JOURNAL OF CATALYSIS 32, 396–414 (1974)

Adsorption Studies at Reaction Conditions—Catalytic Dehydration of *t*-Butyl Alcohol

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Received August 10, 1973

A rapid response technique for measuring the amount of reactant and product adsorbed on a catalyst at reaction conditions was developed. The technique was evaluated using the dehydration reaction of *t*-butyl alcohol over alumina at 195°C and 1 atm pressure. Pure component isotherms were determined for *t*-butyl alcohol, water and isobutylene at 195°C and pressures up to 600 mm Hg as well as binary isotherms for alcohol–water mixtures. Based on the adsorption data, a relatively simple kinetic reaction rate equation was proposed and evaluated. The rate equation gave an excellent correlation of integral conversion data obtained from fixed-bed reactor studies.

NOMENCLATURE

A	Freundlich equation constant
C	Concentration of adsorbate, (mg mole/g)
F	Total feed rate (mole/sec)
k	Reaction rate constant
L	Concentration of unoccupied reactive surface (mg mole/g)
n	Exponent in Freundlich equation
P	Pressure (mm Hg)
r	Reaction rate (g mole/g hr)
W	Weight of catalyst (g)
X	Conversion (moles converted/mole of feed)

Subscripts

a	*t*-Butyl alcohol
0	Initial value
s	Saturation pressure
w	Water
wf	Fast water
wt	Total water
ws	Slow water

Adsorption–desorption processes are generally accepted as elementary steps in heterogeneous catalytic reactions, however, few experimental studies of adsorption have been conducted with a reactive system at reaction conditions. The desirability of such studies has been recognized (*1–3*) but experimental techniques have not been developed for independent adsorption studies at typical reaction conditions. Present kinetic models employ such simplifying assumptions as Langmuir type isotherms and ideal multicomponent relationships to describe the sorption processes and although the resulting kinetic rate expressions have been quite successful in correlating kinetic data, the applicability of such models has been the subject of much discussion. The work reported here describes a technique for studying adsorptive processes at reaction conditions.

Kabel and Johanson (*4*) have made both reaction rate and equilibrium adsorption studies for the dehydration of ethanol over Dowex 50. They compared the Langmuir adsorption constants obtained from the application of the Hougen-Watson type equations to their kinetic data with those obtained from independent single component equilibrium adsorption measurements utilizing a classical equilibrium adsorption device. Good agreement was found at high temperature (100 and 120°C) but poorer agreement at the lowest temperature (79°C). Macarus and Syverson (*5*) reported on transient adsorption–desorption studies carried out at reaction conditions for the decomposition of *n*-hexyl acetate. They were able to develop a simple kinetic model, based on these studies, which gave an excellent correlation of the fixed-bed data of Sashihara and Syverson (*6*).

The purpose of this work was to extend the study of the role of adsorption in surface catalysis employing an improved apparatus for conducting rapid, transient adsorption–desorption studies on a reactive system at reaction conditions. The system selected for this work was the catalytic dehydration of *t*-butyl alcohol over alumina. This reaction is particularly well suited for studies such as these in that the usual side reactions encountered with some of the other alcohols, such as ether formation and isomerization, do not occur.

The dehydration of alcohols has been the subject of many studies; much of the prior work has been summarized by Winfield (*7*). Pines and Manassen (*8*) reviewed the various mechanisms which have been proposed for these reactions over alumina. Most of the dehydration studies dealt with the dehydration of primary alcohols and in particular ethanol. Both Knozinger (*9*) and Notari (*10*) have recently presented reviews which discuss current ideas dealing with the dehydration of alcohols.

Black, Wright and Coull (*11*) studied the dehydration of *t*-butyl alcohol over alumina at atmospheric pressure and temperatures of 480 to 580°F and correlated their data by means of the reactor unit concept. Their studies included both pure and mixed feeds using both water and *n*-heptane as dilutents. The effect of the dilutent on the reaction rate was the same for both materials, indicating that water did not poison the catalyst. Dohse and Kalberer (*12*) studied the dehydration of *t*-butyl alcohol on a bauxite catalyst at 95 to 200°C. These results indicated that the presence of water in the feed lowers the reaction rate while the introduction of isobutylene does not affect the rate. Knozinger and Buhl (*13*) have made extensive studies of the dehydration of alcohols including *t*-butyl alcohol. They have been able to correlate their rate data with an equation of the form:

$$r = r_0 \frac{(p_A)^{1/2}}{(p_A)^{1/2} + bp_w} \qquad (1)$$

where r_0 is the observed zero order reaction rate found to occur above a given alcohol pressure and which is a function of the reaction temperature.

