Semibatch Operation of a Recirculation Reactor for the Hydrogenation of Ethylene

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The purpose of this study was to develop the use of semibatch operation of a recirculation reactor in kinetic studies. Ethylene hydrogenation over a supported copper catalyst was studied experimentally. In semibatch operation one of the reactants is fed at the rate necessary to hold the total pressure in the reactor constant. In ethylene hydrogenation the reaction rate is directly equal to the feed rate, and the kinetics can be studied at constant partial pressure of either of the reactants. Since ethane is inert, this technique permitted the study of reaction rate as a function of one variable at a time.

Although ethylene hydrogenation has been studied extensively, there is not general agreement regarding the kinetics over a copper catalyst. The results are themselves of interest because they indicate the reasons for the apparently conflicting data in the literature.

The design of experiments for the systematic study of the kinetics of a chemical reaction in the gas phase presents a dilemma. Fixed beds of catalyst are commonly employed in flow reactors for studies of heterogeneous reactions, but gas composition and temperature vary over a wide range from inlet to outlet if appreciable conversion is attained. High conversions in the laboratory serve to demonstrate the feasibility of a commercial process, but the data obtained are often difficult to analyze. Differential reactors giving low conversions operate at nearly constant temperature and gas composition, but extremely accurate gas analyses are required if the reaction rate is to be calculated from the necessarily small change in gas composition.

The recirculation reactor provides a technique for overcoming these difficulties. A gas is circulated over a small amount of catalyst in a gas circulation loop, and the advantages of the differential reactor are retained. In batch operation the system is closed, and reaction rate is calculated from measurements of gas composition as a function of time. In continuous operation the reactants and products are fed and withdrawn continuously so as to establish a steady state. The overall conversion can be large though the conversion in the differential bed is very small, so extreme analytical precision is not required. The composition of the effluent is essentially the same as that of the gas in contact with the catalyst.

Batch operation has the disadvantage that the concentrations of both reactants and products change progressively as the experiment proceeds. With continuous operation each test requires a considerable time to reach a steady state and provides but a single value of reaction rate at a particular gas composition. Neither type of operation makes is possible to carry out a systematic kinetic study in which reaction rate is studied by progressive change of a single variable.

For certain types of reactions these difficulties can be overcome by semibatch operation of a recirculation reactor. As employed in this study for the hydrogenation of ethylene the semibatch operation is as follows: the recirculation reactor is placed in continuous operation with constant feed and withdrawal rates and constant pressure, feed and effluent streams are abruptly cut off, and either ethylene or hydrogen is then fed continuously at a rate controlled so as to hold the total pressure constant in the recirculation reactor.

Because of the stoichiometry of ethylene hydrogenation the reaction rate is equal to the rate of feed of reactant required to hold the pressure constant. Total pressure and partial pressure of reactant fed remain constant as the test proceeds. Since ethane is inert, the rate is determined as a function of a single variable, the partial pressure of the reactant not fed. A single experiment can cover a wide range of values of ethylene or hydrogen concentration. The only gas analysis required is that of the reactor contents at the start of the run.

Semibatch operation is not limited to reactions with stoichiometry similar to ethylene hydrogenation; however the method has limitations and complications which may make its use impractical. In a study of the hydrogenation of benzene to cyclohexane the partial pressure of hydrogen might be held constant by supplying pure hydrogen, but in order to maintain constant benzene concentration it would be necessary to feed a mixture containing one-third benzene and two-thirds hydrogen. The ammonia synthesis reaction might be studied at constant nitrogen concentration by feeding an equimolal mixture of hydrogen and nitrogen, but hydrogen concentration could not be held constant in semibatch operation. The variation of rate with concentration of one reactant can be studied in semibatch operation if the stoichiometry is such that the number of moles of reactant disappearing is equal to or less than the total number of moles disappearing. The kinetics of simple decomposition reactions can be studied by the semibatch method, but the complexity of the method makes its use unattractive. The semibatch method of operation is also of no utility where no simple relation exists between reaction rate and the feed rate required to hold the pressure constant. Thus the method could not be used where simultaneous reactions occur, or where there is decomposition of the product formed.

The recirculation reactor is not new. Beeck (*1*) used a batch recirculation reactor as early as 1939 in hydrogenating ethylene, and the continuous recirculation reactor reached a high state of development under Temkin and his associates in Russia in the 1950's (*5, 9, 15, 17*). Similar reactors have been employed in various studies in this country during the last decade (*6, 10, 14*). The semibatch operation appears to be new, though the basic principle was employed with a conventional fixed bed reactor by Toyama (*18, 19*) in 1937.

