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Study on the Pulse Reaction Technique

V. Pulse Reaction Kinetics Coupled with an Irreversibly Adsorbed Reactant

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The theoretical analysis has been made in order to clarify the pulse reaction kinetics coupled with an irreversibly adsorbed reactant. Some of the results were significantly different from those with the reversible adsorption. The conversion is not in agreement with that in the continuous flow technique, even when the contact time is reduced to infinitely small. In a special case, a finite conversion is possible even at an infinitely small contact time. The effect of the pulse width was quite remarkable. The conversion is equivalent to that in the continuous flow technique at a sufficiently large pulse width and increases with a decrease in the pulse width. And at a sufficiently small pulse width, the conversion is determined only by the adsorption capacity of the whole catalyst in the reactor. Some of the results were verified by the published data.

Applications to the kinetic study, i.e., the method to obtain the surface reaction rate constant and the site density separately, and to the mechanistic study were proposed and applied to the dehydration of alcohols.

It is well known that the results obtained with the pulse technique, sometimes, are significantly different from those obtained with the continuous flow technique. The authors made the theoretical analyses of the pulse reaction kinetics in the case of the Henry isotherm (*1*, *2*), of the Langmuir isotherm with not too large adsorption equilibrium constant (*3*), and of the Langmuir isotherm with much larger adsorption equilibrium constant (*4*). It was clarified that the difference between the two techniques mainly arises from the chromatographic separation between the components in the catalyst bed and from the lowering of the concentration due to the broadening of the pulse. The effect of these factors was found to depend on the pulse width, that is, the time required for the pulse to pass through an inlet of the catalyst bed. The results in the pulse technique get closer to those in the continuous flow technique with an increase in the pulse width. When the pulse width is large enough, the pulse technique gives the same results as those in the continuous flow technique, because the continuous flow technique corresponds to the pulse technique with an infinite pulse width. Blanton, Merill, and Byers (*5*) measured the rate parameters of nonlinear reactions by using significantly broadened pulse. Another way to reduce the difference between the two techniques is to reduce the contact time. Toyota and Echigoya (*6*) compared the results from the two techniques for the dehydrogenation of cyclohexane and the hydrogenation of benzene and found that the good agreement could be obtained if the catalyst volume was small enough.

These theoretical predictions, however, cannot be applied to all the reactions. All of the theoretical analyses up to date were based on the assumption of the reversible adsorption. The pulse reaction kinetics coupled with an irreversibly adsorbed reactant may be significantly different from that with the reversible adsorption. Bett and Hall (7) found in the dehydration of 2-butanol that the plot of the conversion against the reciprocal flow rate did not extrapolate to the origin at an infinite flow rate. The authors also found the similar results in the dehydration of alcohols (*8*, *9*). The rate of olefin formation was independent of the flow rate of the carrier gas, and the conversion was independent of the temperature in the low temperature region. The order of these reactions may be zero in the reactant pressure. Some workers theoretically analyzed the pulse reaction kinetics of the zero-order reaction (*6*, *12*) on the basis of some assumptions, such as negligible effects of the axial dispersion and of the mass transfer registances from the gas phase to the catalyst surface, and linear adsorption isotherm (Henry isotherm) instead of more actual isotherm. The effect of these factors may be large in the pulse technique. It would be desirable to clarify the pulse reaction kinetics including all of these terms. But it is difficult to take all of these terms into consideration. The present authors have payed attention to the pulse reaction kinetics on the basis of more actual adsorption isotherm.

In the present study, one more and important type of adsorption has been treated, that is, the theoretical analysis has been made in order to clarify the pulse reaction kinetics coupled with an irreversibly adsorbed reactant, and some applications to the kinetic study and to the mechanistic study have been demonstrated.

Nomenclature

C	Concentration of reactant in gas phase (mol/cm^3 of bed)
C_0	Maximum concentration of inlet pulse (mol/cm^3 of bed)
F	Flow rate of carrier gas (cm^3/sec)
k	Surface reaction rate constant (1/sec)
q	Concentration of adsorbed reactant (mol/cm^3 of bed)
q_s	Site density (mol/cm^3 of bed)
t	Time since pulse is introduced (sec)
t_d	Width of disappeared part of pulse (sec)
t_0	Pulse width (sec)
u	Linear velocity of carrier gas (cm/sec)
V	Volume of catalyst bed (cm^3)
X	Conversion
z	Distance from the inlet (cm)
θ	Contact time (sec)
Ω	Amount of inlet pulse, FC_0t_0 (mol)

THEORETICAL ANALYSIS

Theoretical analysis was made on the basis of the following reaction model:

$$A_g \rightarrow (A)_{ad} \rightarrow B_g, \tag{1}$$

where A_g and B_g are the reactant and the product in the gas phase, and $(A)_{ad}$ is the adsorbed reactant on the surface.

