The Catalytic Hydrogenation of Ethylene at a Nickel Surface.
Part I.   The Chemisorption of Ethylene.

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The adsorption of ethylene and hydrogen on nickel films has been examined. The ethylene undergoes dissociative chemisorption to form an adsorbed acetylenic complex and two chemisorbed hydrogen atoms, requiring four contiguous sites for the process. Gaseous ethylene can rapidly remove the chemisorbed hydrogen and where four contiguous vacancies are formed ethylene in its turn is chemisorbed with dissociation. The final structure on admission of the two gases is some 80% coverage by acetylenic complexes, 10% by hydrogen on double sites, and 10% on single sites. This distribution is confirmed by pictorial filling of squares of 100 sites. The chemisorbed hydrogen on the 10% of double sites on this covered surface is readily removed by ethylene to form ethane. No evidence of chemisorbed ethylene was found.

In spite of the interest which has been devoted to this classical heterogeneous reaction since its discovery by Sabatier, the detailed mechanism of its operation is not yet established. Excellent reviews of the various mechanisms proposed have been written by Eley (*Quart. Reviews*, 1949, **3**, 209), Laidler (" Catalysis," Reinhold Publishing Corporation, New York, 1954, Vol. I, p. 168), and Eyring, Parlin, Wallenstein, and Zwolinski (" General Theories of Heterogeneous Catalysis," 1953, Technical Report XI, 69), as well as that presented in the Faraday discussion on heterogeneous catalysis held in 1950 (Vol. **8**).

There appears to be general agreement that the reaction proceeds through an " associative " adsorption of ethylene, a divergence of opinion existing on whether the subsequent reaction proceeds by the so-called Langmuir–Hinshelwood mechanism with adsorbed hydrogen (Farkas, Farkas, and Rideal, *Proc. Roy. Soc.*, 1934, *A*, **146**, 630; Horiuti, Ogden, and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 663, 1164), or by the alternative mechanism of reaction with gas-phase or van der Waals-adsorbed hydrogen (Rideal, *Proc. Camb. Phil. Soc.*, 1939, **35**, 130; Rideal and Twigg, *Proc. Roy. Soc.*, 1939, *A*, **171**, 55). The " associative " adsorption of ethylene may be formulated

$$C_2H_4 + 2Ni \longrightarrow \underset{Ni}{\overset{CH_2-CH_2}{\diagup\diagdown}}_{Ni} \qquad \cdots \cdots \cdots \quad (1)$$
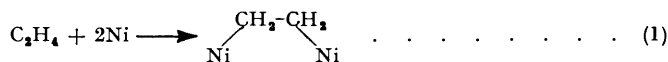
From studies of the exchange reaction with deuterium, it has been concluded that a " dissociative " adsorption of ethylene can also occur (Farkas, Farkas, and Rideal, *loc. cit.*) :

$$C_2H_4 + 2Ni \longrightarrow C_2H_3Ni + NiH \quad \cdots \cdots \cdots \quad (2)$$

Evidence that a " dissociative " adsorption does occur in nickel was first presented by Sabatier (" La Catalyse en Chimie Organique," Lib. Polytechnic, Paris) who records a carbonisation of the catalyst in the presence of ethylene at 300°. Later workers (Beeck, *Rev. Mod. Phys.*, 1945, **17**, 61; Morikawa, Trenner, and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1103; Douglas and Rabinovitch, *ibid.*, 1952, **74**, 2486) found that on admission of

ethylene at lower temperatures a self-hydrogenating reaction occurs, ethane being produced.