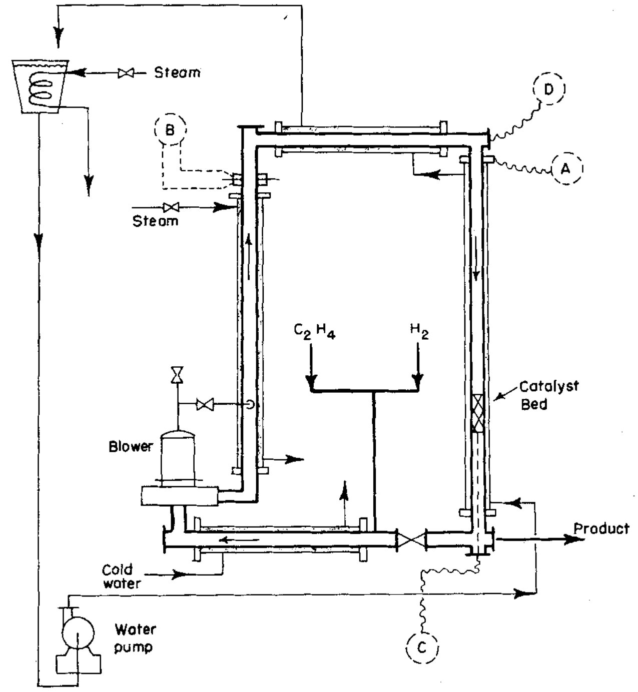

Fig. 1. Recirculation reactor.

APPARATUS

The recirculation reactor is shown on Figure 1. The design of the reactor was such that it could be operated either batch, continuous, or semibatch. The circulating system was built of 1-in. standard IPS red brass pipe. Gas was circulated at a rate of about 2 cu. ft./min. by a rotary blower. A catalyst bed 4 in. deep was located in the downward vertical run of the pipe. Temperature was controlled by passing tempered water at 5 gal./min. through 1½-in. jackets on the 1-in. reactor piping. The gas circulation rate was measured by the orifice *B* between the blower and the catalyst bed. The overall distance from the top section to the bottom section was 57 in. The maximum length of the horizontal section was 41 in.

Ethylene, hydrogen, or both gases were fed to the 1-in. reactor piping at a point 32 in. upstream of the blower suction. Passage of the gas through the blower plus turbulence in the piping ensured that the gas was well mixed when it reached the catalyst bed. In continuous operation the product gas was purged from the system at a point 9 in. upstream of the feed point. Operation was slightly above atmospheric pressure in all tests.

The centrifugal blower was driven by a direct connected electric motor operated at 3,600 rev./min. The gas in the casing of the blower could pass through the lower bearing and enter the motor itself. The motor casing was continuously purged by passing gas from the blower discharge into the top of the casing. Because of mechanical limitations of the blower the entire gas circulating stream was cooled before entering the blower suction. It was then heated to reaction temperature in the vertical jacketed pipe on the blower discharge.

The bed temperature was measured by thermocouple *C* located ¾ in. from the bottom of the bed. Gas temperature was measured at *D* by a thermocouple protected by a polished brass radiation shield. Adjustments were made so that the circulating gas stream and the pipe wall at *A* were at the same temperature as the tempered water flowing through the jackets.

Because of a combination of good heat transfer and low heat generation per pellet the calculated temperature difference between the gas and the surface of the pellet was at all times less than 0.1°C. Although no significant temperature differences existed between the gas and the pellet, the difference between the measured bed temperature and circulating water temperature was of the order of 2°C. By using physical properties of the catalyst and estimated values of the pore diffusion coefficients the effectiveness factor was calculated to be 99% or higher in all cases. In general the adiabatic temperature rise of the gas passing through the bed was 2.5°C. or less.

The catalyst was activated in place by heating the reactor to about 275°C. while passing hydrogen through the bed. Heat was supplied by a Nichrome coil on the outside of the jacket that extended about 1 ft. above and below the catalyst bed. During activation the 1-in. valve in the reactor circulating piping was closed so that hydrogen flowed through the blower (which was not running), down through the catalyst bed, and out the normal purge point. The reaction system itself had an immeasurably small catalytic activity.

