Title	HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS　Part 1-Reproducible Conditions of the Reaction on Evaporated Nickel Film
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Instructions for use

HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 1—Reproducible Conditions of the Reaction on Evaporated Nickel Film

By

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Abstract

Conditions for reproducible observation of the catalyzed hydrogenation of ethylene on evarporated nickel film were investigated with reference to the condition of evaporation and purities of hydrogen and ethylene. The reaction was rendered remarkably reproducible by use of highly pure hydrogen and ethylene, mass spectrometrically free from oxygen and nitrogen, and nickel films coated for every run of rate measurement with nickel freshly evaporated in vacuum of the order of 10^{-7} mmHg.

Under the best conditions thus found the initial rate of hydrogenation of *ca.* 1:1 mixture of hydrogen and ethylene at 30 mmHg initial total pressure on a film coated with freshly evaporated nickel was observed from 0° to 200°C. The optimum temperature was found 130°C and the activation energies 5.6 Kcal or −9.5 Kcal/mole at temperatures respectively below or above the optimum.

Introduction

It is well-known that the catalytic activity of nickel remarkably decreases by repetition of hydrogenation of ethylene, which appreciably obscured the reaction kinetics in former investigations.

According to Beeck[1], Jenkins and Rideal[2] or recently Thomson and Wishlade[3], the hydrogenation of ethylene on nickel catalyst was retarded by some residues of irreversibly prechemisorbed ethylene, *e. g.* acetylenic complex or carbon, but it is not evident whether these residues exist in the course of steady hydrogenation of ethylene. It was reported[2,4], besides, that a small amount of oxygen preadsorbed or contained in reactant gases gave rise to a few minutes induction period.

In the present work the conditions for reproducible observation of the reaction were investigated with evaporated nickel film and under the conditions thus found the temperature dependence of the reaction rate was observed.

Experiment

Fig. 1, (a) and (b) show the whole apparatus and particularly the reaction vessel V all made of Hario glass. Nickel wire of 0.5 mm diameter and *ca.* 34 cm length was spot welded to nickel lead in the reaction vessel, which was fused to the rest of the apparatus at the dotted line shown in Fig. 1, (b), where S is a mica shield to confine the evaporation of nickel underneath. P is a gas circulation pump of *ca.* 100 cc/sec. capacity, T_1 a U-trap of 1.5 mm diameter, M_1 a Hg-manometer of 10 mm diameter for measurement of hydrogenation rate, R_1 or R_2 a reservoir of hydrogen or 1 : 0.93 mixture of hydrogen and ethylene respectively, R_3 a sampling vessel for mass spectrometric analysis of resultant gas and I. G. an inoization gauge. Dead space of the circulation
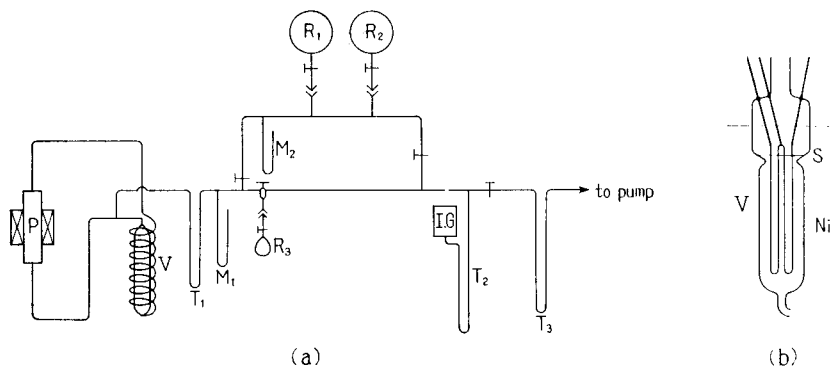

Fig. 1. Reaction apparatus (a) and vessel (b).

system amounts to *ca.* 200 cc. Prior to evaporation V was heated at 500°C in vacuo for a few hours and then in hydrogen of *ca.* 10 mmHg at the same temperature to reduce some oxides possibly remaining. After evacuation of the hydrogen, trap T_1 and T_2 were cooled by dry ice alcohol mixture and T_3 by liquid nitrogen respectively and evacuation was continued, heating the nickel wire electrically with 4.5–5.0 A alternating current, until 1×10^{-6} mmHg or higher vacuum was attained. V was then immersed into an oil bath at a recorded temperature and nickel was evaporated for a few minutes from the white-hot wire heated with *ca.* 6.5 A current. The temperature of the oil bath at the evaporation will be called the appropriate evaporation temperature in what follows.

