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Title	HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS : Part 2-Kinetics of Ethylene Hydrogenation on Nickel Wires
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 12(2), 67-75
Issue Date	1965-01
Doc URL	https://hdl.handle.net/2115/24778
Type	departmental bulletin paper
File Information	12(2)_P67-75.pdf



HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 2—Kinetics of Ethylene Hydrogenation on Nickel Wires

By

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(Received April 21, 1964)

Abstract

The kinetics of catalyzed hydrogenation of ethylene in the presence of nickel wires was studied over a range of partial pressures both of ethylene and hydrogen from about 0.017 to 0.15 mmHg, taking special precautions against the decay of catalytic activity. The catalysts were activated by oxydation followed by reduction and annealing before every series of runs of the catalyzed hydrogenation.

Several series of the catalyzed hydrogenation runs were conducted by evacuating and reducing the catalyst after each run at different hydrogen and ethylene partial pressures. The initial rate of hydrogenation of each run was thus found proportional to the 0.7th power of hydrogen partial pressure P^H but independent of ethylene partial pressure p^E , *i.e.* proportional to $(P^H)^{0.7}(P^E)^0$ as investigated at 0°C and -45°C. The activation energy was determined to be 5.3 ± 0.3 Kcal/mole from the initial rate observed separately at -22°C, 0°C, 11°C and 25.5°C.

Series of another sort were carried out by keeping the catalyst in ethylene vapour (0.03 mmHg) saturated at liquid oxygen temperature and starting every run just by supplementing hydrogen consumed without evacuation or any other preceding treatment of catalyst. The decay of catalytic activity with each run of a series was less than 5% and the rate of hydrogenation was proportional to $(P^H)^{0.7}$ at 0°C, 25.5°C and 40°C. The optimum temperature was thus found about 60°C and the activation energy below the optimum 5.3 ± 0.2 Kcal/mole in coincidence with in case of the series of the first sort. The decay of catalytic activity with each run amounted, however, to 20% or more above the optimum, excluding any quantitative determination of activation energy there.

Introduction

A number of studies have been conducted of the catalyzed hydrogenation of ethylene in the presence of nickel, but there exists scarcely quantitatively reliable observation mainly because of an appreciable decay of the catalytic activity in course of the reaction.

zur STRASSEN¹⁾ reported the clear-cut experimental result that the rate of hydrogenation was proportional to hydrogen pressure but independent of ethylene

pressures lower than 0.2 mmHg and temperatures below the optimum one; he described none, however, as to the decay of catalytic activity.

The present investigation is conducted with a view to establish the kinetics quantitatively with special precautions taken against the decay.

Experimental

The whole apparatus is shown in Fig. 1. The catalysts used are respectively about 50 cm, 300 cm and 12 cm long nickel wires of 0.1 mm diameter and of about 99.9% purity^{*)2)}, which were sealed in reaction chambers RC₁, RC₂ and

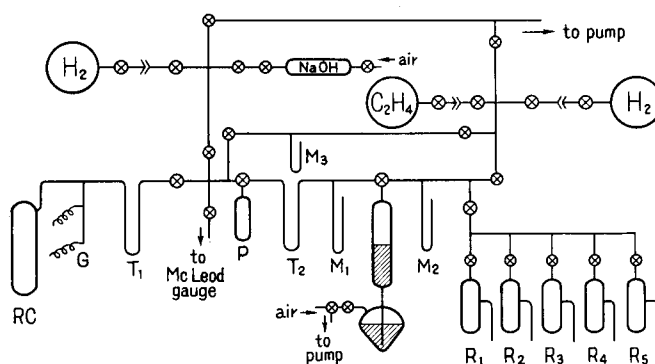


Fig. 1. Apparatus.

RC: Reaction chamber, G: Pirani gauge, T₁ and T₂: Traps cooled by dry ice ethanol mixture, M₁: Silicone oil manometer, M₂ and M₃: Mercury manometer, P: Gas pipette, R₁ etc.: Reservoirs of gas mixtures.

RC₃ in Fig. 2 respectively each of about 100 cc capacity. Pirani gauge, with which the reaction is followed, consists of about 9 cm long tungsten wire of 0.02 mm diameter sealed in a thin-walled tubing of 2 mm bore, which is immersed in ice water. The sealed tungsten wire is set up in a Wheatstone network and calibrated with McLeod gauge. The total pressure in the reaction chamber was measured up to 0.2 mm Hg by means of this Pirani gauge with an accuracy of ± 0.000 , mmHg.

