Influence of Catalyst Particle Size on Reaction Kinetics: Hydrogenation of Ethylene on Nickel

J. W. FULTON and O. K. CROSSER

University of Oklahoma, Norman, Oklahoma

The influence of catalyst particle size upon the reaction rate was studied for the hydrogenation of ethylene with nickel-on-alumina in a packed-bed flow reactor. A threefold increase in particle diameter through a critical size range (0.03- to 0.09-cm. diameter, corresponding to a Reynolds number of around 1) produced a thirtyfold increase in reaction rate per unit external surface area. The behavior of the system indicates that this increase was due to the influence of external gas-solid transport phenomena on the reaction kinetics. *j*-Factor correlations were used to calculate the catalyst surface temperatures and concentrations, which were used to calculate Arrhenius activation energies and reaction rates from available rate expressions.

The rate of a heterogeneous catalyzed reaction is determined by both the chemical reaction kinetics at the solid surface and by the rate of heat and mass transfer to this surface. When the reaction is operating at a steady state, the number of moles of a component destroyed at the catalyst surface by the chemical reaction is exactly equal to the number of moles of that component transported to the surface. Likewise, the heat generated by the reaction must equal the heat removed.

Two systems of heat and mass transfer are involved when dealing with a catalyst pellet. The first system is the hypothetical film or gas layer surrounding the pellet. Both heat and mass transfer occur across this film because the bulk-gas temperature and concentrations are different from those at the catalyst surface. Mass transfer across the gas film occurs by both convection and molecular diffusion. Heat transfer occurs by convection, conduction, and radiation. Catalyst surface temperatures as high as 420°C. above the bulk-gas temperatures may exist (*35*).

The second heat and mass transfer system involves the pores and solid material of the catalyst pellet. Both temperature and concentration gradients may exist through the porous catalyst particle. Mass transfer occurs by Knudsen diffusion, bulk diffusion, and surface migration. Heat transfer occurs by conduction in both the solid and gas phases. Effectiveness factors other than one are the result of temperature and concentration gradients within a porous catalyst pellet.

For any given system involving a porous catalyst, it is difficult to evaluate the relative importance of film and pore effects. The calculations are particularly complicated by strong thermal effects. Unless sufficient data are taken and several variables are analyzed, the pore effects may be confused with film effects. In particular, nonisothermal effectiveness factors may seem to explain experimental data which may be primarily the result of film effects. Therefore, both film and catalyst heat and mass transfer must be considered.

The experimental data from this study indicate that film effects are more important for the system chosen. The extremely active catalyst and low gas flow rates combine to enhance the film effects. All of the reactants which reach the catalyst surface are reacted on the outer surface before they have a chance to diffuse into the pores. For this system, therefore, temperature and concentration gradients across the surface film are of particular interest when studying the kinetics of the reaction and the behavior of the catalyst.

Experimentally, it is difficult or impossible to measure temperatures and chemical concentrations directly on the surface of a catalyst pellet. Generally one can measure only bulk-gas temperatures and concentrations. Therefore the influence of heat and mass transfer phenomena between the bulk-gas phase and the catalyst surface must be considered in order to calculate surface conditions.

These transport phenomena are a function of the catalyst particle size, and this function is of critical influence. Thus, small changes in the size of the catalyst particle may have a profound effect upon the behavior of the reaction. Increasing the size of a catalyst pellet increases the area for heat transfer, mass transfer, and chemical reaction. Increasing pellet size, however, not only changes the area through which these transport mechanisms act but also changes the heat and mass transfer characteristics. This variation in behavior between the transport phenomena and chemical reaction with changing particle size causes a change in character of the reaction kinetic data. Changing temperature and concentration have varying effects on the reaction rate. Reaction rates are approximately first to second order with respect to concentration, but they are exponential with changes in temperature. Therefore, changing the catalyst particle size will have an effect upon the behavior of the reacting system. The purpose of this study was to determine the precise character of this effect.

THEORETICAL CONSIDERATIONS

For a given mass of catalyst, particle size affects the conversion by changing the relative amount of internal and external active areas and the external surface film-transfer coefficients. The effects of Knudsen diffusion through pores to the internal area has been extensively studied (*6, 19, 43, 47*). The role of surface migration or surface

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J. W. Fulton is at Oklahoma State University, Stillwater, Oklahoma.

mobilities of adsorbed molecules is currently being investigated (*42*). Finally, the influence of the interfacial or surface film surrounding the catalyst pellet may also be significant. The influence of the surface film is particularly important when the system involves an extremely active catalyst, a highly exothermic reaction, and operation at low Reynolds numbers. These three extreme conditions were involved in the present study, and, as a result, surface-film effects seemed to be rate controlling. Experimental evidence for this contention will be shown later. In the following discussion of the theory, therefore, only external surface-film transport will be considered.

Mathematical discussions of the reaction steps are presented in several places (*14, 20, 25, 27, 31, 35*). The system of equations for a catalyst particle in a packed bed at steady state reaction is

$$r_{mi} = k_G \, a_m \, \phi \, (p_{iS} - p_{iB}) \qquad (1a)$$

$$r_{mi} \, \Delta H_i = h_G \, a_m \, \phi \, (T_S - T_B) \qquad (1b)$$

$$r_{mi} = k f \text{ (concentrations at solid-gas interface)} \qquad (1c)$$

where

$$k = A e^{-E/RT}$$

k_G and h_G must be presumed to be available from j_D and j_H correlations of packed-bed heat and mass transfer. Both transport coefficients usually are reported as depending upon particle diameter in the same way:

$$j_D = \frac{k_G \, p_f}{G_M} (N_{Sc})^{2/3} = a(N_{Re})^{-b} = a' \, D_p^{-b} \qquad (2a)$$

$$j_H = \frac{h_G}{C_{pM} G_M} (N_{Pr})^{2/3} = a''(N_{Re})^{-b} = a''' \, D_p^{-b} \qquad (2b)$$

For given bulk conditions and other system parameters, the Equations (1*a*), (1*b*), and (1*c*) may have one or three solutions. The three solutions imply a rather large sudden change in catalyst temperature from a kinetic regime to a diffusion regime (*14*). Since h_G and k_G depend upon particle diameter, it is obvious that for a given set of conditions various results will appear as the diameter is changed. Reports of experiments which follow the predictions of equations are few, possibly because the jump behavior is undesirable in kinetics studies. Frank-Kamenetskii (*14*) presents results showing the effect, and the higher temperature data correlating the combustion of coal indicate it. Thus, the experimental study of the effect of particle size should verify the predicted reaction behavior and provide information about the heat and mass transfer correlations.

