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A Batch Reactor to Study Concomitant Adsorption and Heterogeneous Catalysis

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A batch reactor has been devised in which adsorption phenomena important to a heterogeneous catalytic reaction can be followed simultaneously with the overall reaction process. The experimental technique is illustrated with the vapor phase dehydration of ethyl alcohol to diethyl ether as catalyzed by hydrogen ion exchange resin. Directly measured data are vapor phase composition, total adsorption, and total pressure as functions of time. Derived results are adsorbed phase composition data, fractional conversion, the thermodynamic equilibrium constant, and an independent check on internal consistency. The method inherently provides insights characteristic of dynamic experiments while retaining the simplicity of a set of first-order ordinary differential equations for any mathematical treatment desired. For this catalytic reaction the adsorption processes are shown, without recourse to theoretical analysis, to be much faster than the surface reaction.

Prevailing methods for the study of gas solid catalytic reactions often involve steady state flow systems. Such methods offer many advantages such as sampling ease, constant compositions at any point, good mass and heat transfer characteristics, and some similarity to actual operating reactors. Dynamic experiments in flow systems can often provide profound new insights, but the investigations are complicated by the variation of parameters with both space and time. This complexity leads necessarily to partial differential equations in a mathematical treatment. A major shortcoming of flow (and nonflow) reactor techniques is that adsorption data are seldom obtained. The total amount of material adsorbed and the composition of the adsorbed phase as a function of gas phase composition, pressure, and temperature can be important in developing kinetic models to describe catalytic reactions. Thus independent adsorption studies often have to be carried out to provide required information. Multicomponent adsorption experiments are extremely difficult to perform and one usually settles for pure component adsorption data. Such studies, although valuable, do not necessarily represent the actual adsorption processes in the multicomponent reacting mixture. Even multicomponent studies may not be performed at actual reaction conditions.

The experimental technique developed in this work yields adsorbed phase composition, total adsorption, and transient kinetic data in one experiment. The reaction system chosen for study was the dehydration of ethyl alcohol to diethyl ether and water at 120°C over 20–50 mesh Dowex 50-X8, a commercially available sulfonated copolymer of styrene and divinylbenzene in the hydrogen form.

$$2C_2H_5OH \overset{H^+}{\rightleftarrows} C_2H_5OC_2H_5 + H_2O \qquad (1)$$

This reaction was studied in depth under steady state conditions in a flow reactor by Kabel and Johanson (*1*). Fixed bed reactor dynamics in the same system have been described by Denis and Kabel (*2*). No review of these and other related works is provided here. But it is important to note that the reaction rate is profoundly influenced by the adsorbed phase and that ethanol and water are strongly adsorbed while ethyl ether is unadsorbed.

Concepts

The basic concept is the use of a batch heterogeneous catalytic reactor in which the adsorption phenomena important to the catalytic reaction can be followed simultaneously with the overall reaction process. 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, helix length, and vapor phase composition are obtained as functions of time while the various processes proceed toward their respective equilibria. Adsorbed phase compositions, fractional conversion, and the thermodynamic equilibrium constant can be derived from the raw data. Sufficient information remains to provide an independent check on the internal consistency of the experiment.

Catalyst state characterization under reaction conditions by gravimetric methods has been cleverly and valuably achieved by Mars, Scholten, and Zwietering (*3*), Mas-soth and Scarpiello (*4*), and many others. Tamaru and co-workers (*5*, *6*) have succeeded in adsorption measurement during surface catalysis by use of a volumetric technique similar to that used in multicomponent adsorption studies. The method reported here is more versatile than purely gravimetric methods due to the volumetric component, providing information on adsorbed phase composition for example. At the same time the presence of the gravimetric component represents an improvement over purely volumetric techniques by virtue of the very accurate direct indication of total adsorption which provides an independent check on the internal consistency of the experiment and greater accuracy in derived results such as adsorbed phase composition and fractional conversion.

