Adsorption and Kinetics in a Batch Heterogeneous Catalytic Reactor

The utility of a new dynamic experimental technique is illustrated for the specific case of the vapor phase dehydration of ethanol over a hydrogen ion exchange resin. Adsorbed phase composition data are obtained simultaneously with complete vapor phase information, providing new insight into the catalytic behavior. A mathematical model, based upon Langmuir-Hinshelwood kinetics, comprises simply five first-order ordinary differential equations. The model describes all of the important transient and equilibrium characteristics of the reacting system qualitatively and most quantitatively. Experimental data alone are used to show that the surface reaction is the rate controlling step.

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SCOPE

Experiments, coupled with quantitative theoretical interpretation, are crucial to the characterization of heterogeneous catalysis. The kinetics of catalytic reactions, which often depend heavily on adsorption, are currently studied by a variety of steady state and dynamic techniques. When supplemented by appropriate adsorption data, usually obtained independently, these techniques can lead to a thorough understanding of catalytic processes. It would be valuable to have an experimental method which combines the information potential of a dynamic study with the simplicity of a steady state investigation and which also provides concomitant adsorption information.

This research was directed to the development and application of a batch heterogeneous catalytic reactor in which the adsorption phenomena important to the catalytic reaction can be followed simultaneously with the overall reaction kinetics. The experimental method is described in detail by the authors in a separate publication (1974). The reaction investigated is the vapor phase dehydration of ethanol to diethyl ether with a hydrogen ion exchange resin as the catalyst. A small bucket containing the catalyst is suspended from a calibrated quartz helix within an evacuated, constant volume, isothermal chamber. A measured amount of ethanol is injected into the reaction chamber. Data of total pressure, total adsorption, and vapor phase composition are directly measured as functions of time while the various processes proceed toward their respective equilibria. The adsorbed phase composition is calculated from a material balance. Other derived results are ethanol conversion, the thermodynamic equilibrium constant, and an independent check on the internal consistency of the experiment.

In this paper the technique is illustrated with a detailed analysis of the results of a single experiment. The predictions of a mathematical model are compared to the measured and derived data. The findings are interpreted in the context of a variety of previous related studies from this and other laboratories.

CONCLUSIONS AND SIGNIFICANCE

A new experimental technique has been developed for the study of heterogeneous catalytic reactions. Although the experiment described here was continued for almost 15,000 min., data are presented only up to 6000 min. and equilibrium was achieved in 3000 min. (about 2 days). The really strong transients were over within 500 min. The results of the experiment proved to be consistent with all that is known about rates, equilibria, and catalytic character from previous work and provided some new understanding.

The mathematical model consisted of five first-order ordinary differential equations which could be solved routinely by a common computer library program. The simplicity of mathematical analysis is one of the most beneficial aspects of this experimental method. The rates of adsorption and reaction processes were described by an unsteady state variation of Langmuir-Hinshelwood kinetics. Correlations with temperature of the necessary rate and equilibrium constants for adsorption and reaction are presented. The model is shown to be successful in describing all characteristics of the reaction system in a physically significant way, with one exception. The monolayer adsorption limitation of the Langmuir theory precludes proper accounting of multilayer adsorption of water. However, the rate of the overall reaction is still accurately predicted, indicating that only the first layer of adsorbed water affects the catalytic events.

The initiation of the experiment was accompanied by a sharp catalyst temperature rise resulting from the rapid exothermic adsorption of ethanol. This phenomenon subsided after about 100 min. and affected the results only slightly. For the first time in work on ethanol dehydration in this laboratory, evidence of a possible mass transfer limitation has been observed. At the very beginning of the experiment, the diffusion of unadsorbed reaction product ethyl ether out of the catalyst bead seems to be impeded by the shrunken state of the catalyst, due to the previous evacuation. This effect is alleviated soon as the catalyst rapidly swells with the adsorbed ethanol and

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water. Thus these two transport effects are of little consequence, and the interesting transient behavior observed is clearly the result of interaction between adsorption and surface reaction processes.

The dynamic data of this work are compared to the equilibrium adsorption data and correlations of Herlihy (1968). It is evident that, although overall system equilibrium is not established until 3000 min., the adsorbed phase composition is in equilibrium with the existing vapor phase at any time after 60 min. This then is direct experimental evidence that the adsorption processes are rapid and that the surface reaction is the rate controlling step. This conclusion had been reached before by deduction and inference. But such direct information as this demonstrates the value of an experiment which allows one to observe reaction and adsorption processes simultaneously.

NATURE OF REACTION

The vapor phase dehydration of ethanol to diethyl ether is effectively catalyzed by Dowex 50-X8, a sulfonated copolymer of styrene and divinylbenzene in the hydrogen ion form.