The catalysts were activated before every series of runs by oxydation at 600°C for 15 min. in atmospheric air followed successively by reduction at 300°C for 15~40 hr in hydrogen of 15~20 mmHg pressure, annealing at 600°C for 30 min. in vacuo and heating at 300°C in hydrogen of 15~20 mmHg pressure for 15~20 hr.

* The material is a portion of the nickel wire reported in Ref. 2) to be of the mentioned purity.

The reaction temperature was controlled by immersing the reaction chamber in a slush bath of chlorobenzene (-45°C), carbon tetrachloride (-22°C) or melting ice (0°C) or in a bath of water (11°C and 25.5°C) or oil (above 40°C). Thermal transpiration was neglected on the ground of a check in a few cases according to the method of LIANG³⁾, which showed that the systematic error of the total pressure measurement introduced by the neglect was sufficiently small.

Ethylene was prepared by dehydrating ethyl alcohol with orthophosphoric acid and purified by passing it through alkaline hydro-sulphite and concentrated sulphuric acid, and by repeated distillations in vacuo. Hydrogen was prepared by electrolysing ordinary water and purified by passing it through a heated palladium thimble.

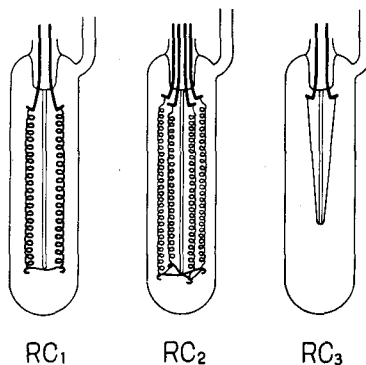


Fig. 2. Reaction chambers.

Results

Preliminary experiments of the catalyzed hydrogenation of ethylene were carried out by evacuating the reaction product and then by reducing the catalyst after each run over a range of initial total pressure from a few mmHg to a few cmHg. The results were unsatisfactory, dependence of the rate on the partial pressures of hydrogen and ethylene being almost masked by an appreciable fluctuation and decay of the catalytic activity.

zur STRASSEN had investigated this reaction at low ethylene pressure below 0.1 mmHg with the clear-cut experimental results, although no description is given as to whether the observation were reproducible or not as mentioned above. Several preliminary series of runs have been carried out under the similar conditions with a hope of reproducible observations, each run being followed by evacuation but not by reduction. The runs were conducted successively at 0.1 mmHg initial total pressure of 1 : 1 mixture of ethylene and hydrogen at 0°C . The result was none the better, the catalytic activity decreasing every run by about 20% or more. Ethylene and hydrogen have now been further purified by passing the former repeatedly through liquid potassium-sodium alloy and by allowing the latter adsorbed at -195°C by molecular sieves^{*)} and then desorbed from it at *ca.* -100°C without any improvement. Two sorts

*) The molecular sieves were preliminarily degased by heating them in vacuo and in hydrogen alternately.

of series of runs were now conducted as described below with mixture of ethylene and hydrogen, each of the initial partial pressure 0.15 mmHg or less.

1) Series of runs each followed by evacuation and reduction.

This sort of series consists of runs successively conducted, each run being followed by evacuation of resultant gas and subsequent reduction at 300°C in hydrogen of 15~20 mmHg pressure for 1 hr. The initial rate of hydrogenation of runs was found reproducible within $\pm 15\%$, without perceptible trend of decay as observed in case of the preliminary experiment mentioned above. The initial rate V_0 was thus observed by varying initial pressures of ethylene and hydrogen at 0°C and -45°C using reaction chamber RC_1 and RC_2 respectively. Fig. 3 and Fig. 4 show the experimental results at 0°C. We see from them

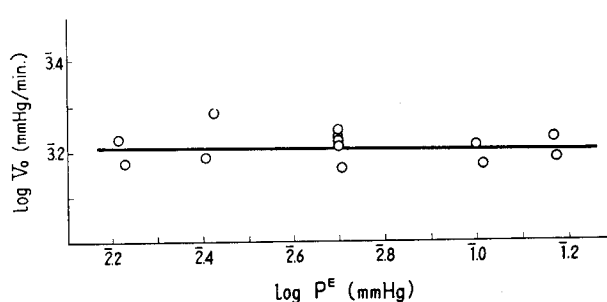


Fig. 3. $\log V_0$ (mmHg/min.) versus $\log P^E$ (mmHg), 0°C: initial partial pressure of hydrogen is $0.051 \pm 0.001_5$ mmHg.