A prime feature of this technique is that it inherently provides the benefits of dynamic experiments while retaining the simplicity of a set of first-order ordinary differential equations. Although mathematical analysis is not a part of this paper, it may be helpful to some readers to show the equations which can be used to describe the behavior of the reaction system.

The concentrations of all the reactants and products on the catalyst can be expressed by material balances on the adsorbed phase.

$$\frac{dy_i}{dt} = \rho_i - r_i \qquad (2)$$

where y_i = concentration of species i on the catalyst surface (moles i/g of catalyst).
ρ_i = net adsorption rate of species i (moles i adsorbed/g of catalyst min).
r_i = surface reaction rate of species i (moles i reacted/g of catalyst min).
t = time (min).

These equations have to be solved in conjunction with corresponding material balance equations for the vapor phase,

$$\frac{1}{W_c}\frac{dn_i}{dt} = -\rho_i \qquad (3)$$

where n_i = moles of species i in the vapor phase.
W_c = mass of catalyst (g).

The rates of adsorption and reaction, ρ_i and r_i, are of course functions of the surface and vapor phase concentrations, y_i and n_i. But leaving the functional forms unspecified does not change the character of the set of first-order ordinary differential equations, which are easily solved by a variety of computer library programs.

EXPERIMENTAL

The apparatus is shown schematically in Fig. 1. An air thermostat enclosed the adsorption-reaction chamber and the manometer system. The temperature of the lower portion of the chamber was more finely controlled by oil circulating through a jacket.

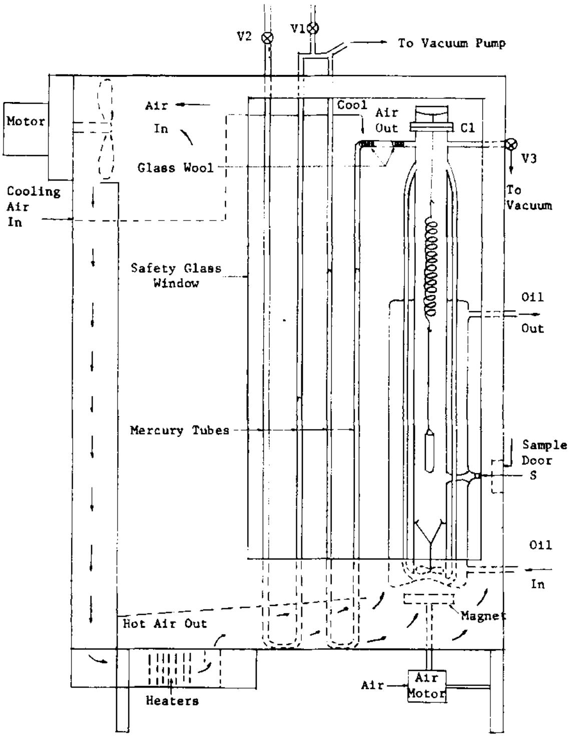

FIG. 1. Adsorption system.

Direct measurement of the total amount adsorbed on the catalyst at any time was achieved by observing the elongation of a quartz helix spring to which an adsorbent container was attached. This catalyst bucket, 3.5 × 1.2 cm, was made of profusely punctured aluminum foil to allow easy access of vapors to the catalyst. A cathetometer was used to read the positions of the spring.

Near the bottom of the chamber, an iron fan suspended from a fishing swivel was rotated by a strong magnet below the chamber. The fan provided turbulent mixing and internal circulation of the vapor in the reactor to improve heat and mass transfer characteristics. Access to the chamber was through a removable top and by syringe through an injection and sampling port, S, fitted with a cylindrical rubber plug.

A dual manometer scheme was employed with a Torricellian manometer (the left one in Fig. 1) actually indicating the chamber pressure. By virtue of a controlled air leak, the pressures on both sides of the other manometer were balanced giving a constant volume reactor (1069 cc in this experiment). In a variety of tests, the apparatus was found to be virtually leak free.