$$2C_2H_5OH \overset{H^+}{=} (C_2H_5)_2O + H_2O \tag{1}$$

Extensive steady state kinetic studies have been performed by Mullarkey (1970) at 90°C, Kabel (1961) at 120°C, and Stula (1972) at 140°C. All results have been successfully correlated by a Langmuir-Hinshelwood rate expression based on the postulates that the reaction occurs by a dual site mechanism and that the surface reaction is the rate controlling step. More sophisticated statistical analyses of the data of Kabel have been performed by Kittrell et al. (1965) and Lapidus and Peterson (1965). The latter work has been commented on by Kabel (1968) and by Mezaki and Kittrell (1968). These results also support the two postulates above. Gates and Johanson (1969), by conducting reaction rate experiments with varying amounts of the hydrogen ions on the catalyst replaced with sodium or lithium ions, provided more evidence that two adjacently adsorbed alcohol molecules are necessary for the reaction to proceed. The other postulate, that the adsorption processes are much faster than the surface reaction, has been supported in investigations of reactor dynamics by Lehr et al. (1968), by Denis and Kabel (1970a, 1970b), and by independent adsorption rate studies by Kabel (1961) and Lehr (1966). Kabel and Johanson (1962) compared the Langmuir equilibrium adsorption constants in their rate equation with those determined independently from pure component adsorption studies and found definite order of magnitude agreement. Thus one gains confidence in the physical picture represented by the Langmuir-Hinshelwood rate equation for this reaction system. All of these studies show water and ethanol to be strongly adsorbed and give no indication that diethyl ether is adsorbed at all. There is no question that water can be adsorbed in multilayers (contrary to the Langmuir adsorption theory) as shown by Waxman et al. (1953) in two adjacent papers. On the other hand, ethanol appears to be adsorbed only to monolayer extent (Kabel, 1961; Herlihy, 1968). All of the above investigations have been free of mass and heat transfer complications. The same is largely true of the present work; however, shortlived effects are noted and commented on at two points in this paper. Much more extensive background information and additional details of all aspects of this work are given by Hsu (1972).

MATHEMATICAL MODEL

From the above physical picture of the reaction system, a quantitative theory can be developed to predict the data to be obtained. Following the usual Langmuir-Hinshelwood kinetics, the following equations represent the adsorption-desorption processes and the surface reaction.

$$A + s = As \tag{2}$$

$$2As = Ws + E + s \tag{3}$$

$$Ws = W + s \tag{4}$$

From this reaction path, rate equations can be written for the three processes.

$$\rho_A = \kappa_A P_A \theta_V - \kappa_{-A} \theta_A \tag{5}$$

$$r_A = k_A \theta_A{}^2 - k_{-A} \theta_W \theta_V P_E \tag{6}$$

$$\rho_W = \kappa_W P_W \theta_V - \kappa_{-W} \theta_W \tag{7}$$

From the Langmuir limitation of monolayer coverage, the fraction of catalytic sites which are vacant is related to the fractional coverages by

$$\theta_V = 1 - \theta_A - \theta_W \tag{8}$$

The model also involves material balances on the vapor and adsorbed phases. Any component i moves between the two phases by the adsorption and desorption processes and is removed from or added to the adsorbed phase by the reaction process. Hence, the rigorous material balances are, for the vapor phase

$$\frac{1}{W_c} \frac{dn_i}{dt} = -\rho_i \tag{9}$$

and for the adsorbed phase

$$\frac{dy_i}{dt} = \rho_i - r_i \tag{10}$$

Because the numerical values of the equilibrium adsorption constants to be used in the model have been determined by classic Langmuir-Hinshelwood correlation of steady state kinetic data, they will be inconsistent with the description embodied in Equations (9) and (10), and the reaction must be treated as if it occurred in the vapor. This point is not obvious or briefly justifiable, but it is explained fully by Denis and Kabel (1970a).

Thus the adsorbed phase material balances for alcohol and water become

$$\frac{dy_A}{dt} = \rho_A \tag{11}$$

$$\frac{dy_W}{dt} = \rho_W \tag{12}$$

For alcohol, water, and ether in the vapor phase, respectively,

$$\frac{1}{W_c} \frac{dn_A}{dt} = -\rho_A - r_A \tag{13}$$

$$\frac{1}{W_c} \frac{dn_W}{dt} = -\rho_W + \tfrac{1}{2} r_A \tag{14}$$

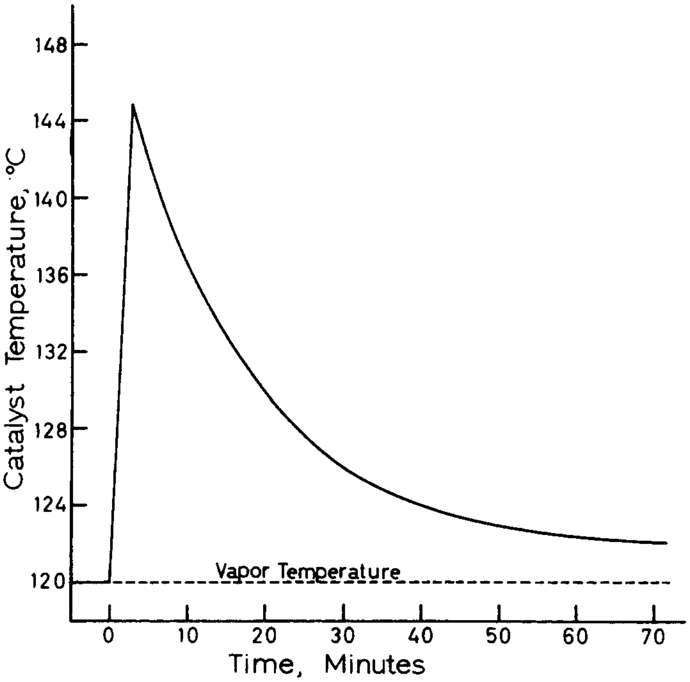

Fig. 1. Temperature at center of catalyst bed.

$$\frac{1}{W_c}\frac{dn_E}{dt} = \tfrac{1}{2} r_A \tag{15}$$

Assuming an ideal vapor phase of constant temperature and volume, Equations (13), (14), and (15) become

$$\frac{V}{W_c RT}\frac{dP_A}{dt} = -\rho_A - r_A \tag{16}$$

$$\frac{V}{W_c RT}\frac{dP_W}{dt} = -\rho_W + \tfrac{1}{2} r_A \tag{17}$$

$$\frac{V}{W_c RT}\frac{dP_E}{dt} = \tfrac{1}{2} r_A \tag{18}$$

The five Equations (11), (12), (16), (17), and (18) are seen to be available to determine the five unknowns y_A, y_W, P_A, P_W, and P_E. Since $\theta_i = y_i/y_m$, the incorporation of Equations (5) through (8) to express the adsorption and reaction rates introduces no new unknowns. The initial conditions are $P_{A0} = n_{A0}RT/V$, $P_{E0} = P_{W0} = 0$, and $y_{A0} = y_{W0} = 0$.