Beeck, Smith, and Wheeler (*Proc. Roy. Soc.*, 1940, *A*, **177**, 62) concluded on somewhat slender evidence that the ethylene was adsorbed on four sites (the ratio of hydrogen to ethylene adsorbed being 2 : 1). When later they observed a decomposition of ethylene, the mechanism of adsorption postulated was

$$C_2H_4 + 4Ni \longrightarrow \underset{Ni}{\overset{CH=CH}{\diagup \diagdown}} \underset{Ni}{} + 2NiH \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
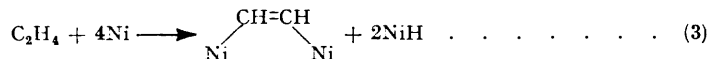
In this computation, however, it was overlooked that the ethylene adsorption on which the ratio was based fails to take into account the fact that the ethane found in the gas phase must have received its hydrogen from the surface, thus rendering more surface available for further ethylene addition.
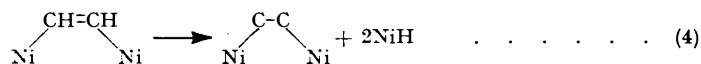
Separate experiments revealed that the addition of ethylene to a hydrogen-covered surface results in a rapid reaction, ethane appearing in the gas phase.

FIG. 1.
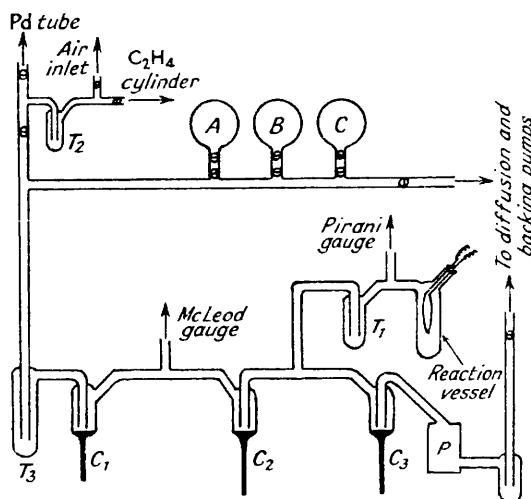
To explain the kinetics of the hydrogenation reaction, Beeck (*Discuss. Faraday Soc.*, 1950, **8**, 118) assumed that some ethylene was also adsorbed " associatively " on that part of the surface not covered with the dehydrogenated complexes formed by (3) but no direct experimental evidence was advanced to support this view.

The carbonisation reaction which Sabatier showed took place at 300° can be formulated as a sequel to (3) :

$$\underset{Ni}{\overset{CH=CH}{\diagup \diagdown}} \underset{Ni}{} \longrightarrow \underset{Ni}{\overset{C-C}{\diagup \diagdown}} \underset{Ni}{} + 2NiH \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Much is known about the behaviour of hydrogen when brought into contact with nickel (Beeck, *Adv. in Catalysis*, 1950, **2**, 151 ; De Boer and Schuit, *Rec. Trav. chim.*, 1953, **72**, 909). In view of the apparent complexity of the ethylene reactions it appeared desirable, before dealing with the actual hydrogenation process, to examine in somewhat more detail the sequence of events when ethylene is brought into contact with nickel. The actual state of the surface when the catalytic reaction is proceeding at a steady rate must be dependent on the result of these reactions. A knowledge of the surface state during hydrogenation, together with data on the kinetics of the process, should assist in revealing the molecular mechanism.

EXPERIMENTAL

Clean and reproducible nickel surfaces were obtained by evaporation of a hairpin filament of spectroscopically pure nickel (26 s.w.g.) spot-welded to tungsten–Pyrex seals. Reaction

vessels of 30 ml. capacity, coated internally with the freshly evaporated nickel films, were employed. A Pirani gauge was attached to the reaction vessel and connected through traps and mercury cut-offs to the McLeod gauge, diffusion and backing pumps, hydrogen and ethylene dosers, and gas-storage vessels in the customary manner, as shown in Fig. 1.

Hydrogen was prepared from cylinder gas by diffusion through a palladium tube, and ethylene by repeated fractionation of the liquefied gas from a cylinder. To minimise the introduction of impurities from the Pyrex glass reservoirs and tubing, prolonged heating under high vacuum was frequently carried out, and no gas sample was retained for more than 24 hr. in the reservoirs.