The experiment was begun by placing the catalyst in the chamber and evacuating the system at <0.001 mm Hg and 120°C until no further change in weight was noted. This established a reproducible catalyst base condition and weight. Pure ethyl alcohol was charged to the chamber and periodic monitoring of all important parameters was begun. Samples of the vapor were drawn into a cooled microliter syringe where they condensed. Analyses were made chromatographically.

RESULTS

Measured Results

Several experiments have been conducted with this equipment; some better in one respect, others in another. For clarity, brevity, and consistency this paper presents the results of just one experiment. Further information on all aspects of the work is given by Hsu (7).

The following data are obtained through direct measurement: total adsorption, total system pressure, and the vapor phase composition as functions of time. The total adsorption curve as a function of time is presented in Fig. 2. The ordinate shows the weight of the bucket-catalyst-adsorbate combination. Using the initial value and the given catalyst base weight, the actual mass adsorbed per unit mass of catalyst is easily calculated. The data show very rapid initial adsorption of alcohol to a maximum value. As the reaction proceeds, ether and water are produced in equimolar amounts, the total produced being equal to the moles of alcohol consumed. 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. This occurs despite the fact that water is more strongly adsorbed than ethanol on a molar basis. Two interesting artifacts due to lapses in temperature control are seen in Fig. 2. The second and more dramatic was the result of a 2-hr campus-wide power failure. Although one could not have been certain at the time, it is now clear that system equilibrium had been reached by the time power was lost. The resulting decrease in temperature produced an abrupt increase in total adsorption. The original equilibrium condition was quickly reestablished when power was restored. This response is an impressive indication of the velocity of the adsorption processes. Any apparent gradualness is probably primarily a function of the thermal inertia of the thermostats.

The total pressure data for the first 400 min of the run are shown in Fig. 3. Beyond 400 min the pressure simply declined gradually to an equilibrium value of 0.7 atm. The initial rapid decrease in pressure corresponds to the early removal of ethanol from the vapor phase by adsorption. Also by careful inspection of this graph one can detect the small, but significant, effect of vapor sample removal. More will be said on this effect later in the paper.

In Fig. 4, the component partial pressures from the gas chromatograph analyses are shown for the duration of the experiment. Alcohol is removed from the vapor by adsorption and from the system by reaction. Of the ether and water produced, the ether is found entirely in the vapor phase while the water distributes itself between the vapor and adsorbed phases. Hence the water data are generally lower than the ether data.

Derived Results

It is also possible to derive additional information of value. Knowing the pressure, temperature, and volume of the reactor, the vapor phase compositions and the amount of alcohol charged (1.3590 g in this experiment), the adsorbed phase compositions can

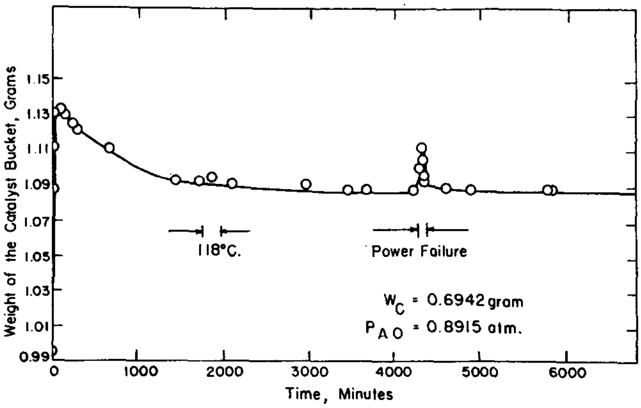

FIG. 2. Total adsorption at 120°C.