EXPERIMENTAL METHODS

General considerations. One of the goals of this work was the design and development of an experimental apparatus which could be used to determine the adsorption isotherms of the reactant and products at reaction conditions. From the work of Macarus and others, it was known that a substantial amount of the adsorption occurs very rapidly, on the order of 1–2 sec or less. Because of this, none of the standard techniques for obtaining adsorption data could be employed. Macarus had designed a rapid response adsorption apparatus which consisted of a constant volume adsorption cell containing the catalyst into which the vapor to be adsorbed was quickly introduced and the amount adsorbed was determined from the pressure drop. While this apparatus was very useful for exploratory studies, which revealed the very high adsorption rates, it became apparent that improvements could be achieved by changing the method of contacting the gas and solid. In order to reduce the time required to bring the adsorbent and adsorbate into contact, an adsorption cell was designed which contained the gas to be adsorbed and into which the solid could be introduced quickly. This was accomplished by sealing the catalyst in a glass capsule and placing it in a holder in the adsorption cell; at the desired time, the capsule was crushed and the pressure–time data were recorded. From these data, the quantity adsorbed could be calculated. This design also provided a convenient means for the pretreatment of the catalyst. The second improvement in the response time was gained by employing a severe environment, rapid response, pressure transducer and a recording oscillograph. Together, these two pieces

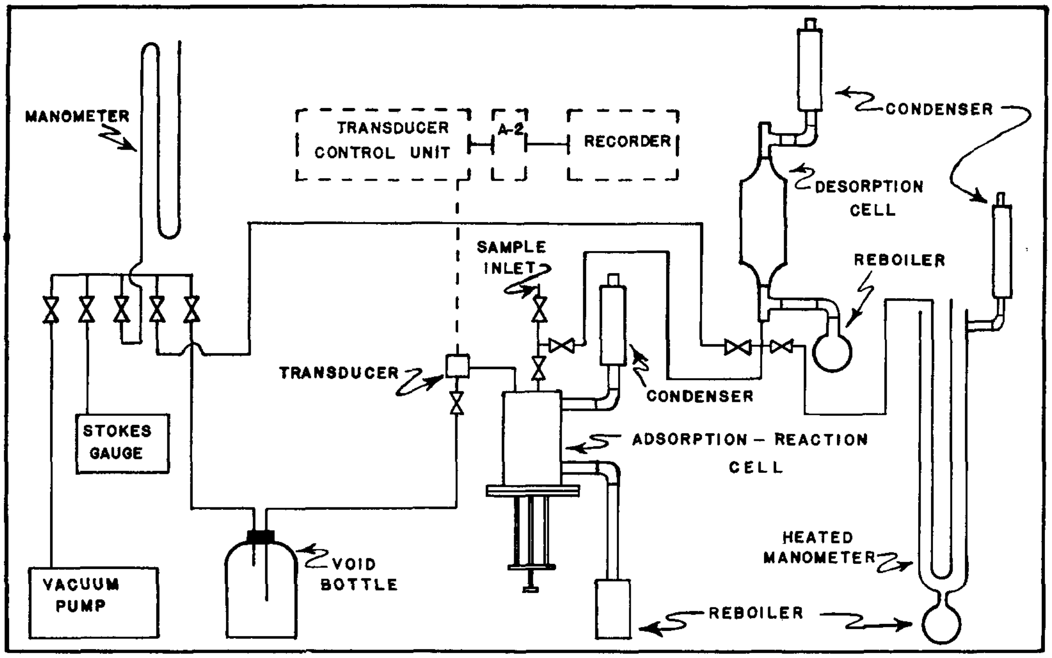

Fig. 1. Adsorption equipment.

of equipment improved the rate of contacting the gas and solid and the rate of response of the pressure measuring system so that the contacting and recording could be accomplished in less than 0.01 sec.