A prepurified grade of commercial hydrogen was used. Though this had a guaranteed minimum purity of 99.9%, it was further purified by passage through a 3 ft. long 1 in. diameter section of steel pipe containing palladium on alumina catalyst to convert traces of oxygen to water. The column operated at approximately 175°C. The hydrogen next passed through a 3-ft. long section of 3 in. diameter steel pipe containing activated alumina in order to remove traces of water.

Commercial CP grade ethylene with a guaranteed purity of 99.5% was obtained in steel cylinders. The ethylene feed purification system was similar to that used for purifying hydrogen, except that traces of oxygen were removed by passing the gas through a column filled with reduced copper and operated at about 170°C.

The flow of hydrogen was measured by one of three capillaries fabricated from stainless steel hypodermic needle stock. A similar system was used for measuring ethylene flow rates. All six capillaries were calibrated by a wet test meter.

The catalyst used to obtain all data, copper on an alumina support (girdler T-317), was in the form of 3/16 × 1/8 in. tablets and contained 9.8% copper. Physical properties of this catalyst are listed below:

Surface area, sq. m./g.	190
True density, g./mliter (helium displacement)	3.54
Pellet density, g./mliter (mercury displacement)	1.75
Pore volume, mliter/g.	0.29
Pore diameter, Å	61

The concentrations of ethylene, ethane, and of hydrogen were of interest, but the stoichiometry was such that it was essential only to measure the ethylene concentration. The latter was measured with an apparatus with a solution of mercuric sulfate in 22% aqueous sulfuric acid as the absorbent (*7*).

PROCEDURE IN SEMIBATCH OPERATION

With the recirculation reactor operating continuously under known steady flow conditions a number of operations were carried out nearly simultaneously. On the assumption that the ethylene concentration was to be held constant, the procedure was: the blowoff was sampled and the product line shut off, hydrogen and ethylene feeds were cut off by closing the main throttling valve, a pressure regulator was put into service to feed ethylene at such a rate that the reactor pressure was held constant, the ethylene throttle valve was opened wide, and the ethylene flow rate was recorded at frequent intervals. The change over from continuous to semibatch operation normally required about 2 min. Experimental runs lasted from 2 to 7 hr.

The key to successful operation of the semibatch system was the development of a simple pressure regulator that allowed precise control of reactor pressure without fluctuations in the flow rate of the gas feed. The capillary and manometer used to measure ethylene flow rates during continuous operation were also used during semibatch operation. The ethylene flow rate was adjusted during the change over so that more ethylene than required was fed. Excess ethylene was bled off at a point just upstream of the flow measuring capillary through an open-ended copper tube extending to the bottom of a 2 in. diameter glass tube partially filled with water; thus the inlet pressure to the capillary was fixed by the water level in the bubbler. If the flow rate to the reactor was too small, the reactor pressure dropped, the differential across the capillary increased, and the flow necessarily increased. If the flow rate was too high, an adjustment occurred in the opposite direction. Thus the system was self-compensating and proved to be extremely stable. A relatively large capillary was selected so that the reactor pressure changed by only about 1 in. of water during a run. About 5 min. was required for the pressure regulation to assume positive control.

In the absence of leaks the reaction rate is numerically equal to the rate required to hold the pressure constant; the concentration of all components at any time can be calculated by a simple material balance if the initial concentrations and the number of moles of gas in the reactor are known. The volume of the reactor was determined under static conditions with the reactor filled with hydrogen alone. A known volume of gas was suddenly withdrawn from the reactor and the pressure decrease noted. Though allowance was made for the different temperatures in different parts of the system the calculation of total moles contained in the circulation loop was subject to an error of perhaps 5%. This showed up in discrepancies between the measured final gas composition and the composition calculated by integration of the feed rate.

Particularly in runs at low catalyst activity it was essential to make corrections for leakage from the system. The reaction rate was simply the feed rate minus the leak rate; however leakage caused the concentration of the reactant being held constant to increase by several percent during most runs. The system was calibrated under dynamic conditions so that the leak rate was known as a function of the pressure at the blower suction, and this calibration was used in making the necessary allowance for leakage to obtain the true reaction rate. The composition throughout the run was readily calculated by simultaneously allowing for leakage and reaction in making the numerical integration.