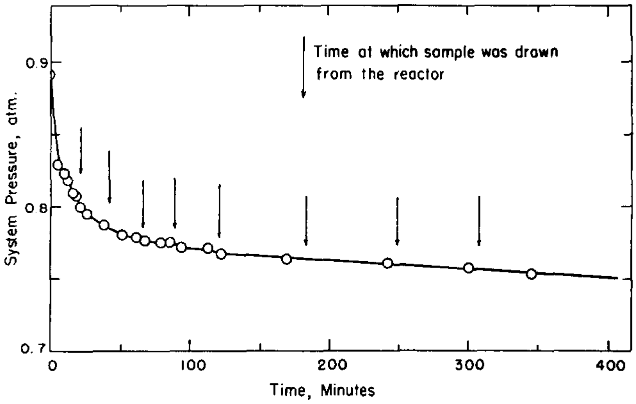

FIG. 3. System pressure in the first 400 min.

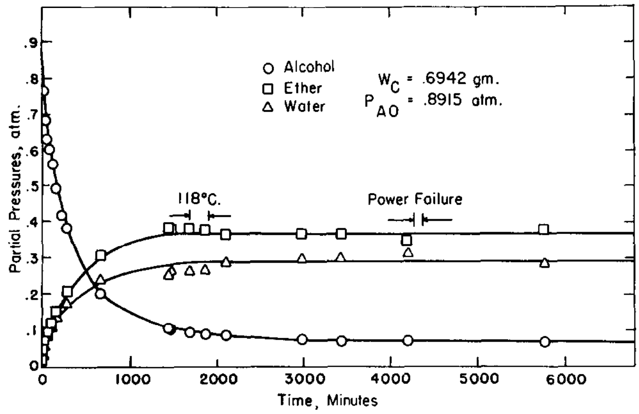

FIG. 4. Partial pressures of alcohol, water, and ether at 120°C.

be calculated independently if ether is considered (*1*) to be not adsorbed at all.

Let WAD be the total adsorption weight in grams at any time and m_A and m_W be the masses of alcohol and water adsorbed on the catalyst at any time, then

$$m_A + m_W = \mathrm{WAD}. \quad (4)$$

From the stoichiometry of the reaction, the molar amount of alcohol reacted must produce an equal molar amount of products, hence

$$\frac{m_{AO}}{M_A} - \frac{(m_A + m_{AV} + \delta_A)}{M_A} = \frac{(m_W + m_{WV} + \delta_W)}{M_W} + \frac{m_{EV} + \delta_E}{M_E}. \quad (5)$$

Solving:

$$m_W = \frac{M_A M_W}{(M_A - M_W)}\left(\frac{m_{AO}}{M_A} - \frac{m_{AV}}{M_A} - \frac{m_{WV}}{M_W} - \frac{m_{EV}}{M_E} - \frac{\mathrm{WAD}}{M_A} - \frac{\delta_A}{M_A} - \frac{\delta_W}{M_W} - \frac{\delta_E}{M_E}\right), \quad (6)$$

where: m_{iV}	mass of component *i* in vapor phase (g).
m_i	mass of component *i* in adsorbed phase (g).
M_i	molecular weight of component *i* (g/mole).
m_{AO}	mass of pure alcohol injected initially (g).
δ_A, δ_W, δ_E	mass of alcohol, water, ether removed from the reactor by sampling up to the time of interest (g).

The mass of alcohol adsorbed can then be solved for using Eq. (4). Using the spring data for the total adsorption weight, the adsorbed phase compositions were calculated. The results for the first 400 min are presented in Fig. 5. The adsorbed alcohol rises rapidly initially, reaching a maximum when the rate of adsorption of alcohol is equaled by its rate of reaction to ether and water. From this point on, the ethanol curve declines gradually to equilibrium. The water, on the other hand, is formed by the reaction and gradually accumulates in the adsorbed phase until equilibrium is achieved. The 121st minute datum is apparently in error, as discussed later in the data consistency check, and probably should be disregarded.

The conversion of alcohol, moles of alcohol reacted per mole of alcohol charged, can be obtained from the following equation:

$$\text{Fractional conversion} = \frac{m_{\mathrm{AO}} - m_{\mathrm{AV}} - m_{\mathrm{A}} - \delta_{\mathrm{A}}}{m_{\mathrm{AO}}}. \qquad (7)$$

The ethanol conversion was rapid at first, with about 60% of the alcohol fed reacted in 400 min. In 1000 min, about 80% of the initial alcohol charge was reacted. As the reaction progressed its rate slowed down considerably and in about 4000 min, a constant conversion of 91.5% was obtained.