Reaction Kinetics

The reaction system chosen for this study was the hydrogenation of ethylene to ethane on a nickel catalyst because the reaction proceeds without any side reactions, the hydrogenation does not occur to a measurable degree in the absence of a catalyst, conversion of any amount may be obtained at moderate operating conditions, and there are substantial data on the kinetics of this reaction.

It is generally agreed that the reaction is unaffected by the presence of ethane, other than through its action as an inert diluent (*10, 22*). There seems to be a reaction mechanism shift between 150° and 200°C. The reaction mechanism at the lower temperatures is generally correlated as first order with respect to the partial pressure of hydrogen (*3, 13*). Beeck's value for the energy of activation at the lower temperatures, $E = 10.7$ kcal./g.-mole, is probably the most appropriate, since it covers a range of −80° to 150°C. Pauls', Comings', and Smith's (*32*) value of $E = 11.6$ kcal./g.-mole is available for purposes of comparison, since it was obtained using a nickel-on-alumina catalyst similar to the one used in this study. The mechanism at the higher temperature is generally correlated as first order with respect to the partial pressures of both hydrogen and ethylene (*11*). A precise value for the energy of activation above 150°C. is not available. Most investigators find values below 3.4 kcal./g.-mole (*45*).

Transfer Processes

Heat and mass transfer processes for a catalyst pellet may be divided into two categories: those processes which occur inside the pellet, and those which occur across the stagnant gas film surrounding the pellet. A review of these processes has been published recently by Hougen (*19*). Mathematical expressions describing the overall behavior of packed-bed reactors are given and solved numerically by Park (*30*) and von Rosenberg (*46*). Textbooks by Satterfield and Sherwood (*39*), Hougen and Watson (*20*), and Smith (*41*) consider general heat and mass transfer correlations for a packed bed. Weisz and Hicks (*47*), Tinkler and Metzner (*44*), and Carberry (*6*) have solved the differential equations resulting from material and energy balances inside a porous catalyst pellet. Theoretical approaches to the influence of operating variables on the external surface gas film have not been especially useful. Five recent papers which have offered models have been presented by Carberry (*5*), Kusik and Happel (*23*), Hoelscher (*18*), Rosner (*37*), and Pfeffer and Happel (*33*).

Although the system of heat and mass transfer through a gas film in a packed bed is complex, the *j*-factor correlations of Chilton and Colburn (*7*) have been extremely useful for the past 30 yr. Reviews of the wide variety of experimentally determined *j*-factors correlations have been made (*16, 35*).

The effect of Reynolds number upon j_D appears to depend upon whether the data were obtained with a sublimating solid or a wetted porous sphere. Experiments where only a gas film existed, such as sublimating napthalene spheres in air or carbon dioxide (*1, 8, 21, 36*) and decomposing hydrogen peroxide on silver (*38*), yield the important relations for gas-solid catalyzed reactions.

A similar variety of results exists for j_H, and the correlations obtained by dielectrically heating plastic particles (*12*) and electrically heating metal spheres (*2, 9, 17*) are more appropriate to this study.

The gas-film *j*-factor correlations show that the exponent on the Reynolds number varies between 0.29 to 0.35. The coefficient multiplying the Reynolds number varies between approximately 0.2 and 1.0. Several investigators have shown that this multiplying coefficient is a function of system variables (*17, 21, 36*). The unreliability of this coefficient is the weakest point in these transport-phenomena correlations. The relationship between the heat transfer factor j_H and the mass transfer factor j_D was demonstrated by Satterfield and Resnick (*38*) to be $j_H/j_D = 1.37$.

APPARATUS

The apparatus used in this study consisted of four units: feed system, reactor, temperature measuring system, and gas analysis system. A schematic diagram of the apparatus is shown in Figure 1. This apparatus operated at atmospheric pressure.

Feed System

Hydrogen and ethylene gases were fed from commercial cylinders with constant pressure regulators. Their flows were measured by capillary tube flow meters. The feed composition for all runs was 80% hydrogen and 20% ethylene on a mole basis. The hydrogen flow rate varied from 1.18 to 3.53 g.-

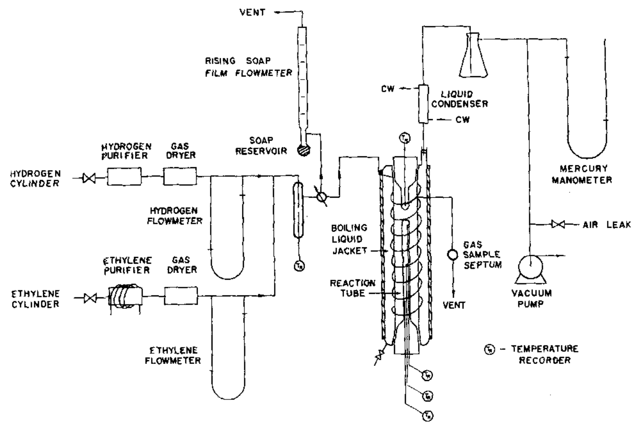

Fig. 1. Experimental apparatus.

moles/hr. Reaction conversions for the various particle sizes ranged from 4 to 60%, but all runs giving more than 28% conversion were repeated with less catalyst in order to get conversions below 28%.

