Kinetics of the Hydrogenation of Ethylene

(On a Nickel Catalyst)

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A differential type of flow reactor, 0.25-in. I.D., was used to study the kinetics of the hydrogenation of ethylene on an alumina-supported nickel catalyst. This is apparently the first investigation made above atmospheric pressures. Data were obtained from 14.7 to 70 lb./sq. in. abs. and feed compositions from 40 to 90 mole % hydrogen. Measurements at temperatures from 30° to 80°C. indicated an apparent activation energy of 11,600 cal./g.-mole.

It was found that the activity of the catalytic surface was reduced by exposure to ethylene, or mixtures containing an excess of ethylene, owing to the formation of acetylene residues. Pretreatment of the catalyst at temperatures of 170°C. with mixtures of ethylene and hydrogen stabilized the catalyst so that reliable rate data could be obtained.

The rate measurements at 70°C. were correlated by an equation. While the mechanism of the reaction cannot be determined from the data, the rate expression and other kinetic studies suggest a process in which hydrogen is adsorbed on the small fraction of the surface not occupied by acetylenic residues and the reaction takes place between this adsorbed hydrogen and ethylene in the gas phase.

The hydrogenation of ethylene has served as a basis for numerous kinetic studies and as a reaction medium for studying surface catalysis [for example, the work of Beeck and coworkers (*1*, *2*)]. Most of the investigations were made by following the decrease in pressure with time in a static system. Wynkoop and Wilhelm (*16*) employed a tubular flow reactor and carried out rate measurements on a copper-chromium oxide catalyst. Their data were taken at atmospheric pressure restricting the possible conclusions concerning the kinetics of the reaction. The objective of the present study was to make a kinetic study of the nickel catalyzed reaction, using a commerical type of catalyst, that is one with porous material as a carrier; (1/8-in., cylindrical alumina pellets were employed for this purpose). To strengthen the kinetic interpretation, data were obtained up to 5 atm.

Table 1 summarizes the previous kinetic studies with a nickel catalyst. Most measurements were made with pure, unsupported nickel in a static system, and all the results were obtained at pressures less than atmospheric. The works of Rideal (*7*, *15*), Twigg (*13*), and their colleagues provided the most extensive measurements. Their efforts, along with those of Beeck (*1*), established the existence of acetylenic residues on the nickel surface. This concept appears to be the most likely explanation for the adverse effect of ethylene on the rate. The ethylene is considered to be adsorbed by a dissociative mechanism, so that there remains an acetylenic complex occupying four adjacent active sites on the catalyst.

The previous studies demonstrated that ethane had no effect on the reaction other than that of an inert diluent. Hence in the present work no data were obtained with ethane added to the feed. As indicated in Table 1, many of the data were consistent with a first-order (with respect to hydrogen) rate equation. This result was not found in the present study, as brought out later in the development. Measurements over a range of partial pressures of each reactant show that ethylene has a significant effect on the rate. The quantitative evaluation of ethylene's part in the reaction is complicated by the side effects that occur, particularly the acetylenic complex formation on the catalyst surface.

EXPERIMENTAL WORK

The apparatus, as shown schematically in Figure 1, consisted of a reactants-purifying section, a gas-metering section, a packed-bed flow reactor, and a gas-analyzing section.

Reactor

The reactor was made of 0.25-in. I.D. stainless steel tubing packed with catalyst pellets and jacketed with a 1-in. brass pipe for a length of 24 in. As depicted in Figure 2, temperatures were measured in a 0.065-in. thermocouple well (stainless steel) extending the length of the reactor. Two copper-constantan thermocouples, prepared from 30-gauge wire, were employed, one inserted through each end of the well.

Gas-Purification System

The hydrogen was first purified (of oxygen) by being passed through an electrically heated converter consisting of a 3-ft. section of 1/4-in. galvanized pipe. It was packed with 6-20–mesh copper-magnesium oxide catalyst. After leaving the converter, the gas was cooled in a 1/4-in. copper tube jacketed for a length of 35-in. with 1/2-in. copper tubing. Water passed through the jacketed section. Finally the gas was dried by flowing through 1/4-in. black iron pipe packed with 6-16–mesh silica gel for a length of 3 ft. To ensure proper operation of the equipment temperatures were continuously recorded at the exit of the converter and the entrance to the dryer.