CORRECTIONS FOR CHANGING CATALYST ACTIVITY

Despite careful purification of the feeds the catalyst activity decreased seriously throughout the series of runs. Months were spent in an effort to correct the situation, but the reason for the rapid decline was not definitely determined. The most probable reason is that substantial quantities of water remained on the alumina carrier even after drying in a stream of dry hydrogen at 325°C. Traces of water are known to poison copper catalysts rapidly (*21*). Even though the water was tied up with alumina by strong chemical types of bonds, the equilibrium between water and alumina is metastable, and water very likely reacted slowly with copper (*4*).

Corrections were made for changing catalyst activity by making check runs before each kinetic run. All check runs were made by the semibatch method under identically the same standard conditions (34% ethylene, 40% hydrogen, 61.3°C.), the resulting reaction rate being defined as the *standard activity* of the catalyst at that time. The standard activity changed significantly with time, some fourfold over the period of nearly two weeks required for the completion of the semibatch runs.

To adjust all runs to the same catalyst activity an activity-adjusted rate was defined. In effect the activity-adjusted rate is a rate normalized to a standard activity of 10×10^{-5} lb. moles/hr. (for a constant mass of 60.2 g. of unreduced catalyst):

$$\text{Activity adjusted rate} = \frac{10 \times 10^{-5}}{\text{standard activity}} \times \text{measured rate}$$

EXPERIMENTAL RESULTS

Initially a series of continuous runs was made. These runs were not successful because of a combination of rapidly declining catalyst activity and long times required to reach steady state conditions. The discouraging results in these runs motivated the development of the semibatch operation.

Semibatch operations were planned so that a minimum number of runs would be required to get a relatively complete picture of the kinetics. At 61.3°C. three runs were made at three different constant partial pressures of hydrogen (Runs 46, 54, and 62). A fourth run was made at constant ethylene partial pressure (Run 66) with the hydrogen partial pressure changing continuously throughout the run. Three runs were made at one partial pressure of hydrogen and at three different temperatures (Runs 46, 50, and 70). A final run (Run 72) was a repeat of the first run but at a much lower catalyst activity. Essentially all meaningful kinetic data were obtained in these runs.

The results of Run 66 at constant ethylene partial pressure are shown in Figure 2. The reaction is clearly first order with respect to the hydrogen partial pressure. First-order kinetics were obeyed despite the fact that the ethylene concentration changed during the run from 26.8 to 32.8% because of leakage during the long run. (Run 66 was the longest of the series of semibatch runs.)

The change in hydrogen concentration was small in all runs at constant hydrogen concentration, with the exception of Run 54 in which it increased during the test period from 22.4 to 30%. Since the results of Run 66 clearly showed the reaction to be first order with respect to hydrogen, the activity-adjusted rates were corrected to the average hydrogen concentration by multiplying each data point by the ratio $(p_{H2})_{avg}/p_{H2}$. Data obtained at constant temperature are shown in Figure 3; data for constant hydrogen partial pressure and varying temperature are shown in Figure 4. In kinetic runs at constant hydrogen concentration the final ethylene concentration was assumed to be correct; stoichiometric calculations were based on this value rather than on the initial concentration. The consistency of the data and stoichiometric calculations was tested by comparing the initial measured ethylene concentration with the calculated concentration; these values checked within several percent. In check runs, and the one run at constant ethylene concentration,

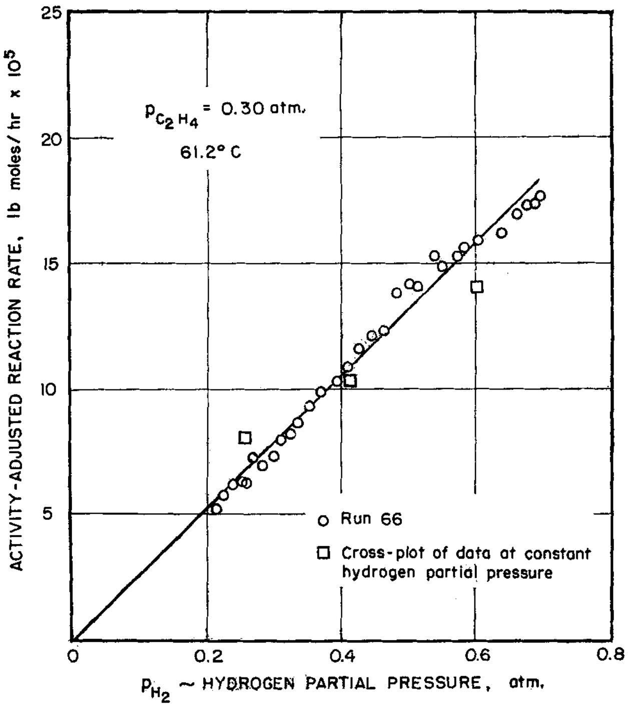

Fig. 2. Run 66. Activity adjusted rates at constant partial pressure of ethylene. Points shown as squares are from Figure 3.