1. The first step is the adsorption of the reactant, and its rate is sufficiently fast, so that the surface is completely covered by the reactant if only the reactant is present in the gas phase. The rate of the reverse direction, i.e., the desorption of the reactant, can be neglected.
2. The second step is the surface reaction of the adsorbed reactant to the gas phase product. Strictly speaking, the second step should be divided into two steps: the surface reaction of the adsorbed reactant to the adsorbed product, and the desorption of the product. But the latter can be neglected, if its rate is fast enough. The reverse reaction, i.e., the reaction of the gas phase product to the adsorbed reactant can be neglected.

Further, the following were assumed: the substance in the gas phase moves as a plug flow with a linear velocity of u, and the influence of the mass transfer onto the catalyst surface is negligible. The effect of the latter can be estimated from the effect of the particle size of the catalyst and can be neglected when the particle size is small enough. The effect of the former can be neglected when the pulse width is much larger than that of the dispersed part due to the axial dispersion. According to the above-mentioned model and assumptions, the basic equations expressing the mass balance is given as follows:

$$\frac{\partial q}{\partial t} + \frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial z} - kq, \tag{2}$$

$$q = q_s \text{ when } C > 0. \tag{3}$$

The initial condition is evident, because no substances are present before the introduction of the pulse.

$$C = q = 0, \text{ when } t = 0. \tag{4}$$

The boundary condition at the inlet of the catalyst bed depends on the shape of the inlet pulse.

$$C = C_0\Phi(t) \tag{5}$$

where $\Phi(t)$ is the shape of inlet pulse and is given as a function of time. For a rectangular pulse,

$$\Phi(t) = 1, \text{ when } t_0 \geq t \geq 0, \tag{6}$$

and

$$\Phi(t) = 0, \text{ when } t > t_0. \tag{7}$$

And for a triangular pulse,

$$\Phi(t) = t/t_0, \text{ when } t_0 \geq t \geq 0, \tag{8}$$

$$\Phi(t) = 2 - (t/t_0), \text{ when } 2t_0 \geq t \geq 0, \tag{9}$$

and

$$\Phi(t) = 0, \text{ when } t > 2t_0. \tag{10}$$

Parameter t_0, pulse width, is determined so that C_0t_0 corresponds to the amount of the inlet pulse.

These equations indicate that the pulse moves through the catalyst bed with the moving velocity of u and that the shape of the pulse does not change except the concentration change due to the reaction and except the disappearance of the pulse at the front of the pulse. According to the above-mentioned model, the molecules at the front of the pulse are all adsorbed and the front of the pulse disappears, because the molecules at the front always come in contact with the fresh surface. By defining dt_d as an increment of the width of the disappeared part necessary to cover the catalyst surface in an increment of the catalyst volume, dV, the following equation is obtained (*4*).

$$q_s\, dV = FC\, dt_d. \tag{11}$$

After the front of the pulse passes through, the surface is completely covered, i.e., $q = q_s$. It follows that Eq. (2) can be reduced to the following one:

$$\left(\frac{\partial C}{\partial \theta}\right)_{t-\theta} = -kq_s. \tag{12}$$

Equation (12) indicates that the concentration decreases according to the same rate expression as in the continuous flow technique.

$$C = C_0\Phi(t - \theta) - kq_s\theta. \tag{13}$$

The width of the disappeared part can be related to the contact time from Eqs. (11) and (13), and the concentration change can be calculated from Eq. (13). It follows that also the conversion can be obtained from these equations.

Rectangular Pulse

The relation between the width of the disappeared part and the contact time can be obtained from Eqs. (6), (7), (11), and (13).

$$t_d = -\frac{1}{k}\ln\left(1 - \frac{kq_s\theta}{C_0}\right), \tag{14}$$

As the amount of the pulse can be expressed by the product of the flow rate of the carrier gas, the concentration, and the pulse width, the conversion is given as follows:

$$X = \frac{kq_s\theta}{C_0} + \frac{1}{kt_0}\left(1 - \frac{kq_s\theta}{C_0}\right)\ln\frac{1}{1 - (kq_s\theta/C_0)}. \tag{15}$$

For a small value of x, the following approximation is useful.

$$\ln\frac{1}{1-x} = x + \frac{x^2}{2}. \tag{16}$$

By substituting Eq. (16) into Eq. (15), and by neglecting the term of the contact time squared, the following equation for a small value of the contact time is obtained.