The current was now broken, the bath around V changed to another one at a reaction temperature, the gas mixture of 30 mmHg total pressure introduced from R_2 into V and the reaction thus started was followed by reading the manometer M_1, time to time stopping the circulation pump P. The circulation pump was kept constantly in operation since the evacuation preceding

the evaporation in order to remove gas held in it. After the first run thus conducted, the subsequent run was started either by supplementing the reactant mixture to make up the initial pressures of reactants or by pumping out the resultant gas from V and by introducing the same initial amount of reactant mixture from R_2. The nickel film was occasionally coated with nickel freshly evaporated at a recorded temperature after the reaction vessel was evacuated at temperature of the foregoing run, filled with 10 mmHg hydrogen, heated subsequently to 500°C and then evacuated at the same temperature. The apparent area of the evaporated film was *ca.* 35 cm².

Two samples of hydrogen of different purity were used; one (A) was purified by an usual method, *i.e.* passing electrolyzed hydrogen through tubes packed with silica-gel, P_2O_5 and Pt-asbestos, and finally through liquid nitrogen trap; this sample contained a few hundredth percent of air as observed mass spectrometrically. The other (B) was obtained from (A) as follows. Molecular sieves were heated in vacuo and in (A) alternately at 300°C and finally evacuated at 300°C. Hydrogen (A) was now allowed to be absorbed by the molecular sieves thus treated and cooled by liquid nitrogen, and then desorbed at *ca.* −100°C. The sample (B) thus obtained was found mass spectrometrically free from oxygen and nitrogen. Ethylene was purified by distilling it a few times in vacuo between two traps reciprocatively from *ca.* −100°C to liquid nitrogen temperature; ethylene thus purified was found mass spectrometrically free from oxygen and nitrogen.

Results

Fig. 2 show remarkable decreases of catalytic activity of film coated with freshly evaporated nickel at *ca.* 130°C and 10^{-6} mmHg caused by repetition of

TABLE 1. Dependence of Catalytic Activity of Nickel Film on Its Evaporation Temperature: Initial Rate of Total Pressure Decrease at 50°C and 30 mmHg Total Pressure of *ca.* 1:1 Mixture.

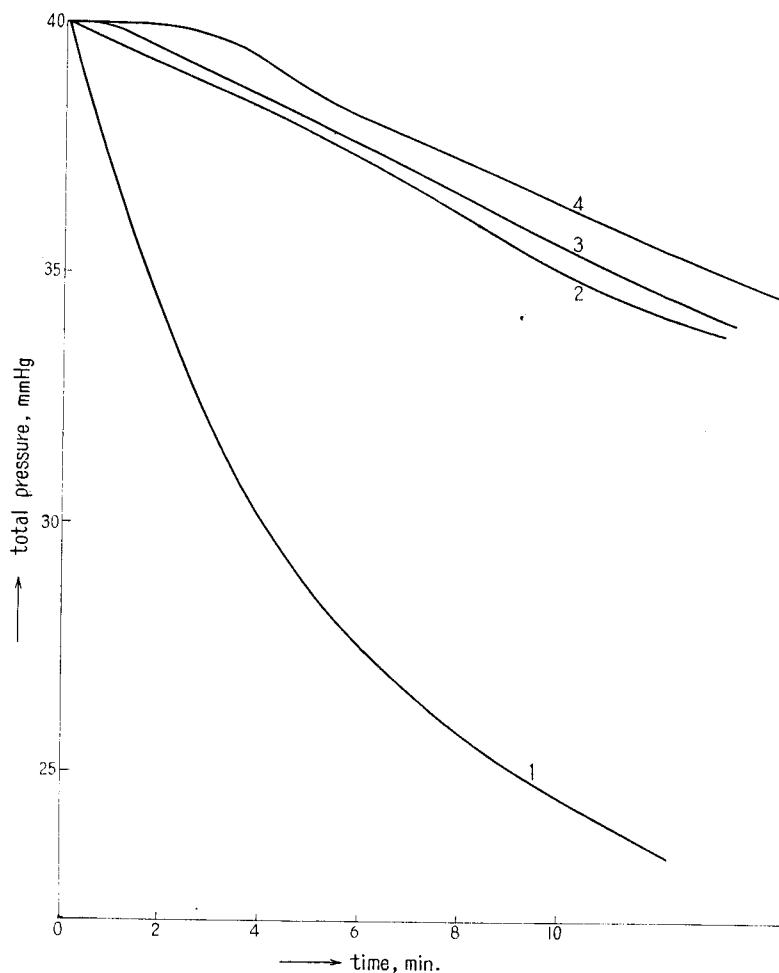| Evaporation temp. °C		130	155	200	223	253
Catalytic activity mmHg/min.	Fresh film	4.2	4.0	3.5	3.7	0.7
	Supplementing gas mixture	3.4	3.0	2.3	2.5	—
	After evacuation at 50°C to 10^{-6} mmHg	3.4	3.2	1.5	1.5	0.2
	After evacuation at 155°C to 10^{-6} mmHg	—	1.3	—	—	—

