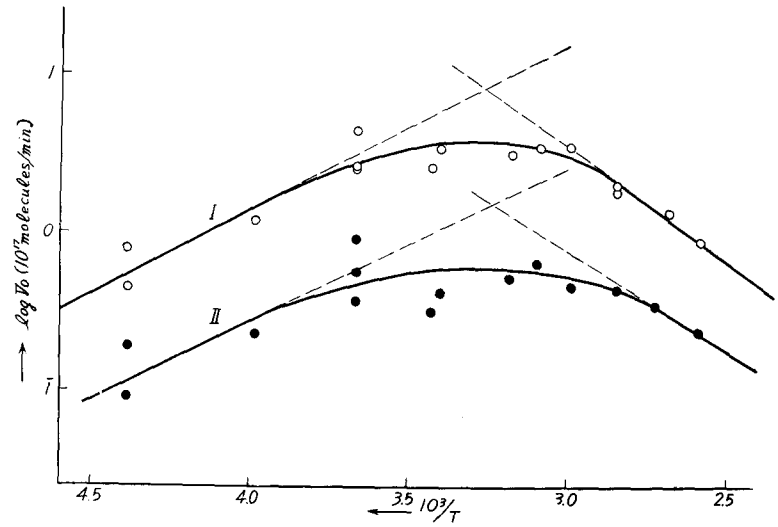

Fig. 3. Temperature dependences of initial hydrogenation rates in the first (I) and the second (II) runs respectively.

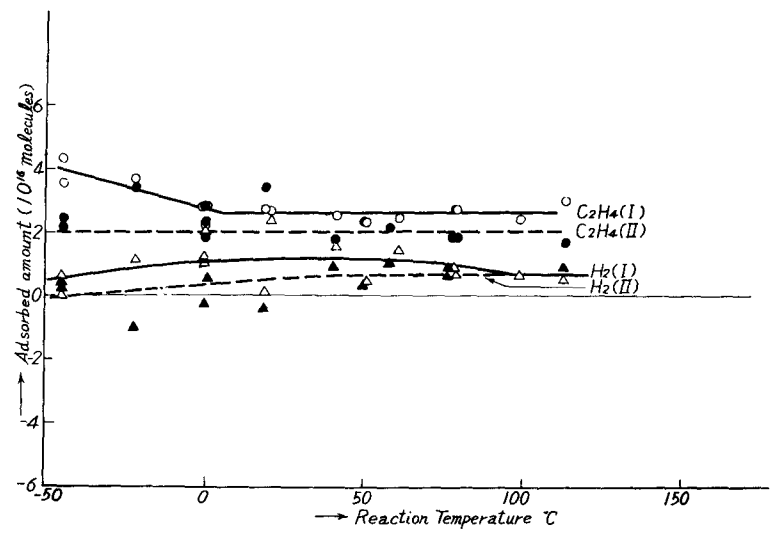

Fig. 4. Temperature dependences of adsorption of H_2 and C_2H_4 in the first (I) and the second (II) runs respectively.

of ethane was adsorbed from the standard mixture of ethylene and ethane at 0°C, whereas the coexistent ethylene was adsorbed by $3.62 \cdot 10^{16}$ molecules.

Results

Fig. 3 shows the logarithm of the hydrogenation rate determined as the negative of the initial inclination of a–b part exemplified in Fig. 2, plotted against $1000/T$; curve I or II is respectively the result of the first or the second runs conducted successively on fresh-coated film. These results are satisfactorily reproducible revealing the optimum temperature at *ca.* 35°C and *ca.* 5 Kcal activation energy at lower temperature. Absence of methane was confirmed by mass spectrometrical analysis of reacted gas of every run.

Fig. 4 shows the typical series of adsorbed amounts of hydrogen and ethylene in course of hydrogenation of the result in Fig. 3. H_2(I) and C_2H_4(I) or H_2(II) and C_2H_4(II) indicate adsorbed amounts of hydrogen and ethylene in the first or the second run respectively. The adsorbed amount of ethylene in the first runs decreases with temperature at lower temperature but is practically constant from 0°C to 100°C through the optimum; the adsorbed amount of hydrogen, smaller than that of ethylene, appears to increase up to the optimum and then decrease with temperature. The adsorbed amounts both of hydrogen and ethylene in the second runs are practically constant independent of the reaction temperature and slightly smaller than those in the first runs.

The adsorbed amounts of hydrogen and ethylene at 0°C or 80°C were found unchanged both in the first and the second runs by doubling the amount of reactant mixture introduced into the reaction vessel.

At 200°C the adsorbed amount of ethylene was found apparently twice the constant value around the optimum, while hydrogen was evolved by the same amount both in the first and the second runs. This indicates the predominance of decomposition of ethylene to form so-called acetylenic complex.

Discussion

SCHWAB's mechanism[1] of optimum temperature is unequivocally contradicted by the present result that the adsorbed amount of ethylene in course of hydrogenation is nearly constant over a wide range of temperature through the optimum, as incorporated with the previous conclusion that there are 10^{15} cm^{-2} seats for the critical complex by order of magnitude, which are occupied by ethylene at temperatures below the optimum but evacuated above according to the SCHWAB's mechanism.

It follows on the other hand from the present result as below that the cover-

age fraction of the catalyst surface is *ca.* $25\pm8\%$ in the first run. Adsorbed ethylene and hydrogen occupy $(5.2\pm0.8)10^{16}$ and $(2.0\pm1.2)10^{16}$ sites respectively in the first run assuming that each ethylene or hydrogen molecule occupies a pair of sites on the catalyst surface when adsorbed. The sum of these number of sites occupied amounts to the above mentioned fraction of total number of sites, *i.e.* $10^{15}\,cm^{-2}$ multiplied the roughness factor 3[6] times the apparent area $120\,cm^2$ of the evaporated film. This conclusion is in conformity with the mechanism of HORIUTI[2], as concluded from the experimental results by premising approximately uncovered catalyst surface.

The adsorption observed in course of hydrogenaiton may be due to nearly saturated adsorption on lattice imperfections leaving the active surface free in the case of the first run. If then, some part of active surface must be additionally covered by poison in the case of the second run, since the hydrogenation rate was then reduced. The poison may be inferred to be formed by evacuation in accordance with the previous result found by one of the present authors[4] that the catalytic activity was considerably reduced by evacuation whereas not by simple replenishment of the reactant mixture without evacuation.

The cause of the apparently saturated adsorption is now under investigation by further observations with nickel film evaporated from purer nickel wire in higher vacuum.

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