$$X = \frac{kq_s\theta}{C_0} + \frac{q_s\theta}{C_0t_0}. \tag{17}$$

The contact time can be varied not only by the catalyst volume but also by the flow rate of the carrier gas. When the contact time is varied by the catalyst volume at a constant flow rate, the width and the concentration of the inlet pulse are independent of the contact time. Therefore, Eqs. (15) and (17) can be applied to such a case. On the other hand, when the contact time is varied by the flow rate, the width and the concentration may depend on the flow rate. Therefore Eqs. (15) and (17) must not be used in such a case. When a six-port valve is used to introduce the reactant pulse into the carrier gas stream, the relation between the conversion and the contact time can be obtained in the following manner. The reactant in the sampling part of the six-port valve, as a first approximation, may be transported to the catalyst bed without mixing with the carrier gas. It follows that the initial concentration is independent of the flow rate, but the pulse width is in inverse proportion to the flow rate of the carrier gas. By substituting these relations into Eq. (15), the equation expressing the conversion for such a case is obtained as follows:

$$X = \frac{kq_s\theta}{C_0} + \frac{q_sV}{\Omega}\,\frac{1 - (kq_s\theta/C_0)}{kq_s\theta/C_0}\ln\frac{1}{1 - (kq_s\theta/C_0)} \qquad (18)$$

The approximate equation for a small value of the contact time is obtained by substituting Eq. (16) into Eq. (18).

$$X = \left(1 - \frac{q_sV}{2\Omega}\right)\frac{kq_s\theta}{C_0} + \frac{q_sV}{\Omega}. \qquad (19)$$

Triangular Pulse

In the case of the triangular pulse, both the width of the disappeared part and the conversion cannot be represented by such simple equations as in the case of the rectangular pulse. When $t_0 \geq t_d \geq 0$,

$$\frac{kq_s\theta}{C_0} = \frac{1}{kt_0}\,(e^{-kt_d} + kt_d - 1), \qquad (20)$$

and

$$X = 2\frac{kq_s\theta}{C_0} - \frac{1}{2}\left(\frac{kq_s\theta}{C_0} + \frac{t_d}{t_0}\right)^2 + \left(\frac{t_d}{t_0}\right)^2. \qquad (21)$$

And when $2t_0 \geq t_d \geq t_0$,

$$\frac{kq_s\theta}{C_0} = \frac{1}{kt_0}\,[1 + k(2t_0 - t_d) + (1 - 2e^{kt_0})e^{-kt_d}], \qquad (22)$$

and

$$X = 1 - \frac{1}{2}\left(\frac{kq_s\theta}{C_0} - \frac{2t_0 - t_d}{t_0}\right)^2. \qquad (23)$$

And the conversion for a small value of the contact time is given as follows:

$$X = 2\frac{kq_s\theta}{C_0} + \frac{q_s\theta}{C_0t_0}. \qquad (24)$$

As mentioned above, these equations can be applied when the pulse width is independent of the contact time. In the other case, that is, when the pulse width is in inverse proportion to the flow rate of the carrier gas and the contact time is varied by the flow rate, the term t_0 in Eqs. (20)–(23) should be replaced with $\Omega\theta/VC_0$. And the conversion for a small value of the contact time is given by the following equation:

$$X = 2\frac{kq_s\theta}{C_0}\left(1 - \sqrt{\frac{q_sV}{2\Omega}}\right) + \frac{q_sV}{\Omega}. \qquad (25)$$

RESULTS

Figure 1 shows the relation between the conversion and the contact time for the rectangular pulse in the former case, that

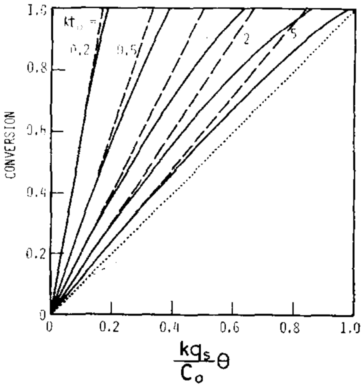

FIG. 1. Relation of the conversion to the contact time for the rectangular pulse, when the contact time is varied by the catalyst volume. (——) from Eq. (15), (- - -) from Eq. (17), (· · ·) continuous flow technique.