stoichiometric calculations were based on the initial ethylene concentration.*

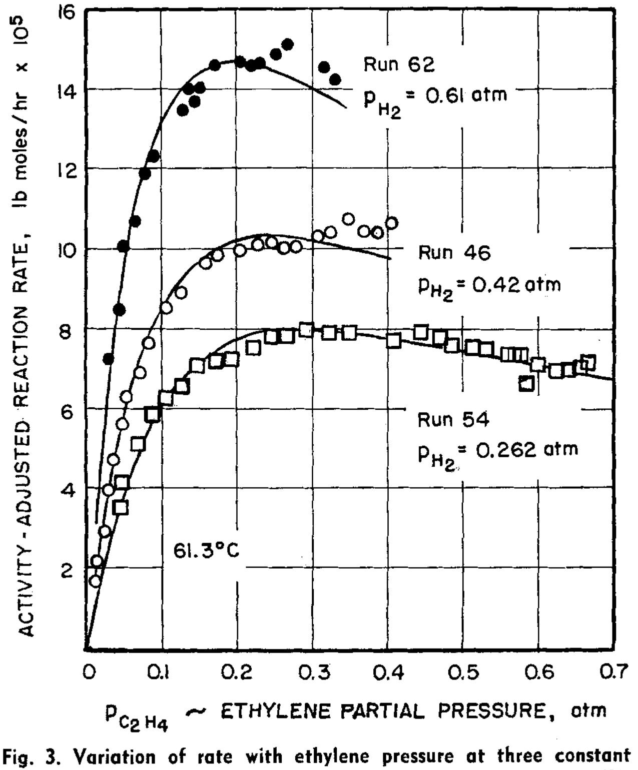

Fig. 3. Variation of rate with ethylene pressure at three constant hydrogen partial pressures. Solid lines calculated by Equation (1).

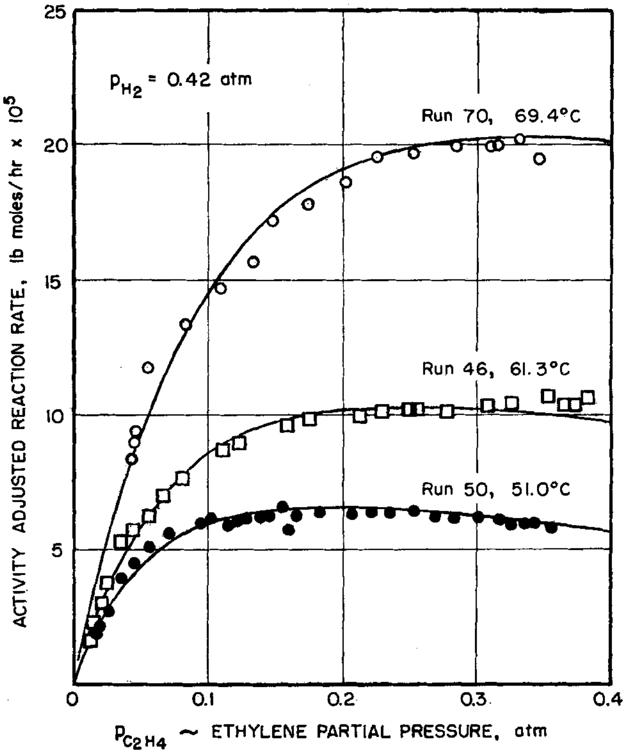

Fig. 4. Rate as a function of ethylene pressure at three temperatures. Solid lines caluculated by Equation (1).

Values of the reaction rate as read from Figure 3 at 0.30 atm. ethylene partial pressure are plotted as squares on Figure 2 for comparison with the results of Run 66. The good agreement suggests that only three runs should suffice at any one temperature, since results at constant ethylene partial pressure could be predicted by cross plotting the data at constant hydrogen partial pressure. It is reassuring to have a fourth run to provide a cross check.

Figures 2, 3, and 4 represent all the useful kinetic data obtained. Data of the type shown in these three figures demonstrate an important advantage of semibatch operation; results are easy to correlate because only one independent variable is changed at a time.