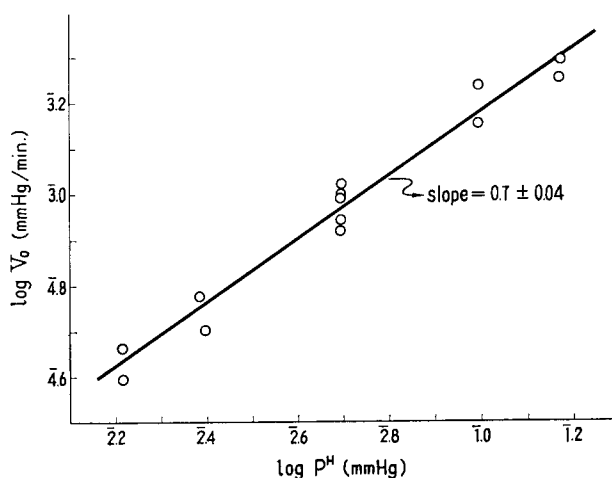


Fig. 4. $\log V_0$ (mmHg/min.) versus $\log P^H$ (mmHg), 0°C: initial partial pressure of ethylene is 0.049 ± 0.001 mmHg.

that V_0 is independent of partial pressure P^E of ethylene but proportional to the 0.7th power of partial pressure P^H of hydrogen, *i. e.*

$$V_0 = k(P^H)^{0.7}(P^E)^0 \quad (1)$$

where k is the rate constant. Fig. 5 and Fig. 6 show that the same rate law holds at -45°C .

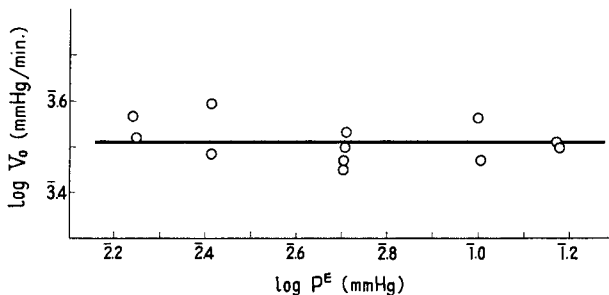


Fig. 5. $\log V_0$ (mmHg/min.) versus $\log P^E$ (mmHg), -45°C : initial partial pressure of hydrogen is $0.052 \pm 0.001_5$ mmHg.

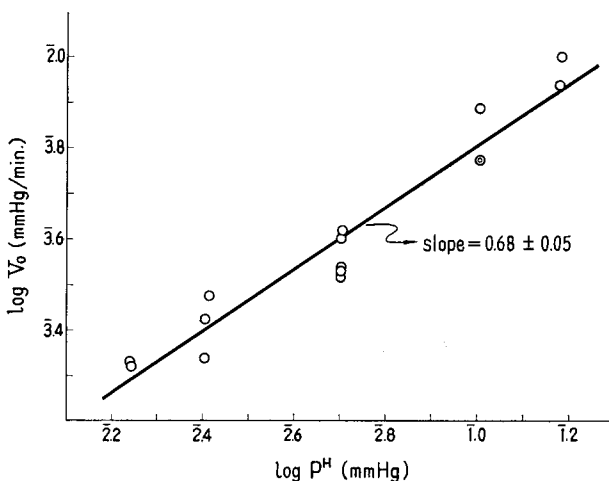


Fig. 6. $\log V_0$ (mmHg/min.) versus $\log P^H$ (mmHg), -45°C : initial partial pressure of ethylene is 0.051 ± 0.001 mmHg.

Fig. 7 shows the Arrhenius plot of the measurements, from which the activation energy is determined to be 5.3 ± 0.3 Kcal/mole.

2) Series of runs each followed neither by evacuation nor reduction.