A catalytic purifier for electrolytic hydrogen was installed in the hydrogen line to reduce any traces of oxygen to water. A heated purifier for removal of oxygen and sulfur was installed in the ethylene line. Both gas streams passed from their purifiers through drying tubes, in order to remove moisture. The gases were thoroughly mixed in a mixing chamber before being fed to the preheater.

Reactor

The reactor was designed with the primary purpose of maintaining an accurate and isothermal temperature level. The entering gases passed through a preheater coil, emptied into the reactor at the bottom, and passed up through the reactor tube containing the catalyst bed and out the top of the reactor. The internal diameter of the packed-bed tube was 2.14 cm. and the length of the packed section was 30.48 cm. The external diameter of the thermowell through the bed was 0.91 cm.

The reactor bed was packed in a particular way in order to hold isothermal conditions and maintain the bed fixed. The method of packing is discussed later.

Temperature Measuring System

All temperatures at the thermocouple points indicated in Figure 1 were sensed by iron-constantan thermocouples inserted in glass thermowells.

Product Analysis System

A vapor phase, partition chromatograph, built and modified in conjunction with previous research projects (*29, 40*), was used to analyze the reacting and product mixtures. A 4-ft. copper tube, ¼ in. in diameter, packed with finely divided silica gel, constituted the column used for the gas analysis. The analysis was determined by comparing the peak heights of the elution curves obtained for the reaction gas samples to those obtained from the standard gas mixtures. Six different compositions of gas samples were used as standards, and their method of preparation is mentioned elsewhere (*16*).

Catalyst

The catalyst used throughout the study was nickel-on-alumina, and an analysis of its physical characteristics were supplied. The internal surface area of the catalyst was 210 sq. m./g. and its weight 10 to 12% nickel. Pore volume contained 0.29 cc./g. below 800°A threshold diameter and 0.27 cc./g. below 140°A threshold diameter determined by the carbon tetrachloride adsorption technique of Benesi, Bonnar, and Lee (*4*).

The catalyst was received as ⅛-in. cylinders and was subsequently crushed in a glass mortar and pestle. The catalyst particles were classified by screening in U.S. Standard sieves to sample sizes varying from 8 to 12 mesh to 200 to 325 mesh. All of the catalyst samples were taken from a single crushing and screening operation.

Hydrogen

The 99.9% pure hydrogen was taken from commercial cylinders manufactured by the electrolytic process. The oxygen and water impurities were removed by converting the oxygen to water after which all water was removed by passing the gas through a drying bed.

Packed Bed Diluent

The inert particles used to dilute the catalyst bed were cleaned Ottawa sand, which was nearly pure quartz of almost spherical shape. The sand was classified by screening in U. S. Standard sieves.

EXPERIMENTAL PROCEDURE

Packing the Reactor

The reactor was packed in a particular way in order to assure essentially isothermal conditions and to maintain the bed fixed. First, 3 in. of 3-mm. glass beads were packed into the reaction tube, after the bottom thermowell had been fixed in place. Then 1 in. of clean 20 to 30 mesh Ottawa sand was packed above the glass beads. This entrance packing served to distribute the incoming gases evenly across the tube diameter before contact was made with the catalyst. Above the initial packing was packed the catalyst diluted in 100 ml. of Ottawa sand. The catalyst sample (0.1 or 0.2 g. weighed accurately to 1 mg.) was diluted in order to spread the reaction throughout the bed, since the exothermic heat of reaction (−32 kcal./g.-mole) was fairly large. The diluted bed reduced the possibility of hot spots developing and allowed the heat of reaction to be carried off by the liquid jacket. Isothermal conditions were thus maintained throughout. During most runs the diluent Ottawa sand was 20 to 30 mesh, no matter what the catalyst particle size. By using the same size diluent throughout a series of runs, changes in the overall bed characteristics could be avoided. There was a limit, however, to how small a catalyst particle size could be mixed with 20 to 30 mesh sand because catalyst particle sizes smaller than 100 mesh could move through the interstices of the 20 to 30 mesh bed. The data resulting from such a condition was erratic, especially with changes in the feed rate. During some of the runs, the Ottawa sand diluent particle size was varied in order to keep it the same size as the catalyst pellets. The catalyst was diluted by rolling a weighed sample of the catalyst with the sand in a round bottom flask until a uniform mixture was observed. One inch of clean sand and another inch of glass beads were packed above the catalyst bed. The reactor was cleaned and repacked for each catalyst particle size and weight of sample.

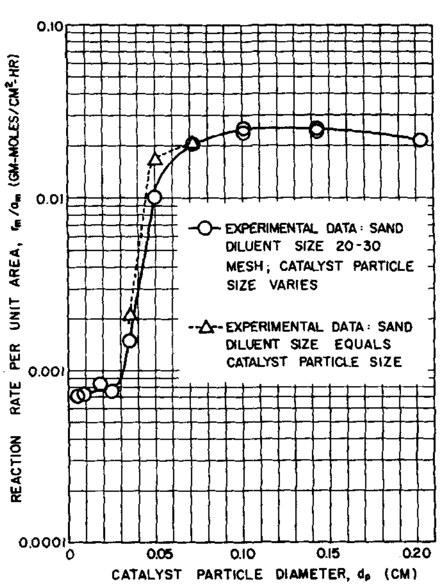

Fig. 2. Influence of particle size on reaction rate (bulk gas temperature 93°C., flow rate 0.498 g.-moles/sq. cm. hr.).

Catalyst Reduction

The catalyst, in the form of nickel oxide on alumina, was reduced in place by passing hydrogen over it at 370°C for 12 hr. After reduction the catalyst was exposed only to hydrogen and ethylene. No air was allowed to contact the catalyst because it was found that oxygen markedly deactivated it.

EXPERIMENTAL RESULTS

The experimental results consisted of values of conversion measured at various flow rates and temperatures. On the basis of catalyst particle sizes, the Reynolds number variations in this study ranged from 0.16 to 5.13. For a bed of 20 to 30 mesh particles the range in Reynolds number was from 0.64 to 1.92. Bulk gas temperatures were varied from 40° to 93°C.