Another derived quantity which can be obtained is the thermodynamic equilibrium constant. It can be calculated by:

$$K_{\mathrm{eq}} = \frac{P_{\mathrm{E}} P_{\mathrm{W}}}{P_{\mathrm{A}}^2} \qquad (8)$$

where the P_i's are partial pressures in atmospheres as shown in Fig. 4. The detailed derivation and justification for this equation is discussed by Hawes and Kabel (*8*). For example, the data of the 3448th minute yielded a K_{eq} of 24.7 and from the data of the 5807th minute, K_{eq} was found to be 26.5. Kabel and Johanson (*9*) had determined K_{eq} for this reaction at 120°C to be 25.2 by a completely different method having extraordinary accuracy. The agreement between the values obtained in this work and that of Kabel and Johanson indicates the kind of accuracy associated with this experimental technique. The precision indicated by the two values of K_{eq} is typical of methods which rely on concentration measurements.

It is also possible to determine equilibrium adsorption constants and the initial rate of ethanol adsorption directly from the experimental results. However the simultaneous solution of Eqs. (2) and (3) is necessary to find the rates of reaction and other adsorption-desorption processes. A quantitative treatment of the catalytic kinetics in this reaction system is to be the subject of a subsequent paper.

Consistency Check

One major advantage in this experiment is that it offers a unique way to check the consistency and hence the reliability of the

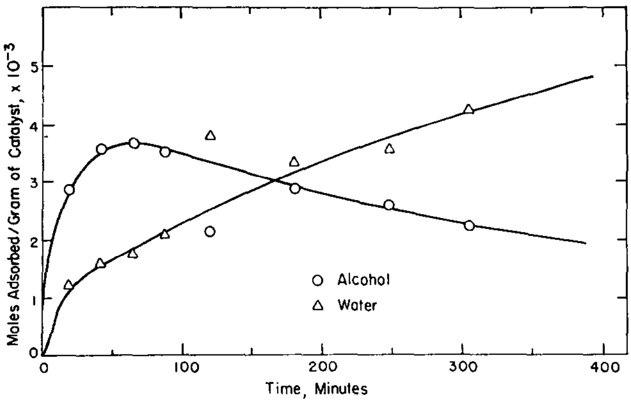

FIG. 5. Adsorbed phase composition in the first 400 min.

data obtained. The total adsorption weight at any time could be calculated from a material balance in terms of the vapor phase compositions:

$$\mathrm{WAD} = m_{\mathrm{AO}} - m_{\mathrm{AV}} - m_{\mathrm{EV}} - m_{\mathrm{WV}} - \delta_T \tag{9}$$

where δ_T is the total mass of material removed from the reactor by sampling up to that time. When the weights calculated from Eq. (9) were compared to the weights determined directly from the quartz spring measurements, the discrepancies between the two quantities would indicate the magnitude of the experimental errors. This method was a very severe test because of the numbers involved. The amount adsorbed at any time was about 0.1 g. Therefore when Eq. (9) was used, the difference between m_{AO} and the sum of m_{AV}, m_{EV}, m_{WV}, and δ_T would be about 0.1 g. Since $m_{\mathrm{AO}} = 1.359$ g this calculation yields a small difference between large numbers. Subsequent analysis reveals that an error of 1 mole% in the composition analyses could propagate to a 20–30% error in the calculated adsorbed weight. The important point here is that this consistency test offers an independent check on the relative accuracy of the data points.