The partial pressure of ethylene in the reaction chamber was kept constant

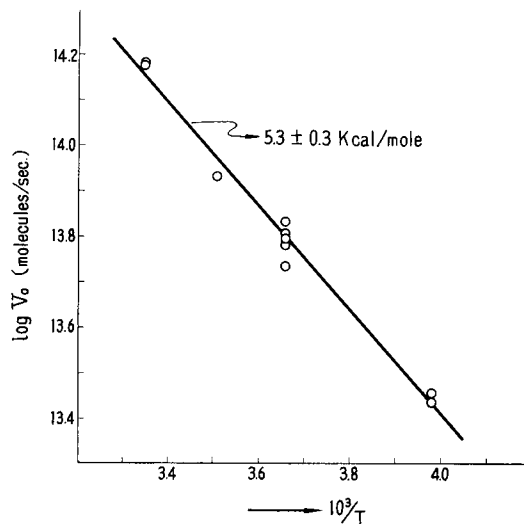


Fig. 7. $\log V_0$ (molecules/sec.) versus $1/T$: initial partial pressures both of ethylene and hydrogen are 0.050 ± 0.001 mmHg.

at the saturated vapour pressure over condensed ethylene in trap T_1 at liquid oxygen temperature throughout the series, each run being started just by supplementing hydrogen in reaction chamber but followed neither by evacuation nor by reduction, *i.e.* heating of the catalyst in hydrogen as in case of 1). Trap T_1 thus keeps the partial pressure of ethane at most at the saturated vapour pressure (0.005 mmHg) at the same temperature. The reaction chamber used was RC_1 at 0°C and RC_3 above 25.5°C . The decay of the rate thus observed, if any, was less than 5% with every run of the series conducted at 0°C , 25.5°C , 40°C and 60°C , but amounted more than 20% at 90°C . The order of reaction was 0.7 with respect to hydrogen as deduced from the linear relation between $(P^H)^{0.3}$ and time observed at 0°C , 25.5°C and 40°C from 0.1 to 0.03 mmHg hydrogen pressure in each run as shown in Fig. 8. This result is in perfect accordance with the relation between the initial rate and the initial hydrogen pressure as observed by method 1).

A series of several runs was now conducted in the reaction chamber RC_3 raising the temperature of a run stepwise from 0°C to 95°C , by following the hydrogen partial pressure in each run from 0.09 mmHg to *ca.* 0.07 mmHg, and returning the temperature of the last run to that of the first run in order to keep check with the activity of the catalyst. Two such series have been carried out, the decay of the catalytic activity during such series being found about 25%. The latter decay might be attributed to that at 90°C , which

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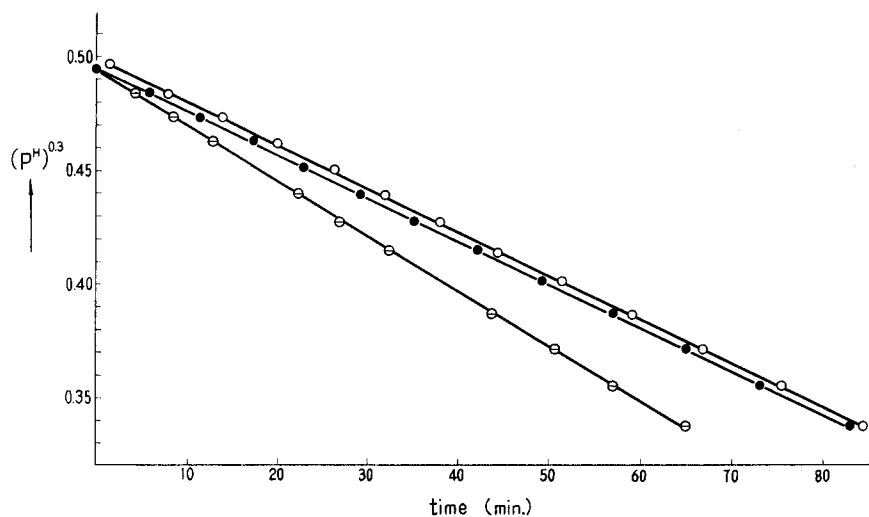


Fig. 8. $(P^H)^{0.3}$ versus time (min.): \circ , 0°C ; \bullet , 25.5°C ; \ominus , 40°C .