is, when the contact time is varied by the catalyst volume at a constant flow rate of the carrier gas. The solid and broken lines were calculated from Eqs. (15) and (17), respectively. The approximate solution, Eq. (17), can be used up to the conversion of 40% within a reasonable error. The exact solution, Eq. (15), also gives essentially a straight line up to the conversion of 70%. Figure 2 shows the relation for the triangular pulse. The solid and broken lines were calculated from Eqs. (20)–(23) and from Eq. (24). The approximate solution holds over the rather smaller range of the conversion than that for the rectangular pulse, but the exact solution gives essentially a straight line up to a considerably large conversion similarly to the case of the rectangular pulse. Thus the relation between the conversion and the contact time in the pulse technique seems to be consistent with the zero-order kinetics in that the relation gives essentially a straight line. However, the reaction rate constant obtained from the slope of the line remarkably depends on the shape of the pulse and on the pulse width, and further it is not identical to that in the continuous flow technique. According to the above-mentioned model, as long as the reactant exists in the gas phase, the surface is completely covered by the reactant, and the reaction rate is equivalent to that in the continuous flow technique. Just after the pulse has left the catalyst bed, the surface is still completely covered. The adsorbed reactant does not desorb, but is converted into the product. It follows that the product can be divided into two parts: one is that formed while the reactant in the gas phase still remains in the catalyst bed, and another is that formed after the pulse has left the bed. The former corresponds to the first term in Eq. (17) which is identical to the conversion in the continuous flow technique, and the latter, to the second term which represents the difference in the conversion between the two techniques. Therefore, the conversion in the pulse technique is always larger than that in the continuous flow technique. And the difference between the two techniques increases with a decrease in the pulse width, as can be seen from Eq. (17).

Figure 3 shows the relation for the rectangular pulse in the latter case, that is, when the contact time is varied by the flow rate of the carrier gas and the pulse width is in inverse proportion to the flow rate. The solid and broken lines were calculated from Eqs. (18) and (19). The approximate solution is useful over a considerably wide range of the conversion, and the exact solution gives essentially a straight line up to a considerably large conversion. The

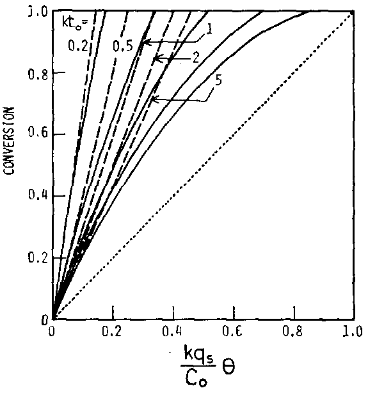

FIG. 2. Relation of the conversion to the contact time for the triangular pulse, when the contact time is varied by the catalyst volume. (——) from Eqs. (20) to (23), (- - -) from Eq. (24), (···) continuous flow technique.

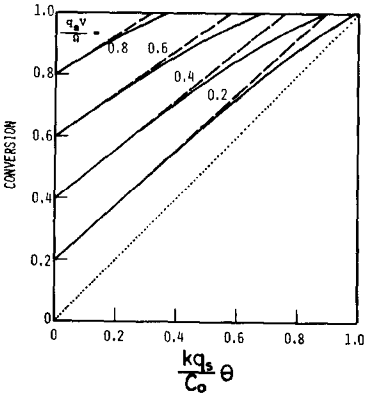

FIG. 3. Relation of the conversion to the contact time for the rectangular pulse, when the contact time is varied by the flow rate of the carrier gas. (——) from Eq. (18), (- - -) from Eq. (19), (···) continuous flow technique.

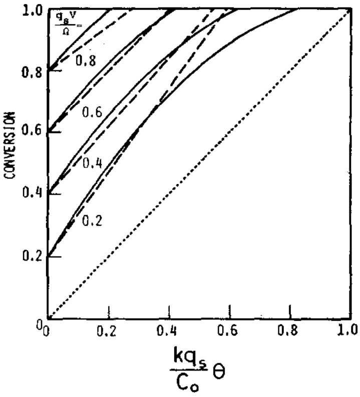

FIG. 4. Relation of the conversion to the contact time for the triangular pulse, when the contact time is varied by the flow rate of the carrier gas. (——) from Eqs. (20) to (23) where t_0 is replaced with $\Omega\theta/VC_0$, (- - -) from Eq. (25), (···) continuous flow technique.