Fig. 2. Courses of hydrogenations with impure (A) hydrogen.

hydrogenation of ethylene with (A) hydrogen on one and the same coating of
the film. Curve 1 is the course of total pressure of reacting gas on a film
coated with freshly evaporated nickel and curve 2 and others are those of
successive runs repeated on the same coating, each being preceded by evacuation
at reaction temperature 50°C. This remarkable decreases of catalytic activity
were almost eliminated by use of pure (B) hydrogen and film coated with
freshly evaporated nickel at *ca.* 130°C in vacuum of $3\sim5\times10^{-7}$ mmHg, as
shown in Fig. 3, where number annexed to each curve denotes that of runs
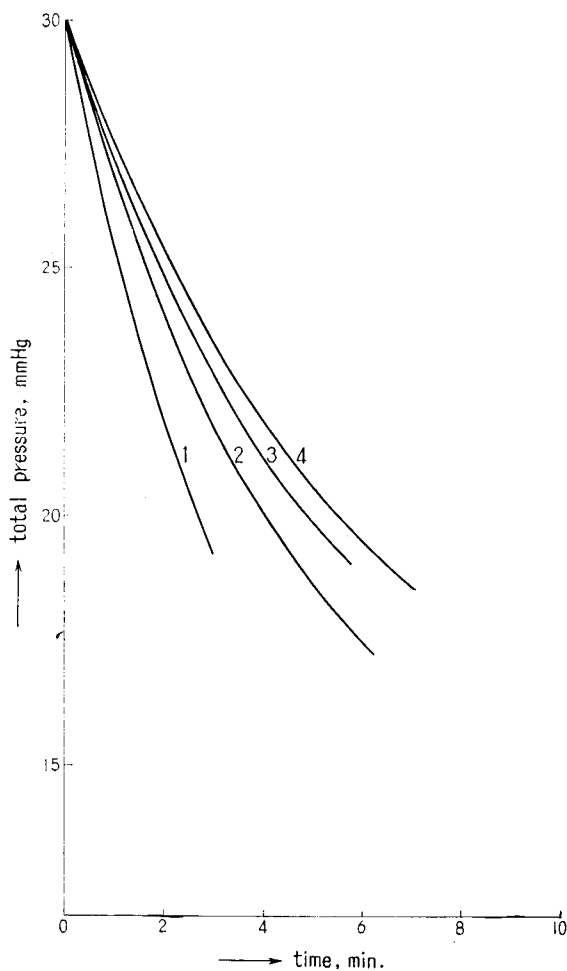repeated similar to those in Fig. 2.

Fig. 3. Courses of hydrogenations with pure (B) hydrogen.

Dependence of the decay of catalytic activity upon the evaporation temperature of film coating was now investigated with films coated with nickel freshly evaporated at different temperatures for two minutes in vacuum of 3×10^{-7} mmHg. The results are shown in Table 1, where the catalytic activity was given in terms of the inital rate of total pressure decrease in mmHg/min. at 50°C. The column headed *e. g.* by 130, indicating the evaporation temperature, shows the results of runs conducted with one and the same coating of evaporated nickel successively; the first one three minutes after the fresh evaporation, the subsequent one just by supplementing reactant mixture to the

resultant of the first run to replace the partial pressures of hydrogen and ethylene respectively to 15.5 and 14.5 mmHg and the last one after evacuating the resultant gas of the second run to 10^{-6} mmHg and introducing the reactant mixture anew to 30 mmHg. In the case of evaporation temperature 253°C the resultant gas of the first run was evacuated without conducting the second run "Supplementing gas mixture". Catalytic activity in this case is appreciably small, which might probably be due to sintering of the film during evaporation. The results on the film coated with nickel freshly evaporated at lower temperatures indicate that the catalytic activity decays much less, yet perceptibly during the course of hydrogenation, as deduced from the comparison of the activity of "Fresh film" with that of the film of the same coating in the second run conducted by "Supplrmenting gas mixture", which could not be extirpated so far as investigated. Nevertheless it has been shown that the relative decay of the hydrogenation rate in course of hydrogenation was much the same for the film coated with nickel evaporated at 200°C or below.