The quantities of gas adsorbed or desorbed are given in units corresponding to a pressure change of 1.00×10^{-3} mm. Hg (*i.e.*, 9.6×10^{15} molecules).

Gas mixtures were analysed by fractional condensation at low temperatures.

Results.—(a) *Complex formation.* When increments of ethylene are admitted to a clean film at 20° two distinct phases are to be observed (Fig. 2). The first few increments (*O—A*) are completely chemisorbed with extreme rapidity. On further addition (*ABC*) more gas is rapidly adsorbed but there is now a concordant rise in the residual gas pressure on each admission. Analysis of the residual gas revealed that it was practically pure ethane up to the point *B*; beyond this point both ethane and ethylene were found in the gas phase.

FIG. 2.
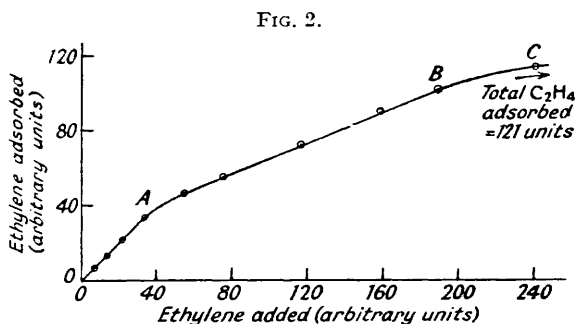
If, when adsorption is complete, the gas be removed and a vacuum maintained for 30 min. there is practically no further adsorption when ethylene is readmitted (see Table 1).

TABLE 1.

Catalyst	Adsorption in phase (ii)	Adsorption after evacuation	Adsorption after repeating evacuation
A_1	65	2·0	0·5
B_1	110	1·0	nil

At the end of phase (i) the volume of ethylene adsorbed is approximately only one-quarter of the amount of hydrogen adsorbed irreversibly at $-183°$ on films of the same area. This ratio was found to be independent of the film thickness, indicating that there is no solution of hydrogen in the metal at $-183°$ during the course of the experiments. The data are given in Table 2.

TABLE 2.

| Catalyst	C_2H_4 adsorbed :		Catalyst	Irreversible H_2 adsorption at $-183°$
	Phase (i)	Phase (ii)		
A_1	37	65	A_2	150
B_1	68	110	B_2	253
C_1	84	—	C_2	290
D_1	41	80	D_2	145

Since molecular hydrogen is chemisorbed to occupy two lattice points, if the surface were completely covered at the end of phase (i) the chemisorbed ethylene would have to occupy at least 8 points. This is highly improbable and we must conclude that a considerable fraction of the surface is bare when the second phase commences. That there are in fact bare sites at the end of phase (i) was confirmed by cooling from 20° to $-78°$ and adding hydrogen, when a marked instantaneous irreversible adsorption occurs. Thus on one catalyst where 84 units of ethylene had been adsorbed in phase (i), no less than 46 units of hydrogen were taken up

irreversibly. Trapnell (*Trans. Faraday Soc.*, 1952, **48**, 160), who observed a similar phenomenon on tungsten films, suggested that the second phase commences when the hydrogen bonding to the catalyst weakens and a detectable quantity of hydrogen appears in the gas phase. The large irreversible adsorption of hydrogen at $-78°$ which we observe, however, shows that this is not so in the case of nickel. Instead, it would appear that as a result of the rapid fall in the heat of adsorption of ethylene on nickel (Beeck, *loc. cit.*, 1945) the reaction of gas-phase ethylene with adsorbed hydrogen becomes energetically more favourable than the adsorption of ethylene before the surface is filled. Removal of hydrogen then increases the available area for adsorption, this process constituting phase (ii) of the isotherm.