CORRELATION OF THE DATA

The clear inhibition of the reaction by ethylene at high partial pressures strongly suggests that ethylene and hydrogen compete for the same adsorption sites on the catalyst surface. The following expression for the reaction rate v_H is based on the assumptions: ethylene is adsorbed very much more strongly than hydrogen, the adsorption is reversible, chemisorption is rapid compared with the surface reaction rate, and both ethylene and hydrogen are adsorbed as molecules:

$$v_H = k\frac{a\,p_{H_2}\,b\,p_{C_2H_4}}{(1+b\,p_{C_2H_4})^2} \qquad (1)$$

This equation can be rearranged to give

$$\left(\frac{p_{H_2}p_{C_2H_4}}{v_H}\right)^{1/2} = \frac{b}{(k\,a\,b)^{1/2}}p_{C_2H_4} + \frac{1}{(k\,a\,b)^{1/2}} \qquad (2)$$

A graph of data as $\left(\frac{p_{H_2}\,p_{C_2H_4}}{v_H}\right)^{1/2}$ vs. $p_{C_2H_4}$ should give a straight line if Equation (1) applies.

Such a test is shown in Figure 5 for the run made over the widest range of ethylene partial pressures (see Run 54, Figure 3). The data for Runs 50 and 70 (51° and 69.3°C.) could also be correlated in a satisfactory manner by Equation (1). The data for Runs 46, 62, and 72 (all at 61.3°C.) fell close to one straight line, but the data for Run 54 (also at 61.3°C.) fell somewhat below the data for the other three runs. The fact that results from Runs 46 and 72 (the first run and the last run, both under identical conditions) fall very nearly on the same

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* Tabular material has been deposited as document 7973 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.

straight line despite a threefold change in catalyst activity shows that there was no fundamental change in the relative adsorption equilibrium of ethylene and hydrogen as the catalyst aged. This indicates that the method of adjusting for changes in catalyst activity by means of check runs is fundamentally sound. No explanation can be given for the fact that the data from Run 54 fell below those from the other three runs at 61.3°C.

It should now be pointed out that the curves shown as solid lines in Figures 3 and 4 (v_H vs. $p_{C_2H_4}$) were calculated curves derived with the constants ka and b for each run. The fit of the calculated curves to the data is reassuring.

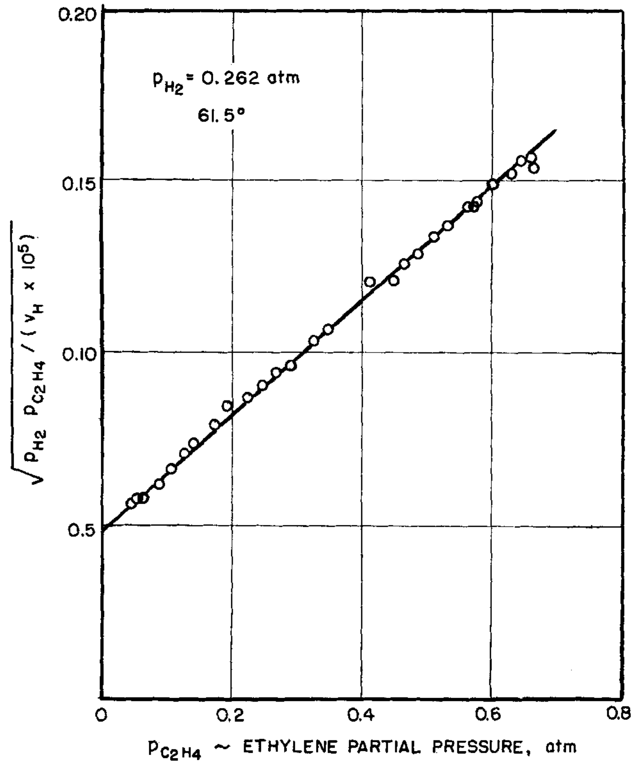

Fig. 5. Test of Equation (1) with data of Run 54.

The logarithm of ka and b were plotted vs. $1/T$. (All four runs at 61.3°C. were averaged to determine the best value of the constants.) The product ka increased with temperature, and b decreased with temperature. From the slopes of these two curves the heat of adsorption of ethylene was determined to be 6.9 kcal./mole; the value $E_a - \lambda_{H_2}$ (the true activation energy minus the heat of adsorption of hydrogen) was found to be 14.1 kcal./mole.