TABLE 1

Adsorbed Weight Check

	Adsorbed wt			
Time (min)	Spring data, W_1 (g)	Eq. (9), W_2 (g)	Delta $W_1 - W_2$, (g)	Deviation W_2 from W_1 (%)
21	0.1075	0.13869	−0.03119	29.0
43	0.1335	0.15892	−0.02542	19.0
66	0.1395	0.15503	−0.01553	11.1
89	0.1385	0.15457	−0.01607	11.6
121	0.1155	0.16098	−0.04548	39.4
181	0.1335	0.16198	−0.02848	21.3
248	0.1295	0.14580	−0.01630	12.6
306	0.1235	0.14603	−0.02253	18.2
676	0.1155	0.13934	−0.02384	20.6
1450	0.0985	0.08667	0.01183	−12.0
1469	0.0975	0.10017	−0.00267	2.7
1696	0.0975	0.10391	−0.00641	6.6
1877	0.0995	0.12110	−0.02160	21.7
2129	0.0958	0.13931	−0.04351	45.4
3007	0.0954	0.15873	−0.06333	66.4
3448	0.0922	0.16290	−0.07070	76.7
4227	0.0922	0.19498	−0.10278	111.5
5807	0.0922	0.13871	−0.04651	50.4
7189	0.0922	0.10671	−0.01451	15.7
8797	0.0922	0.10852	−0.01632	17.7

To illustrate this, the data are analyzed and the results presented in Table 1. The fourth column shows the calculated weights to be almost always larger than the measured weights. Thus a consistent error is indicated. It will be noted that the measured value was taken to be more reliable than the calculated one when determining adsorbed phase compositions. From the percentage deviation column one notices especially large inconsistencies occurring late in the run. This is the result of increased sampling difficulties at high conversion levels. Also the datum at 121 min shows a higher percentage deviation than all other data up to 2000 min. The suggestion of experimental error in this datum made in the discussion of Fig. 5 is reinforced by this internal consistency analysis. Therefore this independent check offers a useful tool to detect any bad data and also indicates whether there are experimental difficulties or otherwise.

Discussion

Some Difficulties

No claim is made that the technique described is optimal. The apparatus descended from previous research and was modified for use in this project. There is no doubt though that the method can be applied effectively to other reaction conditions and systems. Automated indication of pressure and strain gauge responses and in situ analyses would allow convenient treatment of much more rapid reactions as long as mass transfer resistances do not interfere with the well mixed character of the batch reactor. Still it may be worth while to indicate the most severe difficulties, the solutions used, and possible improvements.

The sampling method is critical because any amount of material removed from the batch reactor is going to shift the ultimate equilibrium position to a certain extent.

And this effect is cumulative with continued sampling. Therefore the material removed must be minimized. It must also be accounted for since any theoretical treatment must necessarily be consistent with the conditions of the experiment if valid comparisons are to be made. The composition of each sample was provided directly from the analysis. The sample size was determined by a crude correlation (obtained during calibrations) of the total integral count of the chromatogram with the pressure change in the reaction chamber. Sampling corrections were employed successfully in determining the fractional conversion from Eq. (7) and the calculated total amount adsorbed from Eq. (9). The corrective terms, δ_A, δ_E, δ_W, in Eq. (6) for the adsorbed phase composition were omitted because the accumulated errors of sample size estimation and vapor phase analysis, coupled with the subtraction of large numbers to obtain the small amounts adsorbed, introduced enough scatter into the data of Figs. 5 and 6 to make the fundamental trends less evident. The sampling technique, as described earlier is simple in concept, was quite effective, but required inordinate skill in practice. It is possible that vapor sampling by a gas chromatograph directly incorporated in the apparatus would be a superior technique.

At the start of the experiment an almost immediate catalyst temperature rise to about 145°C occurred followed by a return to within a few degrees of the control temperature at 40 min and to one degree above 120°C at 100 min. These temperature effects correspond to heat released at first by the rapid adsorption and later, when the adsorption processes are near equilibrium, by the continuing exothermic reaction. Heat transfer in the reactor is fairly effective at moderating these effects, as seen from the fact that the adiabatic temperature rise of the catalyst at 40 min would be about 100°C. Nevertheless this thermal effect interferes somewhat with data interpretation. It could probably be reduced considerably by redesign of the catalyst container and perhaps by using a different initial configuration than total evacuation.