A reaction of gas-phase ethylene with adsorbed hydrogen has been postulated. That such a reaction occurs was shown by Beeck (*loc. cit.*, 1945), and this has been carefully studied in this series of experiments by adding ethylene in successive increments to a hydrogen-covered surface at 20° (Fig. 3). The residual gas was found to be entirely ethane up to a point Y. The resemblance of the slopes (ethylene adsorbed/ethylene added) for the reaction of gas-phase ethylene with its own decomposition product on the nickel surface [phase (ii) in the adsorption of ethylene], and the reaction of gas-phase ethylene with hydrogen adsorbed on the surface is at once apparent (Figs. 2 and 3 respectively).

We have seen that at the end of phase (ii) dehydrogenated ethylene residues are present. The surface in this state cannot react with ethylene, and experiments were carried out to see

Fig. 3.
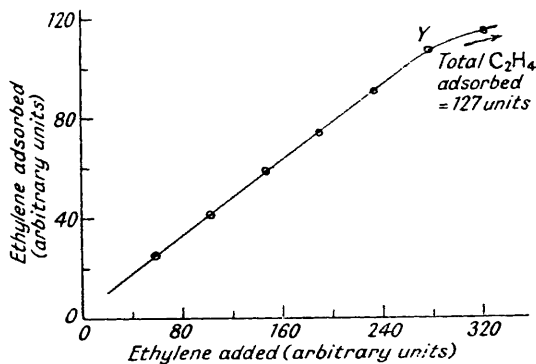
whether any reaction occurred with gaseous hydrogen. Ethylene was added to a clean nickel film at 20° until no further gas was adsorbed. Readmission of ethylene after evacuation for 30 min. resulted in no further adsorption. On further evacuation for 30 min. and addition of a known amount of hydrogen, an instantaneous decrease in pressure was observed, followed by a slow continuous pressure decrease. This slow reaction proceeds at a speed comparable to that observed by Beeck (*loc. cit.*, 1945), who found that hydrogen took 1 hr. to remove 20% of the complexes from a nickel film at 20°, the product consisting of 90% saturated hydrocarbon polymers (C_4—C_8) and 10% ethane. However, in our experiments ethane only was formed, hydrogen being subsequently adsorbed on the sites vacated by the saturated hydrocarbon. The initial rate of this slow reaction was found to be proportional to the initial hydrogen gas pressure (Fig. 4).

The instantaneous fall of pressure observed on admitting the hydrogen might be due either to the hydrogenation of some chemisorbed ethylene adsorbed on two sites (associative adsorption) followed by adsorption of hydrogen on the vacated sites, or to adsorption of hydrogen on bare sites inaccessible to ethylene. That the latter was the case was confirmed by the following experiments. Instead of allowing the slow hydrogenation of the complexes to proceed, the reaction vessel was pumped out for 30 min. Readmission of hydrogen resulted in a similar instantaneous adsorption but no adsorption of ethylene occurred if that gas was admitted. Thus, on a complex-covered surface, there is a reversible adsorption of hydrogen but no adsorption of ethylene.

In agreement with Beeck's conclusions, though not with the evidence with which he supported them, the surface complexes were found to correspond to an acetylenic complex in composition; thus in one experiment, 121 units of ethylene were adsorbed and a further 120

units of gaseous ethylene were converted into ethane.   We have seen that this complex-covered surface has bare sites which are accessible for the chemisorption of hydrogen.   An approximate value for the capacity of the surface, as measured by the low-temperature irreversible hydrogen adsorption, was found to be 145 units or 290 sites.   It is probable that each C_2H_2 complex occupies two sites; the 121 units would thus leave 48 sites bare.   It was found that 12 units of hydrogen could be adsorbed on the complex-covered surface, *i.e.*, on the bare 48 sites.   It would therefore appear that of these 48 bare sites, 24 are in pairs accessible to hydrogen and 24 are isolated single sites accessible presumably only to atomic hydrogen by diffusion through the metal substrate.