The experimental results show the influence of changing the catalyst particle size at various temperatures at a given flow rate and weight of catalyst. An illustration of this influence can be seen from Figure 2, which considers reaction at a bulk temperature of 93°C.

The reaction rate was calculated by using the usual rate equation for a catalytic flow reactor:

$$r_m \, dW = F dx$$

or

$$r_m = \frac{dx}{d\left(\frac{W}{F}\right)} \simeq \frac{\Delta x}{\Delta\left(\frac{W}{F}\right)}$$

The reactor was operated at differential conditions whenever possible. When the x vs. (W/F) plot was not a straight line from the origin (about 20% of the runs), the slope of the curve was used to determine the reaction rate.

The circles (solid line) in Figure 2 represent experimental data taken with the catalyst particles diluted in cleaned 20 to 30 mesh Ottawa sand. The triangles (dashed line) represent data taken with the catalyst diluted in cleaned Ottawa sand having the same particle size as the catalyst.

Beginning with the smaller particles at the left of Figure 2, an increase in particle diameter resulted in a small increase in reaction rate per unit area. At a particle diameter of about 0.03 cm., the reaction rate began to rise sharply. At a particle diameter of about 0.09 cm., the reaction rate arrived at a plateau. The rate continued at this plateau for increasingly larger particle sizes, except for the largest size, where the rate dropped slightly. For a threefold increase in particle diameter of 0.03 to 0.09 cm., the reaction rate jumped approximately thirtyfold. On either side of this transition the reaction rate remained relatively constant.

Over the transition range where the rate rose sharply with increasing particle size, the sand diluent size was varied in order to equal the size of the catalyst pellet. The curve for these data (dotted line in Figure 2) was displaced slightly from but behaved in the same way as the curve describing the data with only 20 to 30 mesh sand as the diluent.

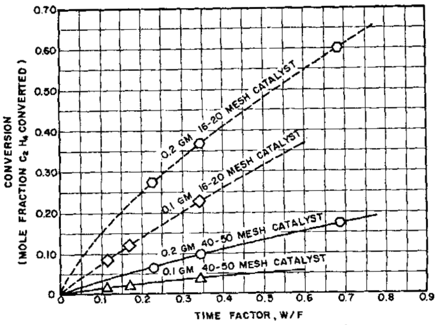

Fig. 3. Test for film diffusion effects.

Two sets of experimental data were considered in determining the relative importance of surface-film effects and catalyst pore effects. The first set of runs, with varying weights of catalysts and flow rates, showed qualitatively that film effects were significant for both the larger and intermediate particles. Figure 3 summarizes this conventional (*26*) test for film diffusion. Series of runs were made for both a large catalyst particle size and a smaller catalyst particle size. A constant weight of catalyst was used in each run, but the time factor W/F was varied. Since the two curves did not coincide for each particle size, surface-film effects were considered important.

The second set of experimental runs was aimed at determining the importance of pore effects for the catalyst particles. The results of several runs at 366°K. and 0.498 g.-moles/sq. cm. hr. are shown in Figure 4. From Figure 4, it can be seen that the reaction rate per gram of catalyst decreases with increasing particle diameter. At a particle diameter of about 0.03 cm., the rate begins to increase sharply. At a particle diameter of about 0.07 cm., the rate reaches a maximum and begins to decrease. In this transition interval from 0.03 to 0.07 cm. particle diameter, the reaction rate per gram of catalyst has increased about tenfold. The reaction rates before and after the transition are directly proportional to the amount of external surface area.

At the end of every reaction run the operating conditions were returned to those at the beginning, in order to check the stability of the catalyst over the period of the run. The same reaction rate was obtained at the end of the run when given the same operating conditions, demonstrating that this catalyst system was stable. Runs for 12 hr. duration failed to show a change in catalytic activity.

Runs were made in order to test the reproducibility of the data. As with all runs, these tests involved cleaning

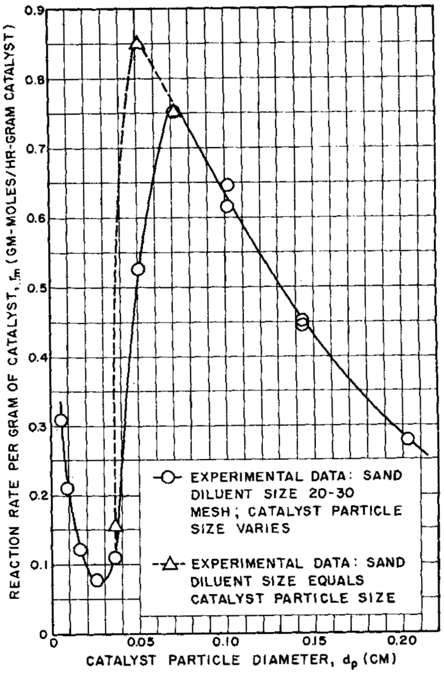

Fig. 4. Experimental data plotted for study of film and intraparticle effects (bulk gas temperature 93°C., flow rate 0.498 g.-moles/sq. cm.hr.).

and repacking the reactor bed between runs. It was found that the conversion reproducibility of ± 1% was well within the range of the estimated maximum deviation of ± 4%.

DISCUSSION OF RESULTS

It has been shown that the catalyst behaved in the same manner in the transition range whether or not it was diluted with a diluent of the same particle size. Therefore, the reaction rate shift could not be ascribed to a caging or shielding effect on the catalyst particle by the diluent. Also, by packing the catalyst in a diluent of equal size, there could be no movement or fluidization of the catalyst particles.

Figure 3 indicates that film effects were influential in this reacting system for both the intermediate and large catalyst particles. Figure 4 further establishes the rate-controlling importance of film effects, since the behavior exhibited is readily explained by film effects but would be difficult to explain on the basis of pore diffusion and internal temperature gradients. The reaction rate per gram of catalyst for the small particles decreased with increasing particle size, in direct contradiction to the behavior of intra-particle effects for an exothermic reaction.