Thermal Transient

To solve Equations (11), (12), (16), (17) and (18), one needs to know n_{A0}, y_m, V, W_c, R, T, and T_c. Numerical values for the first five are constant throughout the experiment and are given in the notation. The reaction chamber and the vapor within it were easily maintained at the desired temperature of $T = 120°C$. However, the adsorption of ethanol is accompanied by a liberation of about 16,000 kcal/mol (Kabel and Johanson, 1962). Thus the abrupt contacting of ethanol vapor with the thoroughly evacuated catalyst at the start of the experiment produced a tremendous thermal pulse in the catalyst which could not be relieved immediately by the mild agitation in the system. Measurement or prediction of the catalyst temperature during the course of the experiment would be difficult at best. So in a separate experiment a thermometer was placed in the bucket and the mercury bulb (0.275 cm^3) was surrounded by catalyst. The system was evacuated as in a real kinetic experiment, alcohol was added, and temperature was observed as a function of time. The amounts of catalyst and alcohol added were kept quite close to the amounts in the actual kinetic experiment. This experiment was repeated with a thermometer of much smaller bulb volume (0.0754 cm^3). To eliminate the effect of the thermometer presence, the two temperatures at each time were linearly extrapolated to zero bulb volume. The resulting profile, Figure 1, should approximate the maximum temperatures which would occur in the center of the catalyst bed since there is no significant mass transfer resistance. It was shown by calculation that the temperature gradient within a catalyst particle would be negligible. Thus the maximum bed temperatures were arbitrarily averaged with 120°C to obtain effective temperature T_c data as a function of time, which could be used directly in calculations.

This method of allowing for nonisothermal effects applies, of course, only to the comparison with a particular experiment. The problem is simpler if an isothermal investigation is accomplished. If the thermal effects must also be predicted, then an energy balance must be added to the model equations. This still does not complicate the model significantly unless one wishes to allow for spatial gradients. Likewise, for comparison to a particular experiment, one must allow in the predictions for the material removed from the reactor for chromatographic analysis. The effect is quite small but sometimes noticeable. All computed results in this paper allow for sampling.

Rate and Equilibrium Constants

To solve the model it is also necessary to have numerical values as functions of temperature of the set of six independent rate coefficients, κ_A, κ_{-A}, k_A, k_{-A}, κ_W, and κ_{-W}, in Equations (5), (6), and (7). From the following relationships a different set can be obtained, namely, κ_{-A}, κ_{-W}, k_A, K_A, K_W, and K_{eq}.

$$K_A = \kappa_A/\kappa_{-A} \tag{19}$$

$$K_W = \kappa_W/\kappa_{-W} \tag{20}$$

$$K_{eq} = k_A K_A^2/k_{-A} K_W \tag{21}$$

The thermodynamic equilibrium constant K_{eq} was accurately determined by Kabel and Johanson (1961, 1962). For use in the present work, their results were expressed as

$$\log_{10} K_{eq} = 824.75/\mathrm{T} - 0.6964 \tag{22}$$

A superior correlation is now available (Hawes and Kabel, 1968). For k_A, K_A, and K_W the authors have used the results of Mullarkey (1970), Stula (1972), and Kabel (1961) to obtain the following correlating equations:

$$\log_{10} k_A = -\frac{5866}{T_c} + 11.28 \tag{23}$$

$$\log_{10} K_A = \frac{2083}{T_c} - 4.767 \tag{24}$$

$$\log_{10} K_W = \frac{2916}{T_c} - 6.575 \tag{25}$$

A more definitive paper on the correlation of steady state kinetic data for this reaction over a range of temperature will appear later. Values of κ_{-A} and κ_{-W} were obtained by Hsu (1972) by recorrelating the transient adsorption data of Kabel (1961) in the light of new information.

$$\log_{10} \kappa_{-A} = -\frac{2416}{T_c} + 2.186 \tag{26}$$

$$\log_{10} \kappa_{-W} = -\frac{2626}{T_c} + 3.295 \tag{27}$$

It is seen that the model comprises simply a set of first-order ordinary differential equations. The equations were solved with the IBM system 360 Continuous System Modeling Program, which is described in detail in IBM publications H20-0240-2 and H20-0367-2. One of the major benefits of this experimental method is that a simulation can be routinely computed regardless of the complexity of the reaction and adsorption rate expressions.

VAPOR PHASE RESULTS

A good overall view of the experiment is provided by Figure 2, in which the partial pressures of ethanol, water, and diethyl ether are shown as functions of time for the duration of the experiment. The ethanol partial pressure drops off rapidly due to adsorption and then continues to decrease as the reaction proceeds. Ether and water build up as they are produced by reaction. Since ether is not adsorbed, all that is formed will appear in the vapor, whereas some of the water formed will remain adsorbed. Thus the ether data are higher than those for water. Although the experiment lasted 6000 min., it is clear that equilibrium was achieved in half that time and that the very rapid changes were confined to the first 500 min. During this time, when the total pressure was highest and the proportion of alcohol in the vapor was the greatest, the vapor phase sampling and analysis was most reliable. Thus the data obtained are the most accurate during the most interesting part of the experiment. In most of the figures that follow, just this early period will be inspected. The agreement between prediction and experiment is seen to be quite good, especially early and late in the run. This is understandable since the constants in the model were originally determined from initial adsorption and reaction rate data or from equilibrium data. The greatest discrepancies, though still not severe, are seen to occur in the high conversion, nonequilibrium region around 1500 min. In the previous paper (Hsu and Kabel, 1973), it is shown how any of the data at or beyond 3000 min. can be used to obtain the thermodynamic equilibrium constant. The agreement with Equation (22) is excellent.