The ethylene adsorption equilibrium constant b decreases with temperature because ethylene is less strongly adsorbed as temperature is increased. The overall constant ka increased with temperature because the true energy of activation of the reaction is greater than the heat of adsorption of hydrogen.

The shift of the maximum rate to higher ethylene partial pressures (see Figure 4) as the temperature is raised can be explained by the fact that ethylene is more strongly adsorbed at low temperatures; hence the surface approaches saturation at low ethylene partial pressures. At higher temperatures ethylene is adsorbed weakly and relatively high partial pressures of ethylene are required to approach surface saturation.

The excellent correlation of the data by Equation (1) is not necessarily proof that the reaction takes place as assumed; it shows only that the data are consistent with the assumed mechanism. Supplementary adsorption studies were made in an attempt to confirm the four underlying assumptions and to find out if a correlation was possible between the ethylene adsorption equilibrium constant b determined by kinetic means and by static means.

Other mechanisms were tested to determine whether the data could equally well be correlated by another method. Most authors (*3*, *20*) claim that chemisorption of hydrogen on metals can reasonably take place only with the formation of atoms. A distinctly inferior correlation was obtained with an equation based on the assumption of hydrogen in the form of atoms.

Still another assumption made in the past (*21*) is that the sites which adsorb hydrogen and ethylene are not of the same type, or at least noncompetitive. A poor correlation of the data was obtained with an equation based on this assumption. Thus neither of these alternative mechanisms was consistent with the data.

SUPPLEMENTARY ADSORPTION STUDIES

Static gas adsorption measurements were made in conventional glass equipment similar to that used by many other investigators. The apparatus was similar in principle to that used in BET determinations, but its construction was considerably simplified. The catalyst was contained in an adsorption bulb with a volume of about 230 mliter. The amount adsorbed as a function of pressure was determined at 51.0°, 61.3°, and 69.4°C. The dead space in the adsorption apparatus was determined by admitting known quantities of helium.

Results were hard to interpret because of difficulty in distinguishing between physical adsorption and chemisorption. The former type of adsorption, which has nothing to do with catalysis, tended to mask the desired effects to an undetermined extent. It appeared likely that a large portion of the ethylene was physically adsorbed; the fraction of the total hydrogen adsorption held by van der Waals forces is debatable.

Sorption of hydrogen was of two types, a very slow sorption or activated adsorption, and a rapid and reversible adsorption. The former almost certainly had nothing to do with catalysis. Once these sites were saturated, study of the second type could be made.

Hydrogen was weakly adsorbed. The adsorption isotherms were curved near the origin, then became linear above approximately 50 mm. of Hg absolute pressure. The heat of adsorption (calculated by the Clausius-Clapeyron equation) was close to zero over the range 51.0° to 61.3°C.; from 61.3° to 69.4°C. the heat of adsorption varied with surface coverage from 5 to 20 kcal./g. mole. The zero heat of adsorption suggests physical adsorption; the values in the range 5 to 20 kcal./g. mole suggest chemisorption. Much less than a monolayer was formed on the gross catalyst surface.

Provided physical adsorption did not mask chemisorption effects, the assumptions behind Equation (1) were generally confirmed. Certainly hydrogen was weakly adsorbed. The second type of chemisorption appeared consistent with the assumption that chemisorption of hydrogen is reversible and rapid compared with the surface reaction rate. Provided hydrogen is adsorbed as molecules, there should be a linear relation between amount adsorbed and pressure at low surface coverage; adsorption as atoms should be proportional to the square root of the pressure. Thus the form of the adsorption isotherms for the amount of hydrogen adsorbed as a function of pressure suggests that hydrogen adsorption as molecules rather than as atoms is more likely.

Ethylene was shown to be adsorbed much more strongly than hydrogen, but this does not necessarily prove that ethylene is more strongly chemisorbed than hydrogen. The measurable adsorption of ethylene was rapid and reversible. The heat of adsorption varied from 6.4 to 7.9 kcal./g. mole, depending on surface coverage. The heat of liquefaction of ethylene is approximately 3.5 kcal./g. mole; however it is common for heats of physical adsorption to be several times the heat of liquefaction. The heat of chemisorption of ethylene on copper is reported to be 18.0 kcal./g. mole. Trapnell (*20*) suggested that values below 8.0 kcal./g. mole of ethylene indicate physical adsorption.