In addition to these experimental results, one can calculate the uppermost limit of the internal temperature variation $(\Delta T)_{\max}$ which could have existed within the particle relative to the boundary temperature by the method of Weisz and Hicks (*47*). With a typical effective diffusivity of 2×10^{-3} sq. cm./sec. and thermal conductivity of 4×10^{-4} cal./(sec. cm./°C.), the internal $(\Delta T)_{\max}$ would have been less than 0.01°C. The steep rise in reaction rate between catalyst particles of 0.03- and 0.07-cm. diameter could have only been due to thermal effects. If these effects could not have been internal, then they must have been external.

A further demonstration of the effects of pore diffusion can be made by calculating effectiveness factors for the catalyst particles. For the larger particles the effectiveness factor was on the order below 0.1, which is consistent with the interpretation that the reaction occurred primarily on the external surface. The effectiveness factor for the smaller particles was around 1.0, which leaves in doubt which surface area one should use in order to calculate the reaction rate per area, but does not alter the interpretation.

These data are presented as evidence to substantiate the conclusion that external surface effects are important, and internal effects are insignificant for the systems and operating conditions under consideration.

The reaction behavior can be explained by gas-film heat and mass transfer behavior of particles in a packed bed. The explanation is, of course, only as good as the previously stated rationale and the heat and mass transfer correlations used.

The heat transfer correlation of Denton (9) was judged the most appropriate for this study for several reasons. First, his data were taken with only a gas film surrounding the pellet and did not introduce the added complexity of a gas-liquid film. Second, Denton's values for the j-factor correlation with Reynolds number is in line with the majority of the other gas-film correlations. Third, and most important, Denton's data were taken in a system similar to the one used in this study. He measured the steady state heat transfer coefficients by generating heat in a single metal sphere randomly packed in a bed of glass spheres. A similar situation exists in the reactor bed used in this study. The catalyst pellet, which generates the heat, is randomly packed in a bed of relatively spherical sand grains. The catalyst pellets are essentially isolated from each other because the volumetric ratio of the reactor bed packing is approximately 1:100 = catalyst:sand. The similarity of the two systems tends to eliminate the problem of variables specific to the particular system in question. For example, the magnitude of pellet-to-pellet heat conduction through the solid point contact cannot be assessed. There has been some recent work on the problem of point-to-point heat transfer (*28*) in a packed bed, but actual calculation of the magnitude of this phenomena is not as yet possible. The situation is further complicated when only one particle among many is generating heat, which was the case in this study. Denton's correlation, however, includes this effect, and calculation of surface temperatures for a particle generating heat among inert particles should be more accurate with his correlation.

The relationship between heat and mass transfer j-factors for a reacting system is found in the research of Satterfield and Resnick (38). They decomposed hydrogen peroxide in a bed of metal spheres, measuring both the heat and mass transfer characteristics of the system. They found the ratio $j_H/j_D = 1.37$.

Utilizing the heat and mass transfer studies of Denton and Satterfield and Resnick, one obtains the correlations

$$j_D = 0.426\,(N_{Re})^{-0.30} \qquad (3a)$$

$$j_H = 0.584\,(N_{Re})^{-0.30} \qquad (3b)$$

When one substitutes Equations (3*a*) and (2*a*) into Equation (1*a*), the partial pressure gradient of a component across the gas film may be calculated:

$$p_{iS} - p_{iB} = \gamma \frac{r_{mi}}{a_m} D_p^{0.30} \qquad (4a)$$

where

$$\gamma = \frac{p_f}{G_m \phi} \cdot \frac{1}{(0.426)} \left(\frac{G_m}{\mu} \right)^{0.30} \left(\frac{\mu}{\rho_g D_i} \right)_f^{2/3} \qquad (4b)$$

The temperature change from the bulk gas stream to the external surface of the catalyst may be calculated from Equations (3*b*), (2*b*), and (1*b*):

$$T_S - T_B = \beta \frac{r_{mi}}{a_m} D_p^{0.30} \qquad (5a)$$

where

$$\beta = \frac{\Delta H}{G_M Cp_M \phi} \cdot \frac{1}{(0.584)} \left(\frac{G_m}{\mu} \right)^{0.30} \left(\frac{Cp_m \mu}{k_t} \right)_f^{2/3} \qquad (5b)$$

The terms γ and β are functions of temperature and were calculated from physical and transport properties available in the literature. The arithmetic average gas-film temperature was used for the physical properties of the gases. The calculations of Δp and ΔT were accomplished by a trial-and-error solution of the four simultaneous Equations (4*a*), (4*b*), (5*a*), and (5*b*).

From these calculations, the smaller particles show only a slight change in surface temperature with increasing particle size. At the 0.03-cm. particle size, the temperature begins to rise abruptly. As the particle size increases, the temperature continues to increase and finally begins to taper off at the larger particle sizes. The partial pressure of ethylene at the surface of the catalyst behaves inversely from that of the surface temperature. As the particle size increases, the partial pressure of ethylene at the surface decreases.

From these calculated values of surface temperatures and concentrations, an Arrhenius type of function of log (rate constant) vs. $1/T$ was plotted in Figure 5. From Figure 5 the energies of activation and frequency factors for the reaction levels can be calculated. For the small particles (lower reaction level), the Arrhenius energy of