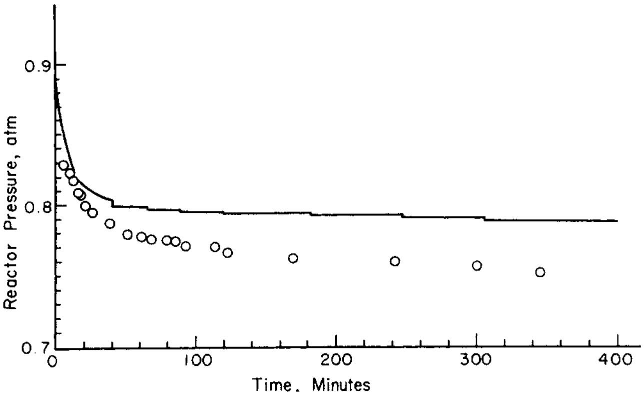

Fig. 4. Total pressure.

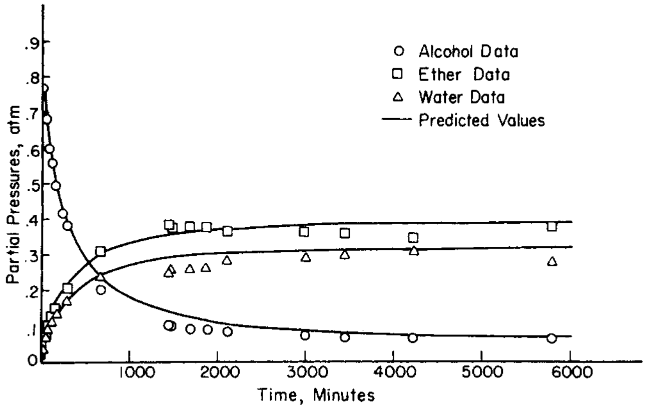

Fig. 2. Vapor phase composition.

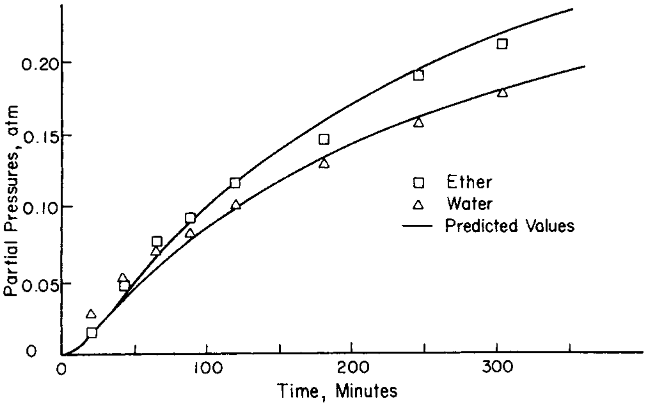

Fig. 3. Early ether and water transients in vapor.

Figure 3 is an expanded graph of the ether and water curves from the early portion of Figure 2. Here one gets a better feeling for the comparisons in the strong transient period. The ethanol results are not shown here to avoid graphical complexity, but the agreement between data and prediction is quite comparable to that exhibited by ether and water. The interesting feature here is that the water data are higher initially than the ether data. It was expected that the ether data would always be higher, as predicted by the model. The early opposite effect can be explained by two experimental phenomena, the initial thermal pulse and an initial resistance to ether diffusion out of the catalyst particle. Hawes and Kabel (1968) and Stula (1972) have shown that ethanol dehydration to ethylene occurs on this catalyst at temperatures above 140°C. Figure 1 shows that such conditions existed in the reactor for about 5 min. Thus there was a time when water was being produced by two reactions, and ether by only one. Also the chromatographic analysis used in this work did not separate ethylene from the other components. In fact, all ethylene formed would be interpreted as water since both had identical retention times. Secondly, the diffusion coefficients of water, ethanol, and ethyl ether in pure dry polystyrene are estimated by the method of Duda and Vrentas (1970) to be 7.8×10^{-6}, 5.2×10^{-8}, 2.2×10^{-9} cm^2/s, respectively. The catalyst is not pure polystyrene, of course, and it is dry only at the beginning of the experiment. When moist it expands considerably. Still these data indicate that ether, once formed, might diffuse out about 3500 times more slowly than water. It is known from previous experience in this laboratory that water diffuses readily through completely evacuated, shrunken catalyst and that ethanol is moderately restricted in this extreme case. Ether should be more limited still. As time goes on, however, increasing adsorption causes the catalyst to swell, which relieves the mass transfer limitation. It is seen from Figure 3 that ether overtakes water at about 60 min. and displays the expected behavior thereafter.