We thus derive the following picture of a catalyst surface in the presence of a hydrogen ethylene gas mixture :

Sites :	occupied by C_2H_2 complexes	occupied by hydrogen as pairs	unoccupied
	242	24	24
	83·4%	8·3%	8·3%

Following the method of Roberts (" Some Problems in Adsorption," Cambridge Univ. Press, 1939) and of Herington and Rideal (*Trans. Faraday Soc.*, 1944, **40**, 505) a pictorial representation of the surface can be made by taking 100 sites, surrounded by a suitable guard ring to eliminate end effects, and filling these in a haphazard manner with ethylene in such a way that each molecule requires four free contiguous sites for adsorption.   Once the pattern has been filled

FIG. 4.

FIG. 5.
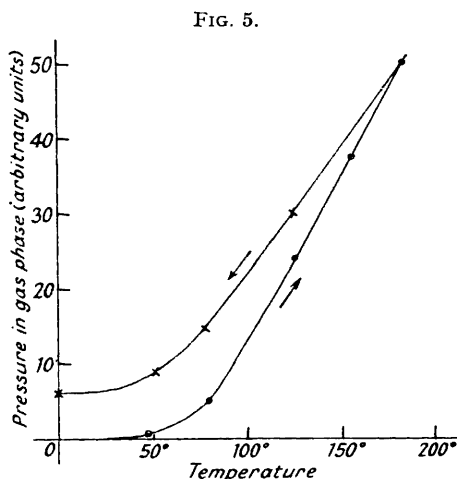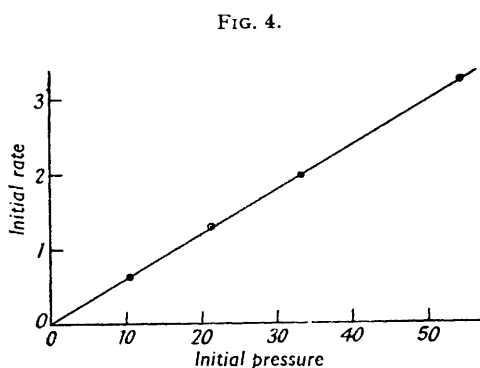
in this manner hydrogen pairs are removed and the vacancies caused by this removal are in their turn filled with ethylene in those places where four contiguous sites are formed by the removal of the hydrogen.   This process is continued until the pattern is completed; the results obtained are :

C_2H_2 complexes, 78%	H_2 as pairs, 13%	Single, 9%

The agreement with the experimentally derived distribution is satisfactory.

(b) *Thermal stability of the complex.*   The surface complex formed on reaction with ethylene is, as we have seen, an acetylenic one ($Ni_2C_2H_2$).   Sabatier noted that at 300° carbonisation occurred and we can infer that this carbide is produced by further dehydrogenation.

When a complex-covered nickel catalyst is heated to 170°, gas, identified as practically all hydrogen, is evolved as indicated in the following analysis.   Thus the decomposition of the complex to carbide appears to be almost complete at 170°.   On cooling, the hydrogen can be readsorbed on the surface (Fig. 5) and the process is reversible.

Catalyst	Surface complexes	Hydrogen desorbed	Catalyst	Surface complexes	Hydrogen desorbed	Catalyst	Surface complexes	Hydrogen desorbed
K_1	60	50	K_2	28	22	K_3	14	11

This adsorption of hydrogen on cooling means that either (i) it can react reversibly with the surface carbide to form acetylenic complexes or (ii) some of the surface carbide has migrated into the interior of the metal, leaving a fresh nickel surface for the hydrogen.

If the former view be correct, addition of hydrogen at 20° after heating should result in a hydrogenation reaction. This reaction does not occur however (Table 3, reactions 1 and 2).