Oxygen was removed from the ethylene stream by passing through a 1/4 in., 3 ft. long, galvanized pipe packed with copper shot or copper-magnesium oxide granules. A cooler and drier system similar to that employed for the hydrogen system was also used in the ethylene feed as illustrated in Figure 1.

Gas-Analysis System

The reactor operation was of the differential type; that is the conversion was limited to a few per cent. This reduces the problem of temperature and composition changes within the catalyst bed, but it requires precise analytical results to determine accurately the small conversions obtained. A thermal conductivity cell, operated at a current of 140.00 ± 0.05 ma., was used in this study. In order to increase the sensitivity of the apparatus for measuring the conversion the outlet gas from the reactor was compared with the inlet gas in a single cell. This is equivalent to using the inlet stream as the reference gas. Used in this way the unbalanced voltage of the bridge circuit of the cell was a direct measure of the increase in ethane concentration due to reaction. However it was necessary in using this method to calibrate the cell for each inlet-gas composition. The cell was calibrated by comparing a known sample mixture of hydrogen, ethylene, and ethane with a known reference mixture of hydrogen and ethylene. In the calibration procedure the ratio of hydrogen to ethylene was the same in the sample and reference gas mixtures. This does not correspond to the operation of the reactor, except when the ratio is unity. The error introduced because of this discrepancy is small because the thermal conductivities of ethane and ethylene are nearly the same, while that of hydrogen is almost seven times larger. Calculations, based upon the assumption that the conductivities are additive, indicate that the error introduced is less than 1.0% over the composition range 20 to 80 mole % hydrogen.

Analysis of the random or accidental errors in the calibration procedure indi-

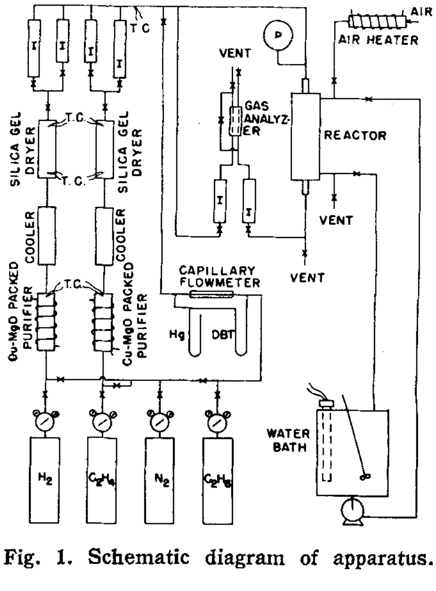

Fig. 1. Schematic diagram of apparatus.

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TABLE 1. SUMMARY OF EXPERIMENTAL INVESTIGATIONS OF THE CATALYTIC HYDROGENATION OF ETHYLENE ON NICKEL

Catalyst	Temperature range, °C.	Total pressure, cm. Hg.	Gas agitation	Activation energy, kcal./mole	Rate relation*	Reference
Ni foil	73–200	12	No	1.8	$r = kp_A$ with B in excess $r = kp_B$ with A in excess	*9*
1% Ni on charcoal	—	—	—	3.6	$r = kp_A$	*10*
Ni ribbon	−10–130	0.003–0.02	—	0 (90°C.)	$r = kp_A$ ($T \leq 67$°C.) $r = kp_A (1 + Bp_A)$(120°C.)	*18*
Ni wire	20	4.2	No	—	$r = k$	*4*
Ni wire	0–17	0.34–1.3	No	0 (140°C.)	$r = k$	*13*
Ni mass	−78–0	20–56	No	6.1	$r = kp_A$ with P and p_B in excess r increases with decreasing p_B at constant P and p_A	*11*
Ni powder	99–165	20–60	No	—	$r = kp_A$ at constant P and p_B $r = \frac{kp_B}{1 + Bp_B}$ at constant P and p_A	*12*
Ni wire	60–207	3.7–7.2	No	14 (60°–100°C.) 0 (207°C.)	$r = kp_A$	*15*
Ni film	0	10–50	Yes	10.7 (−80° –150°C.)	$r = kp_A$	*1* *2*
Ni film	20–180	4–15.4	Yes	10.2 (20°–145°C.) 0 (165°C.)	$r = kp_A$ (114°C.) $r = \frac{kp_Ap_B}{1 + Bp_B}$ (165°C.)	7

*A denotes hydrogen and B designates ethylene.