Also measured directly in the vapor phase is the total pressure, shown on Figure 4. The pressure drops rapidly at the beginning due to ethanol adsorption. Although the reaction is equimolar, see Equation (1), some of the water produced does not return to the vapor. What is more, water is more strongly adsorbed than ethanol on

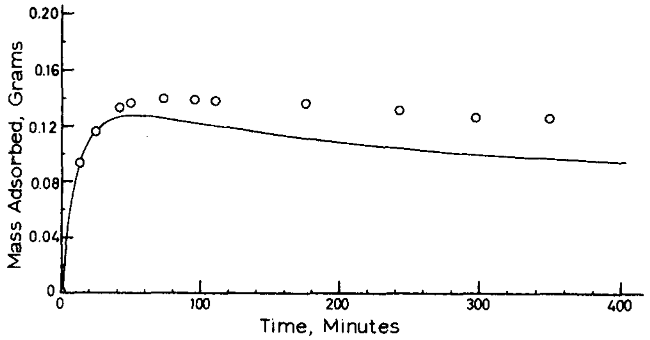

Fig. 5. Total adsorption weight.

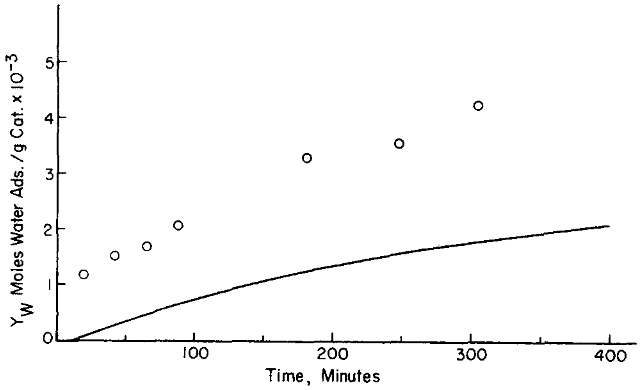

Fig. 6. Water adsorption.

a molar basis. Thus the pressure continues to drop until equilibrium is achieved.

The correction for sampling is most pronounced in this case and is evident in the predicted curve and also, upon close inspection, in the corresponding adjacent experimental points. Without such expanded coordinates, it is too small to be noticed. The agreement between prediction and experiment is not so good here although the expanded ordinate exaggerates the magnitude of the deviation, perhaps. The gap is continued to the end of the experiment. The reason for the discrepancy is thought to be that water is adsorbed in multilayers whereas the model invokes the Langmuir isotherm which implies monolayer adsorption only. Thus less water is found in the vapor phase than the model predicts and the actual total pressure is accordingly lower. Figures 2 and 3 do not bear this hypothesis out fully, but these data depend upon the vapor phase analysis which is the most difficult aspect of the experiment. A variety of very minor discrepancies between experiment and theory are considered in detail by Hsu (1972).

ADSORBED PHASE RESULTS

The final directly measured quantity is the total amount adsorbed, shown in Figure 5. It rises initially with the rapid ethanol adsorption but soon passes through a maximum and declines slowly to equilibrium. As the reaction takes place, each adsorbed pair of ethanol molecules is converted to one molecule each of ether and water. Since ether is not adsorbed and water has a much lower molecular weight than ethanol, the effect of continuing reaction is to decrease the total mass adsorbed even though water is more strongly adsorbed than ethanol on a molar basis. Again a discrepancy between experiment and prediction is seen, and again it is explained by multilayer adsorption of water. That is, more water appears in the adsorbed phase than was predicted by the monolayer theory. The deviations of Figures 4 and 5, which have been attributed to the same phenomenon, can be shown to the consistent by the following calculation. At the 300th min., for example, the difference between predicted and total adsorption on Figure 5 is 0.026 g. Assuming this was all water and using the ideal gas law, the pressure equivalent in this system would be about 0.04 atm. In Figure 4, at the 300th minute, the deviation between the predicted total pressure and the observed datum is 0.034 atm. The difference between 0.04 and 0.034 is within the potential error in pressure measurement, which is estimated to be 0.008 atm. (Hsu, 1972).

Figure 6 shows the amount of water in the adsorbed phase. It is seen to simply increase slowly with time. The amount actually adsorbed is about double the predicted amount. At 300 min. the deviation is 2.15×10^{-3} mol H_2O adsorbed per g catalyst which corresponds to 0.027 g. in weight. This is virtually identical to the 0.026 deviation in the total adsorption case and confirms the hypothesis that the entire deviation was attributable to water.

Figure 7 presents a corollary to the previous observation. That is, the prediction of the amount of alcohol adsorbed is excellent. The data rise sharply with the initial ethanol adsorption, reach a maximum as the adsorption of ethanol is balanced by its removal by reaction, and finally decrease as the alcohol in the system is consumed. Figure 7 displays a somewhat steeper decline from its maximum than Figure 5 because the total adsorption curve is supplemented by the adsorption of water as the quantity of adsorbed alcohol declines. The times of occurrence of the maxima in Figures 5 and 7 are not predicted exactly. These are strongly dependent upon the values of κ_{-A} and κ_{-W}, the least well known parameters in this work. Excellent agreement is easily achieved if desired. However, no adjustments to improve fit have been made in this work in order to retain the maximum physical significance of all parameters used.