solid lines in Fig. 4 were calculated from Eqs. (20)–(23) where the term t_0 was replaced with $\Omega\theta/VC_0$, and the broken lines from Eq. (25) for the triangular pulse. Up to a considerably large conversion, the approximate solution may be useful, and the exact solution gives essentially a straight line, in the same manner as those for the rectangular pulse. However, the slope of the line remarkably depends on the shape of the inlet pulse and is different from that in the continuous flow technique. The most remarkable difference between the two techniques is that the line from the pulse technique does not pass through the origin. The finite intercept is due to the second term in Eq. (19), which represents the conversion due to the reaction after the pulse has left the catalyst bed and is independent of the flow rate. The first term, which corresponds to the conversion due to the reaction while the pulse still remains in the catalyst bed, differs from the conversion in the continuous flow technique. As mentioned above, the width of the pulse decreases with the passage through the catalyst bed. In the case of the rectangular pulse, the width of the disappeared part for a small contact time is given as follows:

$$t_d = t_0(q_sV/\Omega). \tag{26}$$

When the contact time is reduced by reducing the catalyst volume, t_d can be neglected. On the other hand, when the contact time is varied by the flow rate, the ratio of t_d to t_0 has a constant value independently of the flow rate, or, in other words, the decrease in the pulse width cannot be neglected. Therefore, the slope of the line in Fig. 3 is not identical to that in the continuous flow technique.

DISCUSSION

Effect of Pulse Width

In most of the reactions studied in the present series, the effect of the pulse width was quite remarkable. For example, in the reaction with the Langmuir isotherm (*3*, *4*), the conversion in the pulse technique is identical to that in the continuous flow technique at a sufficiently large pulse width and increases with a decrease in the pulse width. But a conversion cannot exceed a certain limit, that is, the conversion in the first-order reaction. The similar results were obtained in the present paper. In the case of the rectangular pulse, the conversion is identical to that in the flow technique at a sufficiently large pulse width, and increases with a decrease in the pulse width, as shown in Fig. 1. However, as can be seen from Eq. (15), the conversion can easily reach 100%, if only the pulse width is small enough. Though the limit of the conversion is not obvious, the amount of the converted reactant, ΩX, can not exceed a certain limit, as can be seen from the following equation derived from Eq. (17).

$$\Omega X = kq_sVt_0 + q_sV. \tag{27}$$

The first term is due to the reaction while the pulse still remains in the catalyst bed, and the second term, the reaction after the pulse has left the bed. The limit is determined by the second term, because the first term can be neglected when the pulse width is sufficiently small. In the case of the triangular pulse, the conversion at a sufficiently large pulse width and a small contact time is twice as large as that in the continuous flow technique, as can be seen from Eq. (24). However, it is equivalent to the conversion in the continuous flow technique calculated on the basis of the averaged concentration of the triangular pulse, i.e., one half of the maximum concentration. The amount of the converted reactant cannot exceed the same limit as in the rectangular pulse, as can be seen from Eq. (24). It is worth noting that the limit is determined only by the adsorption capacity of the catalyst, but not by the reaction rate. The limit in the reaction with the reversible adsorption is determined by the reaction rate of the extreme case, such as the reaction without the adsorption term in the Langmuir-Hinshelwood mechanism (*3, 4*), and the irreversible reaction in the sort of the reaction, $A \rightleftharpoons R + S$ (*2*).

Conversion versus Contact Time

In the reaction with the Langmuir isotherm (*3, 4*), the conversion is equivalent to that in the continuous flow technique, when the contact time is reduced to infinitely small by reducing the catalyst volume. In the present case, however, the conversion even at an infinitely small contact time is entirely different from that in the continuous flow technique. The plot of the conversion against the contact time gives a straight line in the range of not too large conversion. But the slope of the line is entirely different from that in the continuous flow technique, when the contact time is varied by the catalyst volume, as shown in Figs. 1 and 2. Furthermore, even the finite conversion is possible at an infinitely small contact time which is attained by increasing the flow rate of the carrier gas, as shown in Figs. 3 and 4.

The results obtained by Bett and Hall (*7*) are available to verify the relation of the conversion with the contact time. They studied the dehydration of 2-butanol over a series of hydroxyapatite catalysts by the pulse and the continuous flow techniques. The reaction is in good agreement with the above-mentioned model: the reaction order was zero in alcohol pressure, and the surface adsorbed species seemed not to be in equilibrium with the gas phase. When the contact time is varied by the catalyst volume at a constant flow rate of the carrier gas, a plot of the conversion against the contact time is consistent with the zero-order kinetics, that is, the plot gave a straight line which pass through the origin, similarly to Fig. 1. However, the activation energy from the slope of the plot was 14.5 kcal/mol which was much less than that obtained with the continuous flow technique, 39 kcal/mol. As can be seen from Eqs. (17) and (24), the slope of the plot is given as follows:

$$\frac{dX}{d\theta} = n\frac{kq_s}{C_0} + \frac{q_s}{C_0 t_0}. \tag{28}$$

where $n = 1$ for the rectangular pulse and $n = 2$ for the triangular pulse. The first term has the same activation energy as that of the continuous flow technique, but the second term is independent of the temperature. If the first term is so large that the second term can be neglected, the activation energy is in agreement with that in the continuous flow technique. With an increase in the effect of the second term, the activation energy becomes small. Therefore, the activation energy in the pulse technique is smaller than that in the flow technique, unless the pulse width is large enough.