Only in the case of the coating evaporated at 155°C the fourth run was added, evacuating the resultant gas of the third run at 155°C. The result show that the catalytic activity dropped from 3.2 to 1.3 mmHg/min. just by once of the evacuation at 155°C. Another coating of the same evaporation temperature was found to decrease its catalytic activity much slowly by evacuation at 50°C, *i.e.* from 3.8 to 1.4 mmHg/min. by ten times repetition of hydrogenation followed by the evacuation.

TABLE 2. Catalytic Activity of Nickel Coated with Nickel Freshly Evaporated at 200°C: Initial Rate of Total Pressure Decrease at 50°C and 30 mmHg of *ca.* 1:1 Mixture.

No. of runs	1	2	3
Cat. activity, mmHg/min.	3.5	3.6	3.8

The film coated with nickel evaporated at 200°C was further investigated by coating it with freshly evaporated nickel before every run at the same temperature. Table 2 shows the results that the initial rate is remarkably reproducible, if associated at all with the decay in course of hydrogenation mentioned above.

On this basis the temperature dependence of the hydrogenation rate was investigated at reaction temperatures ranging from 0°C to 200°C, every run being conducted three minutes after evaporating nickel freshly on the film for two minutes at the highest temperature of reaction, *i.e.* 200°C. The results
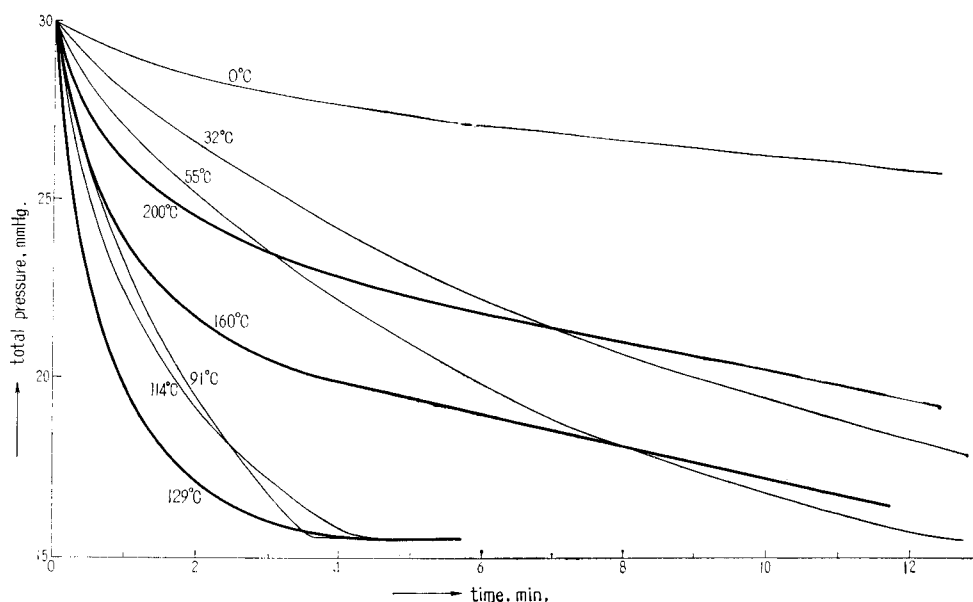
Fig. 4. Temperature dependence of the course of hydrogenation
of 1:0.93 mixture of H_2 and C_2H_4 at 30 mmHg initial
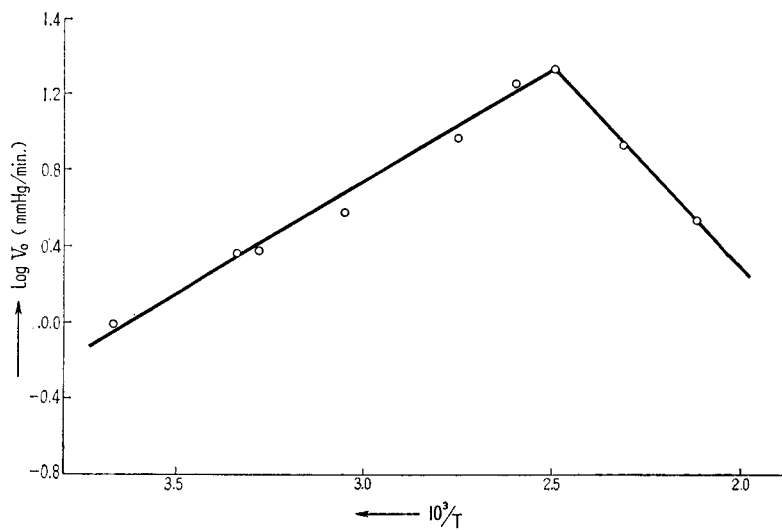total pressure.