INSIGHTS—RATES AND EQUILIBRIA

A derived result which gives good overall perspective on the progress of the reaction is the ethanol conversion. Figure 8 shows this property over the duration of the experiment. The curve is typical of a batch reaction, beginning with a high initial rate and finally leveling off at equilibrium. Not only is the predicted equilibrium conversion of 90% quite close to the experimental value of 91.5%, but so is the rate by which the reaction proceeds well characterized over the entire range of the data. The single substantial weakness of the model, the inability to account properly for all of the adsorbed water, does not seem to restrict the ability of the model to quantify

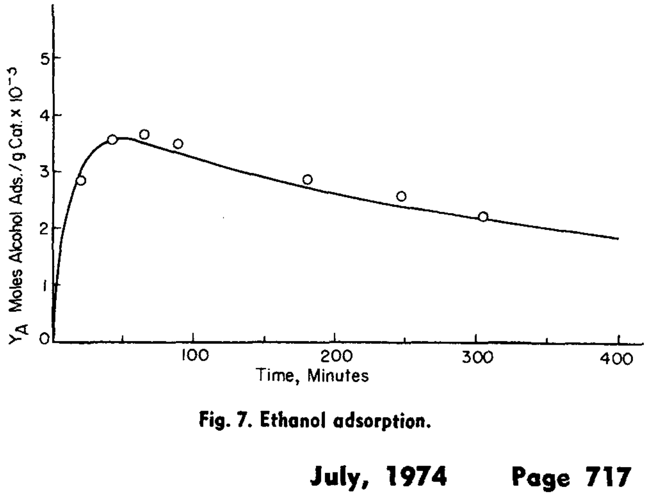

Fig. 7. Ethanol adsorption.

the rate processes important to the reaction.

Valuable insight into the character of the reaction is provided by a comparison of these adsorbed phase composition data to the extremely careful work of Herlihy (1968). Herlihy used a flow system in which fresh feed was continuously introduced so that a constant vapor phase composition was maintained around the catalyst. He obtained pure component adsorption data for water and ethanol at a variety of pressures and also mixed gas adsorption data for the ethanol-water binary system at 1 atm. He employed the thermodynamic analysis technique of Myers and Prausnitz (1965) with his pure component data to predict his mixed gas adsorption results. The agreement he obtained was very good. His results are reproduced on Figure 9.

Herlihy's data display normal behavior with one exception. As one goes to higher and higher vapor phase alcohol concentrations, ultimately to pure alcohol, the amount of water adsorbed does not tend to zero but rather to about 1.4 × 10^{-3} moles of water adsorbed per gram of resin. The reason for this is that his apparatus was really a steady state, not an equilibrium, apparatus. Because of the reaction of adsorbed ethanol, water was formed. A steady state balance between rate of formation and rate of desorption of water resulted in the presence of water in the adsorbed phase despite its virtual absence in the vapor phase. In all of his experiments this phenomenon remains. However, it is effectively unobservable in the data having water vapor mole fractions higher than 0.2 and it does not affect his alcohol data.

Also plotted on Figure 9 are the adsorbed phase composition data obtained in the present work. The differences between the two data sets should be noted. In Herlihy's work the total pressure was constant at 1 atm., whereas in this work it varied from 0.89 to 0.7 atm. Herlihy had a simple binary system, whereas ethyl ether was present in this work as well as alcohol and water. Herlihy worked at 119°C, which is not very different from the 120°C here. And most important, Herlihy used a steady state method to get his equilibrium data in comparison to the dynamic experiment being presented here. The data of the present investigation have been plotted in a way to give the most meaningful comparison. The time corresponding to each data point is shown. There is every reason to believe that ether acts simply as a vapor phase diluent, thus ether free, water-alcohol binary mole fractions were used. Also the indicated pressures for each point are the sum of the partial pressures of water and alcohol rather than the total pressure. It is unfortunate that sampling difficulties late in the experiment precluded the attainment of reliable adsorbed phase composition data in the low ethanol range. But the data which do exist are quite adequate for the comparisons to be made.

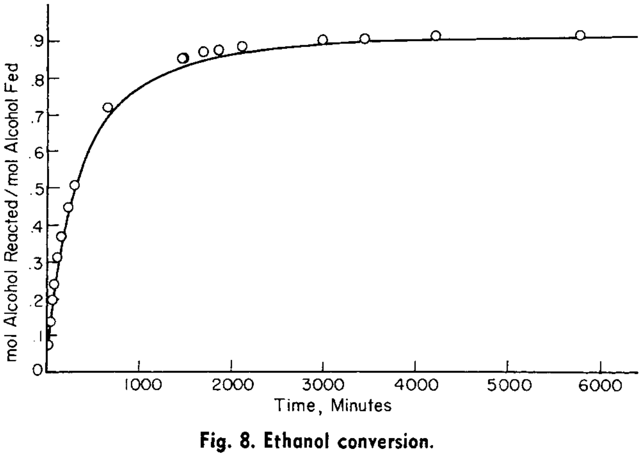

Fig. 8. Ethanol conversion.

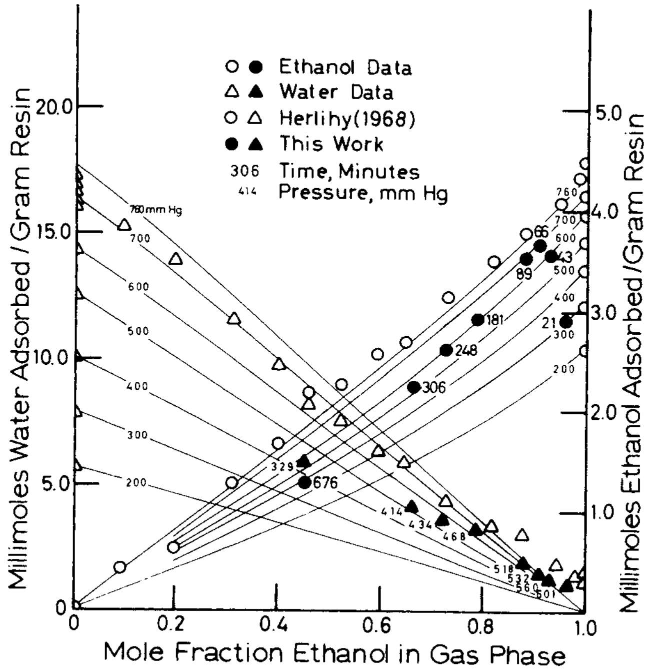

Fig. 9. Ethanol-water mixed gas adsorption. Note: For every ethanol datum of the present work there is a corresponding water datum. The time at which the corresponding data were obtained is noted next to the ethanol point and the sum of the ethanol and water partial pressures which existed at that time is noted next to the water point.