Figure 5 was obtained by varying the flow rate of the carrier gas at a constant volume of the catalyst bed (*7*). Although the conversion linearly decreased with a decrease in the contact time, the line did not extrapolate through the origin; rather, it passed through the finite intercept. Such a tendency is quite similar to that of the theoretical results shown in Figs. 3 and 4. Bett and Hall presumed that finite intercept was a measure of the number of the active site and that the value of the intercept could reach maximum with the temperature at the point where a "site monolayer" of the reactant was adsorbed. They calculated the site densities of a series of hydroxyapatite catalysts from the intercept at the highest temperature. The site densities thus obtained were in good agreement with those calculated from the steady state flow kinetics using absolute

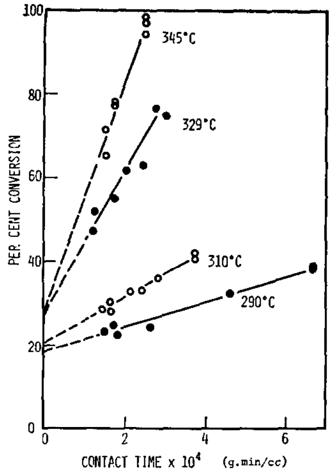

FIG. 5. Relation of the conversion to the contact time in the dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.57), when the contact time is varied by the flow rate of the carrier gas (7).

reaction rate theory and with theoretically expected concentration of surface POH group. Equations (19) and (25) support their presumption: the intercept, or the conversion at an infinite flow rate, is equivalent to q_sV/Ω and therefore the site density, q_s, can be obtained from it. It may be possible that the site density increases with temperature, when the catalyst surface is energetically heterogeneous or when the degree of dehydration of the catalyst surface increases with temperature. It should be emphasized that the intercept of the plot is independent of the shape of the inlet pulse, as can be seen from Eqs. (19) and (25). In other words, the site density can be obtained from the intercept without the precise knowledge of the pulse shape.

The reaction rate also can be calculated from the intercept, X_0, and the slope of the plot of the conversion against the contact time which is varied by the flow rate of the carrier gas, if only the shape of the inlet pulse is known. In the case of the rectangular pulse, the following relations can be obtained from Eq. (19).

$$\frac{dX}{d\theta} = \left(1 - \frac{q_sV}{2\Omega}\right)\frac{kq_s}{C_0}, \qquad (29)$$

and

$$X_0 = q_sV/\Omega. \qquad (30)$$

Therefore,

$$r = kq_s = C_0\frac{dX}{d\theta}\Big/\left(1 - \frac{X_0}{2}\right). \qquad (31)$$

And in the case of the triangular pulse, from Eq. (25),

$$r = C_0\frac{dX}{d\theta}\Big/(2 - \sqrt{2X_0}). \qquad (32)$$

The empty circles in Fig. 6 represent the reaction rate obtained by substituting the slope and the intercept of Fig. 5 into Eqs. (31) and (32), and the solid circles represent the reaction rate obtained with the continuous flow technique by Bett and Hall. The activation energy from the pulse technique agreed well with that from the continuous flow technique, but the absolute value of the reaction rate from the pulse technique was slightly larger than that from the latter. Although the reaction rate from the pulse technique depends on which of the shapes is assumed to calculate the reaction rate, it seems difficult to attribute the difference in the reaction rate to the shape of the inlet pulse. The actual shape of the inlet pulse may not be a good rectangular pulse, because the

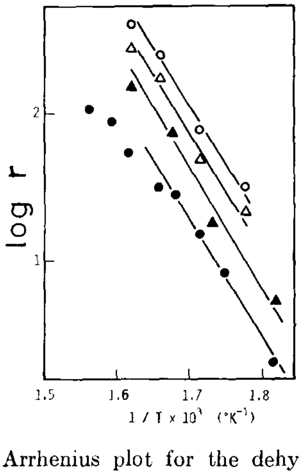

FIG. 6. Arrhenius plot for the dehydration of 2-butanol over a hydroxyapatite catalyst (Ca/P = 1.58). (▲) and (●) continuous flow technique, from Figs. 6 and 7 in ref. 7; (○) and (△) pulse technique, from Eqs. (31) and (32).