Fig. 5. Arrhenius plots of the initial rate of hydrogenation
of 1:0.93 mixture of H_2 and C_2H_4 at 30 mmHg
initial total pressure.

— 7 —

are shown in Fig. 4.

The resultant gas of the hydrogenation at 200°C was analyzed by mass spectrometer and found free from methane, showing that the hydrogenation was not accompanied by cracking hydrogenation of ethylene.

Fig. 5 shows the Arrhenius plots of the initial hydrogenation rate, *i.e.* the negative of the initial inclination of curve in Fig. 4. From Fig. 5 the optimum temperature is determined at 130°C and the activation energies at temperatures below and above the optimum at 5.6 Kcal and —9.5 Kcal/mole respectively for the initial rate of hydrogenation with 1 : 0.93 mixture of hydrogen and ethylene at 30 mmHg initial total pressure.

Discussion

The results of Fig. 2 and 3 show that the removal of a trace of air from reactants or reaction vessel is essential to the reproducible result. Table 1 shows, however, that the catalytic activity, even in the case of pure hydrogen and ethylene free from air, decays perceptibly in course of hydrogenation on freshly coated film. These decays of catalytic activity appear not to be caused by impruity possibly contained in the reactants, since the catalytic activity does not decrease from the second to the third runs for the evaporation temperature 130°C or 155°C as seen in Table 1. JENKINS and RIDEAL[2] have found that the catalytic activity of evaporated nickel film decreased by three times repetition of run of hydrogenation to a steady value similarly as in the case of the so-called carbided film obtained by evacuation at 190°C of ethylene irreversibly prechemisorbed on fresh film. THOMSON and WISHLADE[3], on the other hand, found that only about half of prechemisorbed ethylene containing radioactive carbon was removed from an evaporated nickel film by conducting the hydrogenation of 1 : 1 mixture of hydrogen and ethylene to completion with the same catalyst. On the basis of these experimental results, the decays of the catalytic activity with pure reactants mentioned above might be attributed to irreversible chemisorption of ethylene taking place in course of hydrogenation on freshly coated film.

It might be concluded that this irreversible chemisorption of ethylene proceeds more rapidly at temperatures above the optimum of the hydrogenation, from the result that a markedly slow decrease of total pressure, which followed the initial rapid one, began at earlier stage of the reactions at temperatures above the optimum as shown in Fig. 4.

The so-called self-poisoning effect of ethylene discussed above becomes more remarkable by evacuation of resultant gas at higher temperature, as seen from the remarkable decrease of the catalytic activity caused by evacuation at

155°C, in contrast with its slow decrease by evacuation at 50°C, as mentioned in the foregoing section. The conclusions arrived at above of the self-poisoning effect of ethylene is supported by the recent results of AZUMA and ISHIZUKA[5] in this laboratory, that the deposition of carbon on tungsten tip was remarkably promoted, as observed by field emission microscope, by evacuation of chemisorbed ethylene at higher temperatures especially in the presence of hydrogen. The decay of the catalytic activity still persisting in the present experiment might hence possibly be due to carbon formed by irreversible chemisorption of ethylene.

The optimum temperature and the activation energies of hydrogenation have been carefully determined under the best conditions for reproducible observation, being fundamental to establishing the mechanism of the present reaction on the basis of our structure theory[6]. The activation energy 5.6 Kcal/mole at temperatures below the optimum differs now considerably from those so far observed for nickel[1,4,7] or carbided nickel catalysts[2] under partial pressures of the magnitude near those in the present work. It is hence desirable to reexamine whole series of kinetic data of this reaction under the best conditions mentioned above, the results of which will be reported later.

Acknowledgement

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