It can be seen that the data of this work at and beyond 66 min. have the same behavior as those of Herlihy when an allowance is made for the fact that the pressure is continually decreasing in this work. The data are too high when their respective ether-free total pressures are compared to the pressures indicated on the Myers and Prausnitz lines. (The agreement is better when the actual total pressures of the data are used, but that seems inappropriate.) It was pointed out by Hsu and Kabel (1974) that an error of one mole percent in the composition analysis could propagate to a 20-30% error in adsorbed weights. Also that paper discusses a slight consistent error which is in the correct direction to explain the discrepancy observed here.

These difficulties do not obscure the most important point which is that the data at 21 and 42 min. behave quite differently from the rest. The effect is most obvious in the alcohol data, but can also be seen in the water data. The amount of alcohol adsorbed is seen to increase with time up to 66 min. and then to decrease. The initial transient adsorption of ethanol causes the early rapid rise. The ethanol adsorption evidently achieves equilibrium at about 60 min. Then the adsorbed ethanol decreases consistent with its equilibrium with the vapor as the ethanol in the system is depleted by reaction. The initial nonequilibrium period is complicated by the thermal effect discussed earlier but would exist even in an isothermal experiment. It should be noted that the time of achievement of adsorption equilibrium is consistent with the times at which the reaction begins to dominate the ethanol and total adsorption behaviors, as evidenced by the maxima in Figures 7 and 5. Thus this experiment in which adsorption and overall reaction are followed simultaneously shows dramatically that the surface reaction is

TABLE 1. NONISOTHERMAL EFFECT

Variable	Comparison*	Explanation
P_A	$<$	Higher rates despite lower adsorption
P_E	$>$	Higher rates
P_W	$>$	Higher rates and lower adsorption
y_A	$<$	Lower adsorption and higher rates
y_W	$>$	Higher rates despite lower adsorption

* The comparative equation is nonisothermal variable $\overset{>}{<}$ isothermal variable, for example, $P_{A\,\mathrm{non}} < P_{A\,\mathrm{iso}}$.

much slower than the adsorption processes and can be taken to be the rate controlling step.

In the interpretation of all of the results discussed in this paper, one wonders about the significance of the influence of the high temperatures early in the run. At this point in the work, considerable confidence in the model is justified. Thus it can be used to predict isothermal behaviors for comparison with the results of the nonisothermal model already presented. The increased temperature will produce higher rates of adsorption, desorption, and reaction and yet lower absolute amounts adsorbed at any given time. These effects may be involved singly, be mutually reinforcing, or be somewhat compensatory as shown in Table 1.

Although the directional comparisons given in Table 1 apply over the whole range of the data, the maximum effects occur in the 40- to 100-min. period. In the context of the figures in this paper, the changes which would result if predictions from the isothermal models were plotted would never exceed the dimensions of the data point symbols. Thus slopes of curves may vary somewhat because of the thermal effect, but the general behaviors will be unchanged. Thus, in contrast to most reactor dynamics investigations which derive their characteristics from interaction of reaction rates with heat and mass transfer; in this case, it is the adsorption processes which provide the interesting and informative transients.

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NOTATION

A, W, E = molecule of alcohol, water, ether in the vapor, respectively
As, Ws = adsorbed molecule of alcohol, water, respectively
k_A = forward surface reaction rate coefficient, mol/min-g catalyst
k_{-A} = reverse surface reaction rate coefficient, mol/min-g catalyst-atm
K_A, K_W = Langmuir equilibrium adsorption constants for alcohol, water, respectively, atm^{-1}
K_{eq} = thermodynamic equilibrium constant, dimensionless
n_A, n_W, n_E, n_i = number of moles of alcohol, water, ether, any component i in the vapor phase, resp., mol
n_{A0} = initial amount of alcohol added to the system = 0.02950 mol
P_{A0}, P_{W0}, P_{E0} = initial partial pressures of alcohol, water, ether, respectively, atm
P_A, P_W, P_E = partial pressures of alcohol, water, ether, respectively, atm
r_A, r_i = rate of disappearance of alcohol, any component i, respectively, due to surface reaction, mol reacted/min-g catalyst
R = gas constant, 82.05 atm-cm^3/mol-K
s = catalytic site
t = time, min
T = temperature, K
T_c = effective temperature of catalyst, K
V = reactor volume = 1069 cm^3
W_c = weight of the catalyst (bone dry weight) = 0.6942 g
y_A, y_W = moles of alcohol, water, respectively, adsorbed on the catalyst, mol adsorbed/g catalyst
y_{A0}, y_{W0} = moles of alcohol, water, respectively, initially adsorbed on the catalyst, mole adsorbed/g catalyst
y_m = amount of the monolayer adsorption on Dowex 50-X8 = 0.0054 mol/g catalyst

Greek Letters

$\theta_A, \theta_W, \theta_i$ = fraction of sites in the catalyst monolayer covered with ethanol, water, any component i, respectively, dimensionless
θ_v = fraction of vacant catalyst sites in monolayer, dimensionless
κ_A, κ_W = adsorption rate coefficient for ethanol, water, respectively, mol/min-g catalyst-atm
κ_{-A}, κ_{-W} = desorption rate coefficient for ethanol, water, respectively, mol/min-g catalyst
ρ_A, ρ_W, ρ_i = rate of adsorption of ethanol, water, any component i, respectively, mol adsorbed/min-g catalyst

LITERATURE CITED

Denis, G. H., and R. L. Kabel, "The Effect of Temperature Changes on a Tubular Heterogeneous Catalytic Reactor," *Chem. Eng. Sci.*, **25**, 1057 (1970a).