TABLE 2. SUMMARY OF RESULTS AT 50°C. AND 1 ATM.

Run	Q_i, cc./min.	y_{ai}	y_{c0}	$(p_a)_{avg}$, atm.	$(p_b)_{avg}$, atm.	$r \times 10^5$, $\frac{\text{moles}}{\text{(min.)(g.)}}$	T_i, °C.	ΔT, °C.
3.5	2,010	0.730	0.101	0.716	0.234	122	50	5.5
3.7	2,010	0.730	0.0857	0.718	0.238	105	50	3.75
3.9	2,010	0.730	0.0700	0.721	0.244	87.0	50	2.5
3.12	2,010	0.730	0.0559	0.722	0.250	70.3	50	1.5
3.14	2,010	0.730	0.0489	0.723	0.252	62.0	50	1.0
4	2,010	0.730	0	0.730	0.270	0	50	0

cates a maximum error of about 2%. It is believed that the over-all errors in determining the mole-fraction ethane in the reactor effluent are less than ±5% under all the operating conditions.

CATALYST PREPARATION AND ACTIVATION

The carrier used for the catalyst consisted of 0.14-in. diameter spheres prepared by attrition from ⅜-in. alumina spheres. The internal area of the material was approximately 150 sq. m./g. An aqueous solution of nickel nitrate containing 10 g. of nickel/100 cc. of water was added to a flask containing the alumina carrier under a vacuum. The pellets were agitated for 1 hr. and the excess solution then poured off. After draining for 10 min. on cheesecloth the particles were dried in a laboratory oven at 220°F. for 2 hr. The nitrate was decomposed to nickel oxide by heating in a furnace at 400°C. for 10 hr. The nickel content at this stage was 2.94% by weight.

The reactor was packed with a 17-cm. length of plain alumina spheres preceding the catalyst to allow the entering gases to attain reaction temperature. Preliminary tests showed unimpregnated alumina had no catalytic activity at 110°C. The active bed consisted of a 39-cm. length of tubing packed with a mixture of three parts of plain alumina spheres and one part of catalyst (155 spheres with a mass of 6.27 g.). One thermocouple was placed at the entrance to the catalyst bed and the second 10 cm. prior to the exit of the bed. The reduction of nickel oxide to active nickel was carried out in place at 250°C. with hydrogen flow through the reactor for 24 hr.

SCOPE OF EXPERIMENTAL WORK

The feed-gas composition was varied from 40 to 90 mole % hydrogen and the total flow rate from 800 to 8,000 cc./min., measured at 1 atm. and 70°F. These rates correspond to a space-velocity interval of 66 to 660 reciprocal min. Runs were made at 70°C. over a pressure range from 14.7 to 70 lb./sq. in. abs. At atmospheric pressure data were obtained from 32° to 80°C., although most of the measurements were carried out at 50°, 70°, or 80°C.

RESULTS

With differential type of operation the rate of reaction can be computed directly from the measured ethane content of the product gas and the parameters of the feed. The expression for the rate, in terms of the moles of ethane produced per unit mass of catalyst per unit time, based upon the stoichiometry of the reaction, is

$$r = \frac{N_i}{(1 + y_c)^2} \frac{dy_c}{dW} \qquad (1)$$

Equation (1) applies to a truly differential reactor, that is one in which the change in mole-fraction ethane through the reactor and the mass of catalyst are both infinitesimal. For the actual reactor, approaching differential operation, this expression may be used to compute the rate corresponding to the arithmetic average composition in the reactor.

Equation (1) may be written in difference form:

$$r = \frac{N_i y_{c0}}{W} \left[\frac{1}{(1 + y_c)^2} \right] \cdots \qquad (2)$$

where the term in brackets represents the average value through the reactor.