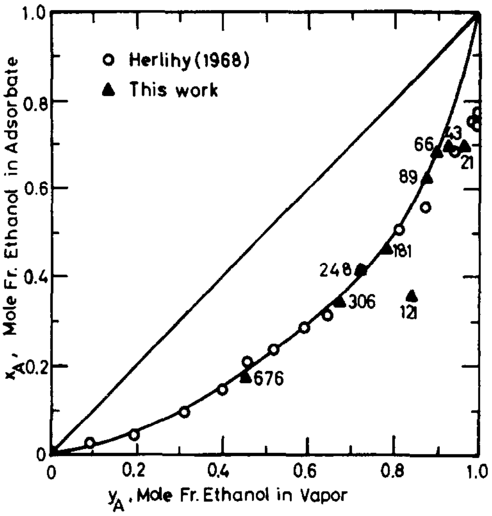

FIG. 6. Vapor–adsorbate phase equilibrium diagram for ethanol–water.

For this work, however, the catalyst temperature was simply measured in a series of separate experiments and incorporated directly in all calculations, etc.

A variety of arguments are given by Hsu (7) to show that mass transfer resistances were inconsequential in this work.

Additional Insight

In this paper an experimental method has been described and characteristic data have been presented and discussed qualitatively. Mathematical analysis applied to the results provides much greater understanding still, but is so extensive that it should be considered separately. Yet additional insight into the nature of this reaction system is possible by simply comparing the adsorption data of this work with those of Herlihy (*10*). Herlihy used a flow system to measure ethanol–water mixed gas adsorption at 119°C and 1 atm pressure. In his series of runs, fresh alcohol–water feeds of differing compositions were continuously introduced so that a constant vapor phase composition was maintained around the catalyst, Dowex 50-X8. His data and those of this work are presented on Fig. 6. A plot of mole fraction ethanol in the adsorbed phase as a function of mole fraction ethanol in the vapor phase is used here because such plots are rather insensitive to temperature and pressure variations and require less supplementary interpretation for understanding. All mole fractions are calculated on an ether free basis.

The data points of this work have their corresponding times of acquisition noted on the graph. Realizing that the 121 min point is faulty, it can be seen that the two sets of data agree up to $y_A = 0.85$. Above this region the trend of Herlihy's points indicates that water is present in the adsorbed phase even when the vapor phase is pure ethanol. The explanation for this is that in his experiment water is present on the catalyst as a result of a steady state balance between its rate of formation by the reaction and its rate of desorption. This effect is most severe at high alcohol concentrations. Taking the $x_A = y_A = 1.0$ point as a valid point, a smooth curve representing equilibrium can be drawn on the graph. Herlihy's five highest data fall off the curve for the reason given above. Only the 21 and 43 min points of this work deviate. These deviations are also in the direction of more water (because of the production by reaction and insufficient desorption) and less alcohol (because of the short time alcohol has had to become adsorbed so far) on the catalyst than would exist at equilibrium. The implication is that even in the present transient experiment the adsorption processes are in equilibrium except in the earliest stages. The first hour of the run has been complicated by the nonisothermal effect described eariler, but even so there would have to be a transient, nonequilibrium adsorption period at the beginning.

Thus one can deduce the adsorption transients are quite short lived (on the order of 1 hr) while the surface reaction transient goes on for days. This observation is consistent with the dynamic studies of Denis and Kabel (*2*). Kabel and Johanson (*1*) found that the surface reaction was the rate controlling step by considering a variety of Langmuir–Hinshelwood models. Now it appears that this conclusion can be deduced directly without recourse to any mathematical model. Thus this single transient experiment, in which the kinetics and equilibria of reaction and adsorption are observed simultaneously, is seen to enhance understanding of a heterogeneous catalytic reaction.

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