leading and the trailing edge may be dispersed in the sampling valve and the pipe line to the catalyst bed. The actual shape may be closer to trapezoid. Then the reaction rate may be expected to lie between the reaction rate based on the rectangular pulse and that on the triangular pulse. The difference in the reaction rate may be due to the difference in the degree of dehydration of the catalyst surface. Bett and Hall reported that the reaction was weakly inhibited by water added into the reactant. In the continuous flow technique, even if water is not involved in the reactant, significant amount of water which is the product of the reaction is adsorbed on the surface. In the pulse technique, however, the surface may be considerably dehydrated, because only purified helium flows through the catalyst bed before the introduction of the small amount of the reactant pulse. It is possible that the inhibition effect of the preadsorbed water is more significant than that of the added water into the reactant.

Application to Kinetic Study

One of the applications is to obtain the same results as those in the continuous flow technique. As can be seen from Fig. 1, it is necessary for such an application that the pulse width is large enough, when the contact time is varied by the catalyst volume. And when the contact time is varied by the flow rate of the carrier gas and the six-port valve is used to introduce the pulse into the carrier gas stream, the ratio of the catalyst volume to the amount of the inlet pulse must be sufficiently small, as can be seen from Fig. 3.

Another and more important application is to obtain the data which cannot be obtained with the continuous flow technique. In the zero-order reaction, the overall reaction rate constant obtained with the continuous flow technique is a product of the site density and the surface reaction rate constant, and it is impossible to measure them separately. On the other hand, the pulse technique may be available for such a purpose. One of the methods is to employ the relation expressed by Eq. (19), as mentioned above on the results shown in Fig. 6. When the contact time is varied by the flow rate and the pulse is introduced by means of a six-port valve, the plot of the conversion against the contact time gives a straight line which passes the finite intercept at zero contact time. The site density can be obtained from the intercept, as shown by Eq. (30), and the surface reaction rate constant can be calculated from the site density and the overall reaction rate constant which can be obtained from the intercept and the slope of the plot, as shown by Eq. (31). However, it requires a special apparatus to vary the flow rate of the carrier gas over a wide range. It is impossible with the conventional apparatus of the pulse technique to vary the flow rate over a wide range, because an increase in the flow rate is accompanied with an increase in the pressure. Furthermore, the dispersion of the pulse in the sampling valve and in the pipe line to the catalyst bed may be more significant than that in the experiment using a microfeeder mentioned below.

In the case of the rectangular pulse, the pulse width can be varied more easily than the catalyst volume and the flow rate of the carrier gas (*10*). The relation between the conversion and the pulse width is given by Eq. (17). The site density can be obtained from the slope of the plot of the conversion against the reciprocal pulse width, and the surface reaction rate constant can be obtained from the ratio of the intercept to the slope. Equation (27) also may be useful: the site density can be obtained from the intercept of the plot of the amount of the converted reactant against the pulse width, and the surface reaction rate constant can be obtained from the ratio of the slope to the intercept. In order to obtain the intercept, the line in the latter plot should be extrapolated to a zero pulse width, while in the former plot, to an infinite pulse width. If the catalyst surface is susceptible to the atmosphere, that is, to whether the catalyst is in the reactant vapor or in the carrier gas, the former plot may be superior to the latter. Furthermore, when the former plot is employed, one should take care not to use so small a pulse width that the width of the dispersed part due to the axial dispersion cannot be neglected.

More simple method is to use Eq. (17) with a constant pulse width. The conversion decreases with a decrease in the temperature, but it does not fall to zero even at sufficiently low temperature; rather it approaches X_0 given by Eq. (30) or by the second term of Eq. (17), because X_0 does not depend on the temperature. The site density can be obtained from X_0, and the surface reaction rate constant can be obtained by substituting X, X_0, and t_0 into the following equation derived from Eq. (17).

$$k = \frac{1}{t_0}\left(\frac{X}{X_0} - 1\right). \qquad (33)$$

Therefore, the site density and the surface reaction rate constant can be obtained, if only the conversion is measured at various temperatures.