The error, as a function of conversion or exit value of ethane mole fraction, introduced in the use of Equation (2) can be established from a rate equation. Since an expression of the form

$$r = \frac{kp_Ap_B}{1 + K_Bp_B} \qquad (3)$$

best fits the experimental data, Equation (3) was used with Equation (1) to obtain the correct rate at the average composition in the reactor. These correct

TABLE 3. SUMMARY OF RESULTS AT VARYING TEMPERATURE AND CONSTANT COMPOSITION AND PRESSURE

Run	Q_i, cc./min.	y_{ai}	y_{c0}	$(p_a)_{avg}$, atm.	$(p_b)_{avg}$, atm.	$r \times 10^5$, $\frac{\text{moles}}{\text{(min.)(g.)}}$	T_i, °C.	ΔT, °C.
8	814	0.730	0.0036	0.729	0.269	1.9	34.5	0
11	814	0.730	0.0069	0.729	0.268	3.7	43.2	0
14	814	0.730	0.0081	0.729	0.267	4.3	50.4	0
19	814	0.730	0.0183	0.727	0.264	9.7	61	0
21	814	0.730	0.0340	0.724	0.259	17.7	72.5	0
23	814	0.730	0.388	0.667	0.139	158	81	2.0

Table 4. Summary of Results at 80°C. and 1 Atm.

Run	Q_i, cc./min.	y_{ai}	y_{c0}	$(p_a)_{avg}$, atm.	$(p_b)_{avg}$, atm.	$r \times 10^5$, moles/(min.)(g.)	T_i, °C.	ΔT, °C.
42	912	0.909	0.0188	0.908	0.083	11.1	80	0
53	1,633	0.582	0.0210	0.578	0.411	22.2	80	0
54	1,034	0.579	0.319	0.512	0.329	172	81	4.2
57	1,812	0.904	0.0151	0.903	0.089	17.9	80	0.25
80	1,802	0.534	0.1288	0.504	0.432	137	81	2.2
84	1,047	0.912	0.0145	0.912	0.081	9.9	80.8	0.25
92	1,541	0.859	0.0246	0.857	0.131	24.5	80.2	0.5
100	1,944	0.630	0.1193	0.608	0.332	137.8	80	1.2

results, when compared with Equation (2), indicated that the error in the use of Equation (2) is less than 2% for feed gases containing 40 to 70 mole % hydrogen at values up to 20 mole % of ethane in the reactor effluents and that at 80 mole % hydrogen in the feed the error reaches 2% at 14.2% of ethane in the effluent.

In the experimental program the conversion was maintained well within these limits, so that the use of Equation (2) was justified. This analysis indicated that maintenance of small temperature gradients is more significant than small conversions, if precise rates of reaction are desired.

The temperature of the reactor was controlled by circulating water at the reaction temperature through the jacket around the catalyst tube. With this system and the diluted catalyst bed it was possible to reduce radial temperature changes to less than an estimated 2°C. Longitudinal temperature changes were a function of the extent of conversion and the pressure, and in a few instances these changes, at the highest pressures, reached values of 10° to 20°C. The rate computed from Equation (2) was given a temperature corresponding to the arithmetic average of the entrance and exit values. It was then corrected to the nominal run temperature by the use of an activation energy of 11,600 cal./g. mole. (This value was determined from experimental rate measurements at different temperatures.)

Tables 2 to 5* show the results of the rate measurements and include in successive columns the entrance flow rate (at 70°F. and 1 atm.); the inlet mole-fraction hydrogen; the exit mole-fraction ethane; the average partial pressures of hydrogen and ethylene, $(p_a)_{avg}$ and $(p_b)_{avg}$; the reaction rate; the inlet gas temperature; and the increase in gas temperature through the reactor, ΔT. Tables 2 and 4 depict a part of the preliminary data showing the effect of time and pretreatment upon the activity of the catalyst.

ANALYSIS OF THE DATA

Poisoning Reactions

Exposure of the catalyst to ethylene reduces its activity for the hydrogenation reaction. The data in Table 2 at a constant feed composition of 73 mole % hydrogen and a temperature of 50°C. illustrate this behavior. The decrease in rate and temperature rise is depicted for some of these runs in Figure 3.