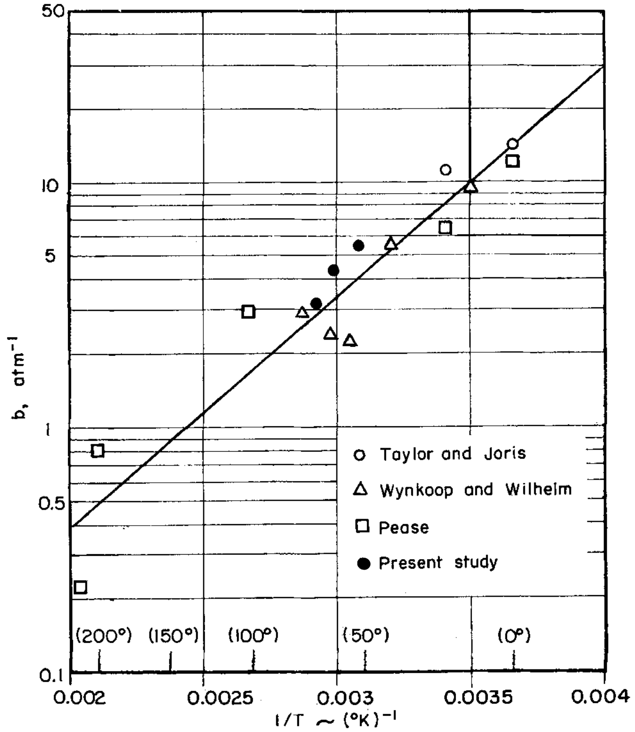

Fig. 6. Comparison of data of four studies of ethylene hydrogenation on copper.

Although physical adsorption masked chemisorption to a very significant extent, there was no evidence of irreversible adsorption of ethylene. Thus the behavior of ethylene on the supported copper catalyst used appears to differ markedly from the behavior on nickel catalysts where ethylene is irreversibly adsorbed as acetylenic residues and polymers (*2, 8*).

One of the basic assumptions in calculating the results of semibatch operation was that the amount of ethylene and hydrogen adsorbed on the catalyst was negligible in comparison with that in the gas phase of the reactor. The static adsorption experiments showed that the amount of ethylene adsorbed on the catalyst was less than 2% of that in the gas in the reactor system, and that the amount of hydrogen adsorbed was negligible.

An attempt to correlate adsorption equilibrium constants determined from kinetic experiments with adsorption equilibrium constants determined in static adsorption measurements was a failure. Although the kinetics could be correlated in a very satisfactory manner by an equation based on the Langmuir isotherm, this isotherm did not even approximately correlate the data in static measurements of ethylene adsorption and was only a fair representation of the hydrogen adsorption data. Whether or not such a comparison is possible is open to question; inability to distinguish clearly between physical adsorption and chemisorption prevented such a comparison.

COMPARISON WITH PREVIOUS INVESTIGATORS

A careful analysis was made of the data of three previous studies of the hydrogenation of ethylene over copper catalysts. Both Pease (*11, 12, 13*) and Taylor and Joris (*16*) found behavior similar to that of the authors, although neither attempted a quantitative correlation by a Langmuir-Hinshelwood type of equation. Wynkoop and Wilhelm (*21*) reported the reaction to be first order in hydrogen and zero order in ethylene. They explained this behavior by postulating that the sites which adsorbed hydrogen and ethylene were not of the same type, or at least noncompetitive.

The authors attempted to correlate the results of all three studies by means of Equation (1). A good correlation of the data of the first two investigators was obtained; the correlation in the third case was moderately satisfactory. No attempt was made to compare the average deviation of the results of Wynkoop and Wilhelm by Equation (1) with the average deviation based on their correlation. All that can be said is that their data are not inconsistent with Equation (1). A comparison of the ethylene adsorption equilibrium constant b (for all four investigations) as a function of $1/T$ is given on Figure 6.

NOTATION

a = hydrogen adsorption equilibrium constant, atm.$^{-1}$
b = ethylene adsorption equilibrium constant, atm.$^{-1}$
E_a = true activation energy, cal./g. mole
k = specific reaction rate constant, lb. moles/hr.
p_{H_2} = partial pressure of hydrogen, atm.
$p_{C_2H_4}$ = partial pressure of ethylene, atm.
T = absolute temperature, °K.
v_H = reaction rate, lb. moles/hr.
λ_{H_2} = heat of adsorption of hydrogen, cal./g. mole

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