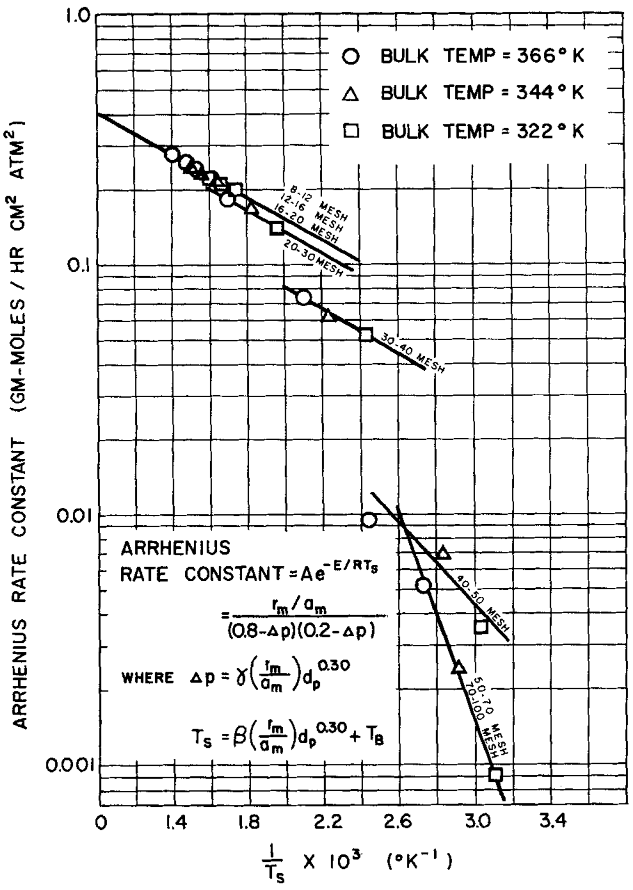

Fig. 5. Arrhenius plot for activation energy and frequency factor.

activation is 9.6 kcal./g.-mole and the frequency factor is 2,900 g.-moles/hr. sq. cm atm.^{2}

The energy of activation for the small particles, 9.6 kcal./g.-mole, is somewhat lower than Beeck's (3) value of 10.7 kcal./g.-mole. The value of 9.6 kcal./g.-mole is, however, close enough to Beeck's value to be sure that the chemical reaction kinetics is primarily the rate controlling step. The calculated catalyst surface temperatures for the small particles (50 to 70 and 70 to 100 mesh) in this study find the surface temperatures essentially the same as the bulk gas temperatures, 40°, 71°, and 93°C. These surface temperatures are within the range of Beeck's study. If the reaction were diffusion controlled, the rate would be considerably lower than the 9.6 kcal./g.-mole value.

The energy of activation for the increasingly larger particles decreases and then levels out at a value of 1.96 k.cal./g.-mole. The calculated surface temperatures for the larger catalyst pellets (8 to 12, 12 to 16, and 16 to 20 mesh) show that they have considerably higher surface temperatures than the smaller pellets, ranging from 381° to 443°C. The literature reports that for temperatures above 150° to 200°C. the energy of activation decreases. The reports differ on the energy of activation found, and there seems to be no agreement on what should be a reasonable value. However, most of these studies do agree that the energy of activation above 150° to 200°C. should be below 3.4 kcal./g.-mole. Therefore, the energy of activation of 1.96 kcal./g.-mole found in this study seems reasonable, although possibly somewhat low. The value of 1.96 kcal./g.-mole was obtained from the calculated surface temperatures and partial pressures and is considerably lower than Beeck's 10.7 kcal./g.-mole. Thus, the drop in activation energy must result from a change in the reaction mechanism rather than from a diffusion controlling condition.

Also, the decrease in equilibrium constant with increasing temperature does not become a limiting factor. A surface temperature of about 1,000°K. would be required before the reversible reaction would become significant. The equilibrium constant for the hydrogenation of ethylene is 3.2×10^{17} at 300°K., 3.2×10^{8} at 716°K. (the highest calculated surface temperature), and 0.35 at 1,000°K.

A more graphic description of this reaction process can be given by plotting the reaction rates for the two mechanisms from the calculated catalyst surface temperatures and partial pressures and the evaluated Arrhenius energies of activation and frequency factors. The reaction rates can be calculated from the following equations:
Available rate equation:

$$\frac{r_m}{a_m} = A\, P_{H_2}\, P_{C_2H_4}\, e^{-E/RT_s}$$

For small particles:

$$\frac{r_m}{a_m} = 2{,}900\ (0.8 - \Delta p)\,(0.2 - \Delta p)\ e^{-9{,}600/RT_s}$$

For large particles:

$$\frac{r_m}{a_m} = 1.18\ (0.8 - \Delta p)\,(0.2 - \Delta p)\ e^{-1{,}960/RT_s}$$

The experimentally evaluated data were substituted into these last two rate equations, and the resulting reaction rates were plotted in Figure 6. In these calculations, a_m was based on the average particle size as determined from the sieve screen sizes.

Beginning at the lower left of Figure 6, one can see that the first reaction rate (for small particles) began to rise at a catalyst particle diameter of 0.03 cm. The rate increased sharply, rising over two orders of magnitude before it began to level off. During this rise, which could only be due to an exponential rise in temperature, the

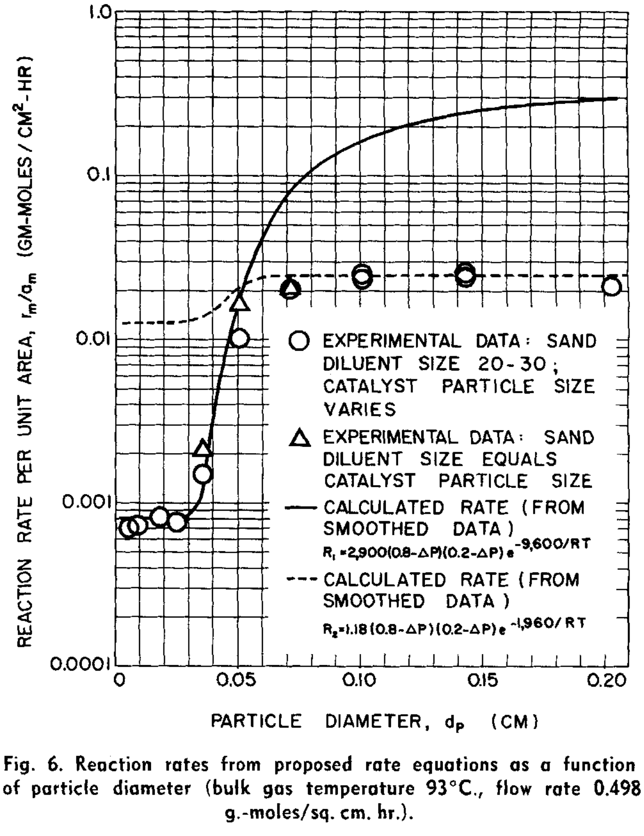

Fig. 6. Reaction rates from proposed rate equations as a function of particle diameter (bulk gas temperature 93°C., flow rate 0.498 g.-moles/sq. cm. hr.).