These results fit the general model of ethylene poisoning of pure nickel films proposed by Jenkins and Rideal (7). It is postulated that ethylene is adsorbed and dissociates into an acetylenic residue plus two adsorbed hydrogen atoms. The hydrogen atoms are then available to react with ethylene, resulting in the so-called "self-hydrogenation reaction." The sites vacated by this reaction will adsorb more ethylene until all the groups of four sites capable of dissociatively adsorbing ethylene have been utilized. In Rideal's model the remaining sites are assumed to catalyze the hydrogenation of ethylene by adsorbing hydrogen, which then reacts with ethylene in the gas phase.

Pretreatment of the catalyst with ethylene at relatively high temperatures partially stabilizes the rates. Figure 4 has been drawn from the data in Table 3, which were obtained after passing ethylene through the reactor at 170°C. Although these rates were measured at 80°C., they are less than those shown in Figure 3 for the freshly activated catalyst. In terms of the Rideal model the high-temperature ethylene treatment results in breaking down the acetylenic complexes into hydrogen and carbide residues. Presumably the rate of reaction is stabilized because the rate of removal of the carbides by hydrogen in the feed gas is low at the normal reaction temperatures, that is 50° to 80°C.

The dependence of the rate on the partial pressures of hydrogen and ethylene is shown in Table 4 and Figure 5. These data are for a total pressure of 1 atm. and illustrate the combined effects of changes in both p_A and p_B. The circles show the results when the activated catalyst has been treated with ethylene at 170°C. for 12 hr. The squares represent the rates after the catalyst had been subsequently exposed to mixtures containing an excess of ethylene at 80°C. The decreased rate shown by comparing the squares and circles evidently results from the formation of additional acetylenic residues. The rates corresponding to the upright triangles were observed after the catalyst had been further exposed to hydrogen for 14 hr. at room temperature. From the results it is clear that the acetylenic residues are removed by hydrogen at relatively low temperatures. If the catalyst is exposed to ethylene for long periods of time, the acetylenic residues practically cover the surface as indicated by the results depicted by the inverted triangles. These low rates were measured after the catalyst had been treated for 48 hr. with ethylene at room temperature.

These preliminary data demonstrated that the catalyst surface was dependent upon its previous history and that a procedure for obtaining reproducible data

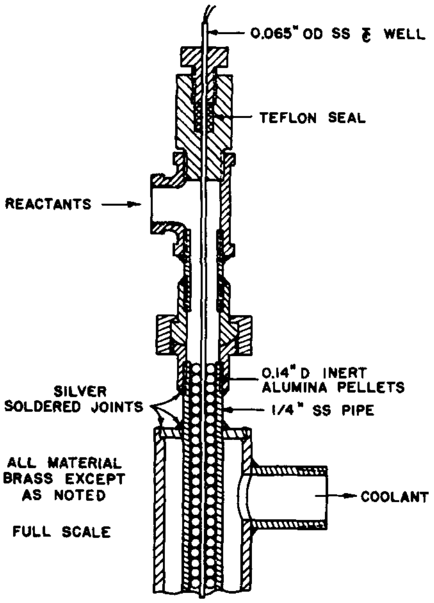

Fig. 2. Reactor detail.

Table 5. Summary of Results at 70°C. and Varying Pressure and Composition

Run	Q_i, cc./min.	y_{ai}	y_{c0}	$(p_a)_{avg}$, lb./sq. in. abs.	$(p_b)_{avg}$, lb./sq. in. abs.	$r \times 10^5$, moles/(min.)(g.)	$r_{70°} \times 10^5$	ΔT, °C.
212	4,048	0.50	0.0126	7.6	7.6	33.3	31.4	1.2
217	8,710	0.50	0.1600	31.0	31.0	805	280	22.6
218	3,370	0.40	0.00703	6.0	9.0	15.5	15.3	0.2
223	7,280	0.40	0.1534	24.0	38.6	645	257	19.5
224	1,404	0.80	0.0707	11.6	2.52	61.4	49.8	4.2
229	3,070	0.80	0.1789	53.2	8.71	312	173	12.2
235	3,970	0.90	0.0921	60.6	3.93	222	152	7.8
236	1,616	0.70	0.0536	10.2	4.13	54.2	44.0	4.2
241	3,580	0.70	0.1913	45.9	15.9	382	203	13.2

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*Tabular material has been deposited as document 6050 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

would have to be developed before kinetic studies were possible. It was found that pretreatment at 170°C. with feed mixtures of the same composition as those used for the following rate measurements results in a stable surface, presumably because the poisoning reactions reached a steady state. All the kinetic data at 70°C. were obtained by this procedure and are shown in Table 5.