TABLE 3.—28 *Complexes on the surface.*

	Hydrogen added	Pressure after :		
Pre-treatment		$\frac{1}{2}$ min.	6 min.	12 min.
Complex-covered surface :				
(1) before heating (acetylenic surface)	60·9	53·5	40·7	36·3
(2) after heating (carbide surface)	60·2	55·0	53·5	53·4
(3) addition of C_2H_4	55·2	49·3	42·0	40·6

If migration has occurred there should be an appreciable quantity of hydrogen adsorbed at 20°. Addition of ethylene should then result, as we have seen previously, in an adsorption with ratio (ethylene adsorbed)/(ethylene added) of 0·4. That this is in fact the case was shown in a number of experiments. Furthermore, this surface having been treated with ethylene, the complexes reacted with hydrogen as expected (Table 3, reaction 3).

Solution of the carbide at 170° was finally established by adding large increments of ethylene (38·2 units followed by 36·1 units) to a surface previously saturated at 20° with 14 units of complexes. The surface remained active for the decomposition, the hydrogen being disengaged at the following rate :

	Pressure recorded after (min.)			
Ethylene added	$\frac{1}{2}$	4	8	60
31·6 units	47·3	57·5	59·8	60·5

(c) *Adsorption of ethylene and hydrogen on the carbided surface.* Hydrogen but no ethylene or ethane is adsorbed on the complex-covered surface. The surface was carbided by heating it to 170° for 30 min. in the presence of ethylene (5 mm. Hg). The ethylene was pumped out and the catalyst was cooled. Again hydrogen was adsorbed but no ethylene or ethane (Table 4).

TABLE 4.—*Number of complexes adsorbed* = 50 *units.*

Surface	Hydrogen		Ethylene		Ethane	
	Added	Adsorbed	Added	Adsorbed	Added	Adsorbed
Complex-covered (20°)	13·4	6·5	35·5	None	30·0	None
Carbide-covered (20°)	13·0	2·5	47·8	None	31·2	None
Carbide-covered (170°)	14·0	1·0	46·0	None	—	—

DISCUSSION

These adsorption studies show that in fact " associative " adsorptiom does not occur. On the contrary, we find that (1) ethylene on chemisorption is dissociated to an acetylenic complex and chemisorbed hydrogen and (2) there is no reversible adsorptiom of ethylene in the isotherm. (3) Any small quantity of ethylene adsorbed by two-site contact should react quickly with hydrogen, leaving sites available for an equivalent readsorption of ethylene. No such readsorptiom occurs.

This applies to the complex-covered surface. When the surface has been heated and the complex has lost its hydrogen and become carbided, again no adsorption of ethylene is observed. In view of this, two mechanisms seem possible in the formation of ethane from ethylene.

(a) *Hydrogenation of the complexes.* Assuming that the first-order dependence of this reaction (Fig. 4) holds at an initial pressure of 5 cm. of hydrogen, 4×10^{-2} cm. of ethane would be produced in 5 min. (500 c.c. volume). In the same volume and with a similar film area the hydrogenation reaction using 5 cm. of hydrogen and ethylene goes to completion in under 5 min. This factor is thus only of secondary importance in the hydrogenation reaction.

(b) *Adsorption of hydrogen followed by reaction with gas-phase ethylene.* It has been observed that an adsorption of hydrogen does occur on both complex and carbided surfaces. Also, that the reaction of adsorbed hydrogen with gaseous ethylene occurs rapidly. It might be concluded that the hydrogenation of ethylene occurs by a Rideal-type mechanism, gas-phase ethylene reacting with hydrogen adsorbed on vacant sites on a complex-covered surface producing ethane, more hydrogen then being adsorbed.

Indeed, this type of mechanism involving the reaction between a chemisorbed and a van der Waals or gas-phase species, seems to be general in this system since, as we have seen, the chemisorbed complexes can co-exist with chemisorbed hydrogen on the surface and are only hydrogenated by an excess of hydrogen in the gas phase.