temperature increase at the catalyst surface caused a shift in the chemical reaction mechanism. As a result, the mechanism shifted to the second rate expression, shown by the dashed line in Figure 6. This second reaction rate became controlled by the diffusion step and leveled off in line with the experimental data points. Therefore, two shifts occurred during the transition phase, both of them resulting from an increase in surface temperature due to an increase in catalyst particle size. First, the increase in temperature induced a change in reaction mechanism. This mechanism change has been documented in the literature and discussed earlier. Second, the increase in temperature shifted the rate controlling step from reaction-kinetics controlling in the lower thermal regime to film-diffusion controlling in the upper thermal regime. This second shift was the cause of the levelling off of the experimental reaction rates for the larger particles and was also the reason calculated values for the second reaction rate expression level off along with the experimental values.

CONCLUSIONS

The demonstrated experimental agreement with literature values for activation energies and transfer correlations is believed to justify the following conclusions:

1. Catalyst particle size exerts a strong influence upon the observed reaction rate for an exothermic surface reaction in a packed-bed flow reactor.
2. The j-factor correlations for gas-film systems adequately evaluate changes in catalyst surface temperatures and concentrations. Furthermore, the j-factor correlations are satisfactorily employed with a diluted catalyst bed, and the inert diluent particles may be either larger, equal to, or smaller than the catalyst particles.
3. The shift from reaction-kinetics controlling to film-diffusion controlling regimes has been observed.
4. The published chemical reaction mechanism shift at around 150°C. for this reaction has been verified.

NOTATION

a = coefficient for j-factor, dimensionless
a_m = external surface area of the catalyst particles per unit weight, sq. cm./g.
A = Arrhenius frequency factor, g.-moles/hr. sq. cm. atm.^{2}
C_{pm} = heat capacity per unit mass at constant pressure, cal./g. °K.
C_{pM} = molal heat capacity at constant pressure, cal./g.-mole °K.
D_p = average catalyst particle diameter, cm.
D_i = gas phase diffusion coefficient of component i, sq. cm./sec.
E = Arrhenius energy of activation, cal./g.-mole
$f(\ )$ = mathematical function
F = feed rate to the reactor, g.-moles/hr.
G_m = superficial mass velocity of the gas based upon the total cross sectional area of the bed, g./sq. cm. hr.
G_M = superficial molal velocity of the gas based upon the total cross sectional area of the bed, g.-moles/sq. cm. hr.
h_G = gas phase heat transfer coefficient, cal./sq. cm. hr. °K.
j_D = mass transfer number, dimensionless
j_H = heat transfer number, dimensionless
k_t = gas thermal conductivity, cal./sq. cm. hr. °K.
k = reaction rate constant, g.-moles/hr. sq. cm. atm.^{2}
k_G = gas phase mass transfer coefficient, g.-moles/sq. cm. hr.
n = constant
p = partial pressure, atm.
p_f = pressure factor, defined as the logarithmic mean value of the partial pressure over the boundary limits of the gas film, atm.
N_{Pr} = Prandtl number
r_m = rate of reaction per unit weight of catalyst, g.-moles/hr. g. catalyst
R = ideal gas constant, cal./g.-mole °K.
N_{Re} = Reynolds number, $\left(\frac{D_p G_m}{\mu}\right)$, dimensionless
N_{Sc} = Schmidt number
T = temperature, °K.
W = weight of catalyst, g.
x = conversion, g.-moles converted/g.-mole of entering feed

Greek Letters

β = heat transfer group [see Equation (5b)], °K. sq. cm. hr. cm.$^{-0.3}$
γ = mass transfer group [see Equation (4b)], atm. sq. cm. hr. cm.$^{-0.3}$
ΔH = heat of reaction, cal./g.-mole
μ = gas viscosity, poise or g./cm. sec.
ρ_g = average density of the gas phase, g./cc.
ϕ = particle shape factor as defined by Gamson (*15*), equal to the ratio of actual external surface area available for mass transfer to the total external surface area, dimensionless

Subscripts

B = bulk gas phase
f = average film characteristic
i = component i
m = mass basis
M = mole basis
S = catalyst surface

LITERATURE CITED

1. Bar-Ilan, M., and W. Resnick, *Ind. Eng. Chem.*, **49**, 313 (1957).
2. Baumister, E. B., and C. O. Bennett, *A.I.Ch.E. Journal*, **4**, 69 (1958).
3. Beeck, O., *Disc. Faraday Soc.*, **8**, 118 (1950).
4. Benesi, H. A., R. U. Bonner, and C. F. Lee, *Anal. Chem.*, **27**, 1963 (1955).
5. Carberry, J. J., *A.I.Ch.E. Journal*, **6**, 460 (1960).
6. *Ibid.*, **7**, 350 (1961).
7. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).
8. Chu, J. C., J. Kalil, and W. A. Wetteroth, *Chem. Eng. Progr.*, **49**, 141 (1953).
9. Denton, W. H., "Institute of Mechanical Engineers and American Society of Mechanical Engineers' Proc., General Discussion of Heat Transfer," p. 370-386, Inst. Mech. Engrs., London, England (1951).
10. Eley, D. D., "Catalysis," Vol. 3, p. 49, Reinhold, New York (1955).
11. Eyring, H., C. B. Colburn, and B. J. Zwolinski, *Disc. Faraday Soc.*, **8**, 39 (1950).
12. Eichhorn, J., and R. R. White, *Chem. Eng. Progr. Symposium Series No. 4*, **11** (1951).
13. Foss, T. G., and H. Eyring, *J. Phys. Chem.*, **62**, 103 (1958).
14. Frank-Kamenetskii, D. A., "Diffusion and Heat Exchange in Chemical Kinetics," Princeton University Press, Princeton, New Jersey (1955).
15. Gamson, B. W., *Chem. Eng. Progr.*, **47**, 19 (1951).
16. Fulton, J. W., Ph.D. thesis, Univ. Oklahoma, Norman, Oklahoma (1964).
17. Glaser, M. B., and George Thodos, *A.I.Ch.E. Journal*, **4**, 63 (1958).
18. Hoelscher, H. E., *ibid.*, p. 300.
19. Hougen, O. A., *Ind. Eng. Chem.*, **53**, 509 (1961).