Effect of Temperature

The data in Table 3 show the effect of temperature on the rate using the stabilized catalyst, that is after the surface has been treated with ethylene at 170°C. The plot of the results in Figure 6 indicate an apparent activation energy of 11,600 cal./g.-mole. The linear nature of the data strengthens the conclusion that diffusion of the reactants to the catalyst surface is not a significant resistance in the over-all process from reactants in the gas to product in the gas.

This activation energy was used to correct rate data for individual runs to the nominal temperature of the run series.

Rate Equation

The rate data of Table 5 were first used to determine the empirical dependence of the rate on the partial pressures. The method of least squares gave the following result:

$$r = 2.73 \times 10^{-5} p_A{}^{0.93} p_B{}^{0.33} \qquad (4)$$

The first-order dependence on hydrogen partial pressure confirms the results of earlier studies (*2, 9, 10, 11, 12, 15, 18*). The one-third power effect for ethylene suggests a Langmuir type of mechanism, in which the adsorption of ethylene on the surface is significant.

The derivation of rate equations based upon the Langmuir adsorption theory and the equilibrium postulate have been treated extensively in the literature (*5, 6, 17*). The equations are derived by the assumption of a mechanism for the reaction and then the supposition that the rate is determined by a single step in the process, the remaining steps occurring under equilibrium conditions. Within this framework the concept of the reaction which best fits the data is as follows.

If the adsorption on the active part of the surface for the reaction is ideal (that is Langmuir adsorption), and if the rates of all the steps except one in the over-all reaction are sufficiently fast that pseudo-equilibrium conditions are maintained, then the process is one in which ethylene is adsorbed on single sites, hydrogen and ethane are not adsorbed, and the controlling step is the reaction between adsorbed ethylene and gaseous hydrogen. The corresponding rate equation is

$$r = \frac{A p_A p_B}{1 + B p_B} \qquad (5)$$

and a least-squares fit of the data yields the numerical form

$$r = \frac{0.86 \times 10^{-5} p_A p_B}{1 + 0.079 p_B} \qquad (6)$$

Figure 7 shows both the experimental data and the line corresponding to Equation (6).

The catalyst-activity studies, Figures 3 to 5, and the work of Jenkins and Rideal (*7*) are not in agreement with the concept of a reaction between adsorbed ethylene and gaseous hydrogen. These studies suggest instead that ethylene dissociates when adsorbed, forming acetylenic or carbide residues. On this basis the hydrogenation reaction can occur only on those sites not occupied by the residues and only by reaction between adsorbed hydrogen and gaseous ethylene. The mechanism may be represented as follows:

$$H_2 + Ni_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2Ni_2 \qquad (7)$$

$$H_2Ni_2 + C_2H_4 \xrightarrow{k_3} C_2H_6 + Ni_2 \qquad (8)$$

Jenkins and Rideal used a steady state approach to derive a rate equation for this mechanism. In this method it is supposed that the concentrations do not vary with time once a steady state has been reached. It is not assumed that a single step is controlling, as in the development of Equation (5). In this sense the steady state method leads to more general equations, and indeed the single-step controlling equations can always be obtained from the steady state development by making additional assumptions.

If the fraction of the surface (available for the reaction) occupied by adsorbed hydrogen is θ, the steady state concept requires that $(d\theta/dt) = 0$. Hence from Equations (7) and (8)

$$\frac{d\theta}{dt} = 0 = k_1 p_A (1 - \theta) - k_2\theta - k_3\theta p_B \qquad (9)$$