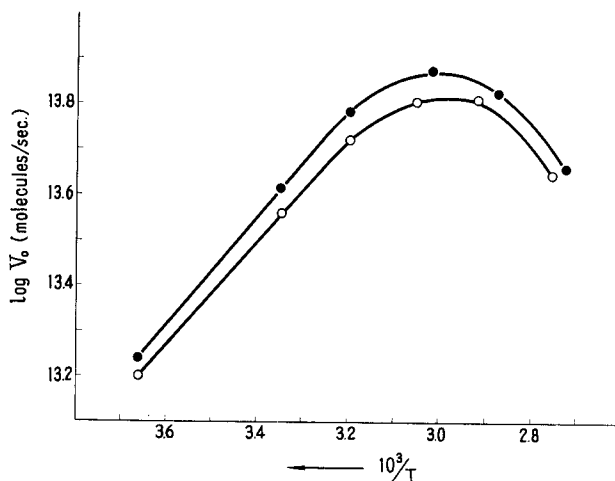


Fig. 9. $\log V_0$ (molecules/sec.) versus $1/T$: \circ , first series; \bullet , second series. Partial pressures of hydrogen, ethylene and ethane are 0.09, 0.03 and 0.005 mmHg respectively.

amounted more than 20% as mentioned above; the observations below 60°C would then be taken almost reproducible in accordance with the above results that the catalytic activity decays, if at all, by less than 5% every run. Fig. 9 shows the result of the series, from which the optimum temperature is determined to be 60°C and the activation energy below the optimum 5.3 ± 0.2 Kcal/mole.

The activation energy at temperatures above the optimum is quantitatively hardly accessible on account of the above-mentioned rapid decrease of the catalytic activity. The observed optimum temperature is in accordance with that observed by zur STRASSEN under the similar condition, while the activation energy below the optimum is in perfect coincidence with that determined by method 1).

Conclusive Remarks

It has been presumed above that the observations at temperatures below the optimum are almost reproducible, which is indirectly evidenced by the quantitative coincidence of the rate law as well as of the numerical value of activation energy as observed respectively by methods 1) and 2).

The present results might be compared with the two important contributions in this field, *i. e.* those of zur STRASSEN¹⁾ and of JENKINS and RIDEAL⁴⁾. The present results on the optimum temperature and the dependence of the rate on the partial pressure of ethylene are in accordance with those of zur STRASSEN but that on P^H differs from that proportional to P^H as reported by zur STRASSEN¹⁾. The latter author determined the dependence of the rate on P^H by a method similar to method 2) in the present paper. It is possible, that the exponent of the power of P^H , to which the rate is proportional, is apparently increased from 0.7 to 1.0 by an appreciable decay of the catalytic activity in course of a run.

The activation energy has been observed coincidentally at 5.3 Kcal/mole by the two methods 1) and 2), which contrasts with the value 10.2 Kcal/mole as observed by JENKINS and RIDEAL on carbided nickel films. These data different from each other may be coordinated with reference to the recent observation of MIYAHARA⁵⁾; he found the activation energy to be 5.6 Kcal/mole on a fresh evaporated film at temperatures below the optimum, by determining the initial rate at different temperatures every time on a freshly evaporated surface. He conducted the second run at each temperature after evacuating the product of the first run at the same temperature. The initial rate of the second run was found to have been reduced to about one fourth of that of the first one at the same temperature and the activation energy appropriate to the second runs 7~8 Kcal/mole below the optimum temperature. The temperature was now raised to 200°C in some of the cases and the runs each followed by evacuation, were successively carried out at the same temperature; the initial rate thus decreased steadily attaining a constant value which amounted to about one tenth of the initial rate on the fresh surface at the same temperature. The activation energy relevant to the final constant rate at each temperature

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was found 11.0 Kcal/mole in accordance with that on carbided surfaces as observed by JENKINS and RIDEAL⁴).

The present results have shown on the other hand that each run followed by evacuation reduces the activity of the catalyst by more than 20% as observed in preliminary experiment, whereas without the evacuation the rate is reproduced within a few percent according in method 2). These results suggest that the carbiding of the catalyst surface is promoted by evacuation, which decreases the rate, but increases the activation energy of the catalyzed hydrogenation, especially markedly at higher temperature above the optimum.

The present author wishes to express his sincere thanks to Professor J. HORIUTI for his kind advices and valuable discussions in the present work.

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