20. ———, and K. M. Watson, "Chemical Process Principles. Part III," Wiley, New York (1957).
21. Hurt, D. M., *Ind. Eng. Chem.*, **35**, 522 (1943).
22. Jenkins, G. I., and E. Rideal, *J. Chem. Soc. (London)*, **158**, 2490 (1955).
23. Kusik, C. L., and J. Happel, *Ind. Eng. Chem. Fundamentals*, **1**, 163 (1962).
24. Laidler, K. J., and R. E. Townshend, *Trans. Faraday Soc.*, **57**, 1590 (1961).
25. Lapidus, L., and M. L. McGuire, paper presented at A.I.Ch.E. Fifty-Sixth Annual Meeting, Houston, Texas (December, 1963).
26. Levenspiel, O., "Chemical Reaction Kinetics," Wiley, New York (1962).
27. Liu, S-L., and N. R. Amundson, *Ind. Eng. Chem. Fundamentals*, **2**, 183 (1963).
28. Masamune, S., and J. M. Smith, *ibid.*, p. 136.
29. Norris, T., M.S. thesis, Univ. Oklahoma, Norman, Oklahoma (1957).
30. Park, W. H., Ph.D. thesis, Univ. Minnesota, Minneapolis, Minnesota (1960).
31. Ostergaard, K., *Chem. Eng. Sci.*, **18**, 259 (1963).
32. Pauls, A. C., E. W. Comings, and J. M. Smith, *A.I.Ch.E. Journal* **5**, 453 (1959).
33. Pfeffer, Robert, and John Happel, *A.I.Ch.E. Journal*, **10**, No. 5, 605 (1964).
34. Prater, C. D., *Chem. Eng. Sci.*, **8**, 284 (1958).
35. Ramaswami, D., Ph.D. thesis, Univ. Wisconsin, Madison, Wisconsin (1961).
36. Resnick, W., and R. R. White, *Chem. Eng. Progr.*, **45**, 377 (1949).
37. Rosner, D. E., *A.I.Ch.E. Journal*, **9**, 321 (1963).
38. Satterfield, C. N., and H. Resnick, *Chem. Eng. Progr.*, **50**, 504 (1954).
39. Satterfield, C. N., and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley Publishing Co. Reading, Massachusetts (1960).
40. Skinner, J. L., Ph.D. thesis, Univ. Oklahoma, Norman, Oklahoma (1962).
41. Smith, J. M., "Chemical Engineering Kinetics," McGraw-Hill, New York (1956).
42. Smith, R. K., and A. B. Metzner, *A.C.S. 38th National Colloid Symposium*, June 11-13, 1964, Austin, Texas.
43. Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).
44. Tinkler, J. D., and A. B. Metzner, *ibid.*, **53**, 663 (1961).
45. Twigg, G. H., *Disc. Faraday Soc.*, **8**, 152 (1950).
46. von Rosenberg, D. U., P. L. Durrill, and E. H. Spencer, *Brit. Chem. Eng.*, 320 (March, 1962).
47. Weisz, P. B., and J. S. Hicks, *Chem. Eng. Sci.*, **17**, 265 (1962).

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Forced Convection Mass Transfer:

Part I. Effect of Turbulence Level on Mass Transfer through Boundary Layers with a Small Favorable Pressure Gradient

DAVID G. THOMAS

Oak Ridge National Laboratory, Oak Ridge, Tennessee

The effect of free stream turbulence level on forced convection through laminar and turbulent boundary layers on a flat plate was studied in a wind tunnel with a small but nonzero favorable pressure gradient by means of the naphthalene sublimation technique.

With the small favorable pressure gradient used in this study, the rate of forced convection through laminar boundary layers agreed with Polhausen's theoretical equation for turbulence levels less than 2.8% but increased in a regular fashion for turbulence levels greater than 2.8% and was almost tripled at a free stream turbulence level of 11%. There was no evidence of an interaction between pressure gradient and turbulence level which would produce disproportionate effects on the rate of forced convection through laminar boundary layers. Substantially no effect of turbulence level on forced convection through turbulent boundary layers was observed for turbulence levels up to 7%.

The subject of forced convection through boundary layers on flat plates has been extensively studied, and the broad outlines are well known (*13, 14, 15*). When the partial pressure or concentration differences causing mass transfer are sufficiently small that the velocity normal to the surface can be neglected, the forced convection heat and mass transfer relations are identical, provided the appropriate form of the Stanton number is used and the Prandtl and Schmidt numbers are interchanged. However, there are some notable details which remain unresolved. Among these are the combined effects of turbulence level and pressure gradient on forced convection through laminar and turbulent boundary layers and to a lesser extent the effect of the value of the Prandtl (or Schmidt) number on the rate of forced convection through turbulent boundary layers. In general, the Stanton number is proportional to the $-\frac{1}{2}$ power of the Prandtl number for values of the Prandtl number near unity, to the $-2/3$ power for values from 10 to 100, and to the $-3/4$ power for very large Prandtl or Schmidt numbers (*15*).

Despite numerous investigations of forced convection through boundary layers (*11, 13*), it was not until the studies of Kestin et al. (*1, 12*) that conclusive evidence was presented showing that the coefficient of heat transfer