In the formulation of this equation it is supposed that of the available surface part is occupied by hydrogen and part is bare. From Equation (9)

$$\theta = \frac{k_1 p_A}{k_2 + k_1 p_A + k_3 p_B} \qquad (10)$$

The rate of reaction is obtained from Equation (8):

$$r = k_3 \theta p_B = \frac{k_1 p_A p_B}{k_2 + k_1 p_A + k_3 p_B} \qquad (11)$$

Keii (*8*) found it necessary to postulate a very low surface concentration of adsorbed hydrogen in order to explain the rates of formation of the deutero-ethylenes and deutero-ethanes in the reaction between light ethylene and deuterium. Also the studies of the parahydrogen conversion on nickel (*4, 14, 15*), in which ethylene was found to inhibit the conversion, indicate that the concentration of adsorbed hydrogen must be very low. These separate studies suggest that the term k_1p_A in the denominator of Equation (11) is negligible, so that Jenkins and Rideal's final form of the rate equation

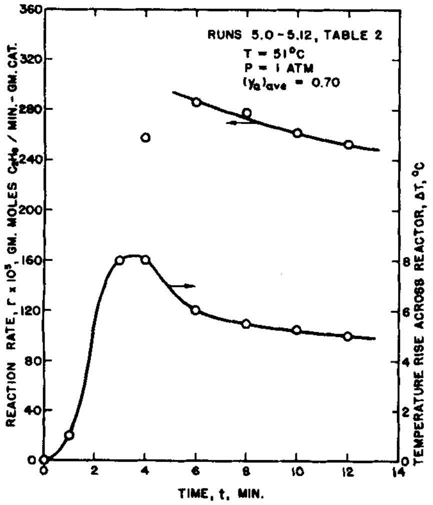

Fig. 3. Variation of catalyst activity with time.

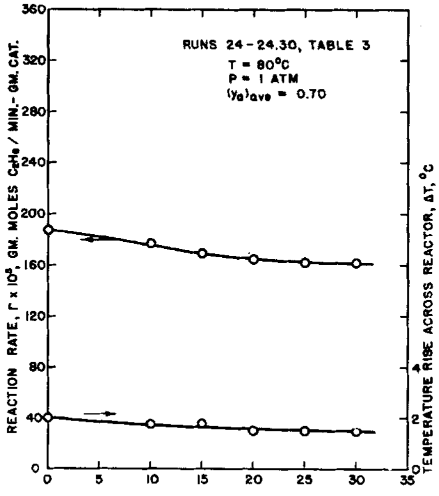

Fig. 4. Variation of catalyst activity with time.

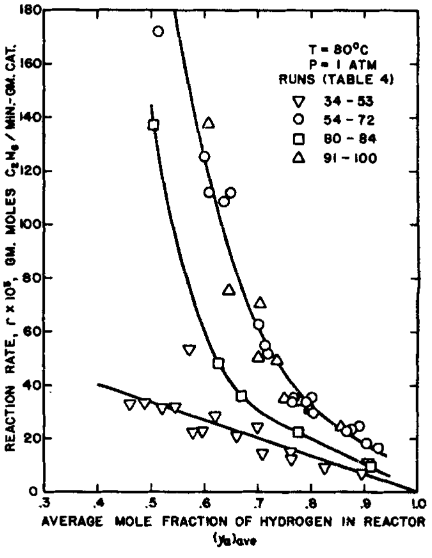

Fig. 5. Effect of catalyst treatment on reaction rate.

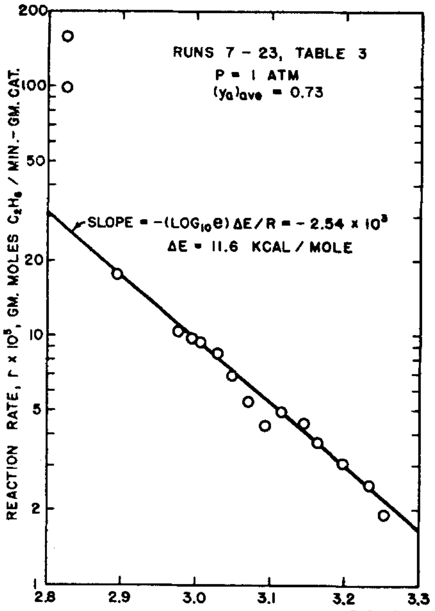

Fig. 6. Temperature dependence of reaction rate.

$$r = \frac{k_1 p_A p_B}{k_2 + k_3 p_B} \qquad (12)$$

is obtained.