———., "The Effect on Conversion of Flow Rate Variations in a Heterogeneous Catalytic Reactor," *AIChE J.*, **16**, 972 (1970b).

Duda, J. L., and J. S. Vrentas, "Diffusion in Styrene Polymers," in *Encyclopedia of Polymer Science and Technology*, Vol. 13, Wiley, New York (1970).

Gates, B. C., and L. N. Johanson, "The Dehydration of Methanol and Ethanol Catalyzed by Polystyrene Sulfonate Resins," *J. Catalysis*, **14**, 69 (1969).

Hawes, R. W., and R. L. Kabel, "Thermodynamic Equilibrium in the Vapor Phase Esterification of Acetic Acid with Ethanol," *AIChE J.*, **14**, 606 (1968).

Herlihy, J. C., "Adsorption of Ethanol and Water Vapor on Ion Exchange Resins and Catalysis of Ethanol Dehydration," Ph.D. thesis, Univ. of Washington, Seattle (1968).

Hsu, S. M., "Experimental and Theoretical Analysis of Adsorption and Reaction Kinetics in a Batch Heterogeneous Catalytic Reactor," M.S. thesis, Pennsylvania State Univ., University Park (1972).

———., and R. L. Kabel, "A Batch Reactor to Study Concomitant Adsorption and Heterogeneous Catalysis," *J. Catalysis*, **33**, 74 (1974).

Kabel, R. L., "Homogeneous Verusus Heterogeneous Rate Equations for Catalytic Reactions," *AIChE J.*, **14**, 385 (1968).

———., "Reaction Kinetics, Adsorption, and Equilibrium in the Vapor Phase Dehydration of Ethanol to Diethyl Ether as Catalyzed by Ion Exchange Resin," Ph.D. thesis, Univ. of Washington, Seattle (1961).

———., and L. N. Johanson, "Reaction Kinetics and Adsorption Equilibria in the Vapor-Phase Dehydration of Ethanol," *AIChE J.*, **8,** 621 (1962).

———., "Thermodynamic Equilibrium in the Ethyl Alcohol-Ethyl Ether-Water System," *J. Chem. Eng. Data*, **6,** 496 (1961).

Kittrell, J. R., Reiji Mezaki, and C. C. Watson, "Estimation of Parameters for Nonlinear Least Squares Analysis," *Ind. Eng. Chem.*, **57** (12), 18 (1965).

Lapidus, Leon, and T. I. Peterson, "Analysis of Heterogeneous Catalytic Reactions by Nonlinear Estimation," *AIChE J.*, **11,** 891 (1965).

Lehr, C. G., "A Study on the Transient Response of a Tubular Heterogeneous Catalytic Reactor to a Step Change in Feed Rate," M.S. thesis, Pennsylvania State Univ. University Park (1966).

———., Sergei Yurchak, and R. L. Kabel, "Response of a Tubular Heterogeneous Catalytic Reactor to a Step Increase in Flow Rate," *AIChE J.*, **14,** 627 (1968).

Mezaki, Reiji, and J. R. Kittrell, "Nonlinear Least Squares for Model Screening," *ibid.*, 513.

Mullarkey, T. B., "Kinetic Study of the Heterogeneous Catalytic Dehydration of Ethanol," M.S. thesis, Pennsylvania State Univ., University Park (1970).

Myers, A. L., and J. M. Prausnitz, "Thermodynamics of Mixed Gas Adsorption," *AIChE J.*, **11,** 121 (1965).

Stula, R. T., "A Kinetic Study of Heterogeneous Catalytic Ethanol Dehydration," M.S. thesis, Pennsylvania State Univ., University Park (1972).

Waxman, M. H., B. R. Sundheim, and H. P. Gregor, "Studies on Ion Exchange Resins. VI. Water Vapor Sorption by Polystyrenesulfonic Acid," *J. Phys. Chem.*, **57,** 969 (1953).

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Application of Quasilinearization to Methane Pyrolysis

The rate constants appearing in differential equations derived from proposed mechanisms for methane pyrolysis were estimated from published integral conversion data. Quasilinearization, capable of fitting the differential equation solutions directly to the integral data and therefore not requiring differentiation or transformations, was used. Since differential equations representing free radical reactions have coefficients varying over many orders of magnitude, implicit numerical integration was used to obtain the numerous particular and homogeneous solutions required in the execution of the algorithm. Convergence was achieved by replacing the concentrations after each iteration with values near the solution at that point and by repeatedly estimating a small number of parameters in a cyclic manner in order to improve starting estimates of all parameters simultaneously. The mechanisms attempted were considered plausible when they led to adequate data fits and reasonable rate constant estimates. The major contribution of the work is that the algorithm is capable of testing a mechanistic model over a relatively wide range of conditions with minimal experimental data.

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SCOPE

The modeling of complex reactions as a sequence of free radical reactions is an important objective of chemical kinetics. With such models, yields and conversions for commercially important reactions such as hydrocarbon pyrolysis and oxidation can be predicted.

Most of the previous work in this area consisted of the simultaneous solution of numerous differential equations by numerical methods using a digital computer. This task is made difficult by (1) the large number of differential equations to be solved and (2) the necessity to simultaneously estimate the necessary rate constants for the

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