Figure 7 shows the results of such an application to the dehydration of 2-propanol on a zinc sulfate catalyst. The catalyst was prepared in the following manner. Guaranteed reagent of zinc sulfate was calcined at 200°C, sifted to 28 ~ 48 mesh after powdering, and dried at 350°C for 2 hr in the stream of nitrogen just before the reaction. The other experimental apparatus and procedures were essentially the same as those in the previous paper (*10*) except that described in the legend of Fig. 7. First of all, the shape of the inlet pulse was measured. 2-Propanol was introduced just before the detector by the aid of a microfeeder. The partial pressure of 2-propanol could be regarded as constant during the time corresponding to the pulse width, and the leading and the trailing edges of the pulse were sufficiently sharp. Secondly, the effect of the axial dispersion was evaluated in the following manner. The reactor packed with inert particles (fused almuina) was installed just before the detector, and the pulse was introduced just before the reactor. The chromatogram thus obtained was essentially the same as that of the inlet pulse mentioned above, or, in other words, the width of dispersed part was sufficiently small compared to the pulse width which was larger than 15 sec. It follows that the pulse could be regarded as a rectangular pulse and Eqs. (17) and (33) can be applied to the present case. It should be noted that the length of the catalyst bed was only a few millimeters, and that the sample inlet was directly connected to the reactor, i.e., the pipe line between the sample inlet and the catalyst bed was composed of a straight pipe with an uniform inside diameter of 4 mm and with a length less than 20 cm.

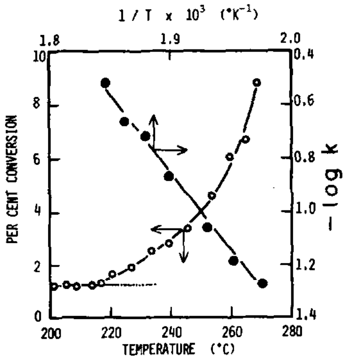

FIG. 7. Effect of the temperature on the dehydration of 2-propanol on a zinc sulfate catalyst. Catalyst, 11 mg; pulse size, 1.24 μmol/sec × 20 sec; carrier gas, N_2 (60 ml/min) dried with silica gel column; chromatographic column, PEG-1500 2 m at 70°C; detector, F.I.D.

Empty circles show the effect of the temperature on the conversion, which was in good agreement with that expected from the theory: the conversion decreased with a decrease in the temperature, but, below 215°C, it had a constant value of 1.24%. The site density obtained from the conversion below 215°C was 0.007 mmole/g, which is in good agreement with the number of the acid site: 0.0048 mEq/g for $H_0 < 3.3$ and 0.0073 mEq/g for $H_0 < 4.8$ (*9*). The solid circles represent the Arrhenius plot of the surface reaction rate constant obtained from Eq. (33). The activation energy was 26.8 kcal/mol, which also is in good agreement with that in the previous paper, 26.1 kcal/mole.

Application to Mechanistic Study

The heterogeneous catalytic reaction is, sometimes, interpreted by either the Langmuir-Hinshelwood mechanism or the Rideal-Eley mechanism. But it is not easy to determine which of the mechanisms can explain the experimental results better. The pulse technique can give some information on that subject.

Figure 8 shows the effect of the pulse width on the amount of ethylene and ethyl ether formed in the dehydration of ethanol on an alumina catalyst. The relation between the amount of ethylene formed and the pulse width was consistent with that expected from Eq. (27). The amount of ethylene formed decreased linearly with a decrease in the pulse width and had a finite intercept at zero pulse width. On the other hand, the amount of ether formed passed through the origin. As mentioned above, the intercept, i.e., the second term of Eq. (27), represents the amount of the product formed after the pulse has left the catalyst bed. It follows that ethyl ether is scarcely formed after the pulse has left the bed, although the significant amount of ethylene is formed even when ethanol does not exist in the gas phase. de Boer and co-workers (*11*) concluded from the kinetic study that the formation of ethyl ether occurred according to the Rideal-Eley mechanism and to the Langmuir-Hinshelwood mechanism simultaneously. As mentioned above, Fig. 8 indicates that the most of ethyl ether is formed only when ethanol exists in the gas phase. In other words, ethyl ether formed according to the Langmuir-Hinshelwood mechanism, i.e., the reaction between the adsorbed alcohols, may be a little.

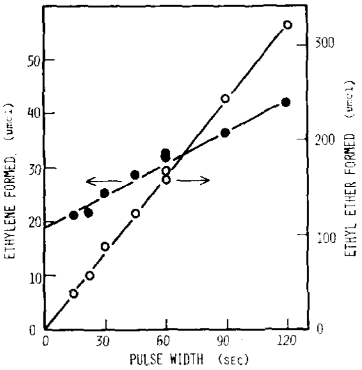

FIG. 8. Effect of the pulse width on the dehydration of ethanol on an alumina catalyst. Catalyst weight, 100 mg; temperature, 280°C; carrier gas, H_2 (50 ml/min); ethanol feed rate, 48.8 μmol/min; chromatographic column, PEG-1500 2 m + LP 2 m at 70°C.

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