Equation (12) is of the same form as Equation (6), which was found to fit best the experimental data. However the mechanisms upon which the two equations are based are different. In view of the catalyst activity studies and the considerable amount of kinetic data from other sources supporting the dissociation of ethylene on the catalyst the Jenkins and Rideal approach is favored.

Several other theories for the reaction have been proposed (*1, 3, 14*) and rate equations developed for them, either in the present investigation or by those suggesting the mechanism. None of these agree with the experimental rate data. Twigg's concept (*14*), which has enjoyed some popularity in the literature, requires that ethane be formed by the reaction between adsorbed ethyl radicals and adsorbed hydrogen atoms. Ethylene is adsorbed by the associative process, and hydrogen is adsorbed only through the interaction of a gaseous hydrogen molecule and an adsorbed ethylene complex. The data of this study do not fit such a picture. The arguments in favor of the Twigg concept are based not so much on the dependence of the rate on pressure and concentration as on the variation of first-order rate constants with temperature and on information for related reactions.

CONCLUSIONS

Studies of the rate of the reaction on an alumina-supported nickel catalyst from 14.7 to 70 lb./sq. in. abs. indicate complex kinetics. The commonly proposed simple rate equation, first order with respect to hydrogen and independent of ethylene partial pressure, is not valid.

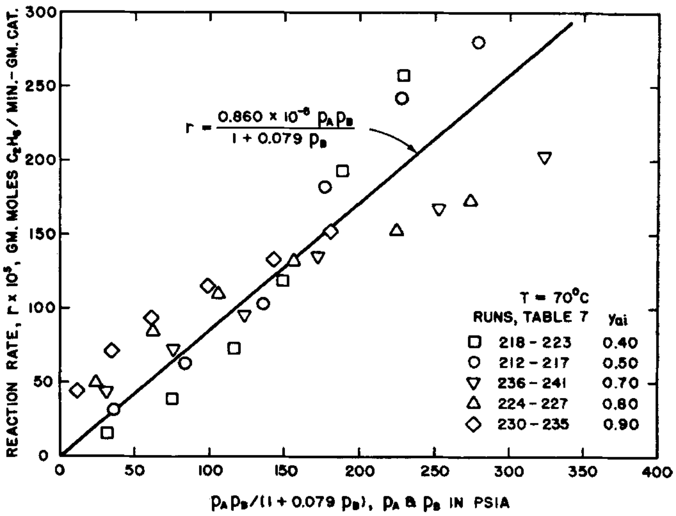

Fig. 7. Rate-data correlation.

Ethylene is a poison for the nickel-alumina catalyst, presumably owing to surface complexes of acetylene polymers formed when ethylene is adsorbed at low temperatures. These residues are only slowly removed by hydrogen at temperatures below 80°C. but are completely eliminated at high temperatures. Comparable rates of reaction, suitable for kinetic study, can be obtained by pretreating the catalyst at 170°C. with mixtures of hydrogen and ethylene. Rate data are then taken at lower temperatures with a feed of the same composition as used in the pretreatment.

The rate data alone are not sufficient to determine the mechanism of the reaction. The same satisfactory rate equation can be obtained from at least two concepts of how the reaction occurs. The previously available data for the nickel catalyzed reaction and the activity studies for the present catalyst suggest a reaction between adsorbed hydrogen and ethylene in the gas phase.

ACKNOWLEDGMENT

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NOTATION

A = constant in Equation (5), dependent on temperature
B = constant in Equation (5), dependent upon temperature
ΔE = apparent activation energy
K = equilibrium constant
k = reaction-rate constant
N = molal flow rate, g.-moles/min.
p = partial pressure, atm.
Q = volumetric flow rate, cc./min. at 70°F. and 1 atm.
r = reaction rate, g.-moles/(min.)(g. of unreduced catalyst)
T = temperature
t = time, min.
W = mass of catalyst, g.
y = mole fraction
θ = fraction of catalyst surface covered by adsorbed hydrogen [Equation (10)]

Subscripts

A, a = hydrogen
B, b = ethylene
C, c = ethane
i = reactor inlet conditions
0 = reactor outlet conditions

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