Apparatus. A schematic diagram of the apparatus is shown in Fig. 1. The adsorption–reaction cell was a constant volume apparatus designed as shown in Fig. 2. The cell consisted of a well insulated, jacketed cylinder which could be maintained at the desired temperature by condensing vapors in the outer jacket, the temperature being monitored by various thermocouples. Several openings at the top permitted connections to be made to the cell for the purpose of measuring the cell pressure, introducing adsorbate, and for evacuating the cell. The bottom of the cell was sealed with a gasketed flange which also held the catalyst capsule support and breaking mechanism.

The pressure of the adsorption–reaction cell was measured by means of a Consolidated Controls Corp. severe environment absolute pressure transducer which had a pressure range of 0–15 psia. The output of the transducer was recorded on a recording oscillograph. Further details concerning the experimental equipment are available elsewhere (*14–16*).

Materials. The catalyst used in these studies was Houdry Hard Alumina grade

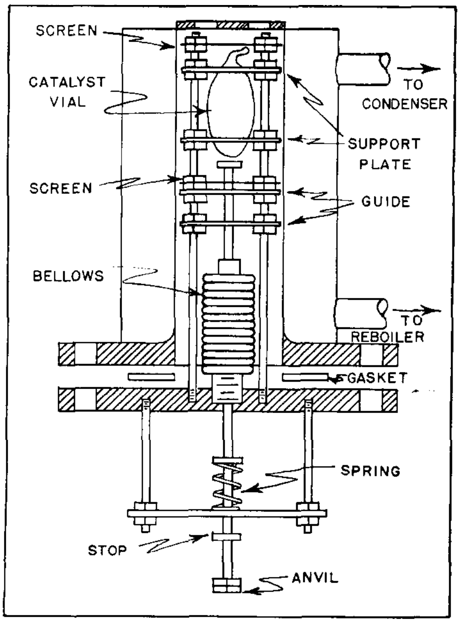

Fig. 2. Adsorption–reaction cell.

100S, received in the form of 3/32 in. diameter pellets of varying lengths. These pellets were reduced in size by means of a laboratory pulverizer and classified into the following mesh sizes: 10–20, 20–40, 40–60, 60–80, 80–100. Each sample was screened at least three times to assure good separation of the fines. The uniformity of the particle size of each size fraction was good when viewed under a microscope. The physical properties of the catalyst are shown in Table 1.

t-Butyl alcohol was obtained from Matheson, Coleman, and Bell and was shown to contain no measurable amounts of impurities by chromatographic studies. CP grade isobutylene obtained from the Matheson Co. was used. Distilled water was used in the water adsorption studies.

Catalyst activation and treatment. The desired amount of catalyst (10 g) was placed in a previously prepared capsule and heated in a constant temperature oven at the desired activation temperature under a pressure of 150–200 μm Hg for a period of 4 hr after which the bulbs were sealed. For the study on activation temperature, the catalyst was activated at 195, 275, and 400°C. Catalyst prepared in this manner has been termed "untreated catalyst."

In a series of experiments planned to improve the stability of the catalyst, water vapor at a given pressure was readsorbed on the catalyst after it had been prepared as described above. This was accomplished by admitting water vapor at 760 mm Hg into the catalyst capsule from a heated water cell. This pressure was held for a period of 2 hr and then the cell was evacuated to 150–200 μm Hg for 4 hr prior to sealing. Catalyst prepared in this way has been termed "treated catalyst." In the multicomponent studies following the exposure of the catalyst to water vapor at 760 mm Hg, the water reservoir was cooled to the temperature corresponding to the desired vapor pressure of water. This pressure was held for 4 hr after which the capsule was sealed.

TABLE 1
PROPERTIES OF HOUDRY 100S ALUMINA (*17*)

Chemical:	Al_2O_3	98.5%
	Na_2O	0.1–0.2%
Physical:	Surface area	75–85 m²/g
	Bulk density	0.78–0.82 kg/liter
	Pellet density	1.28–1.34 kg/liter
	True density	3.6–3.7 kg/liter
	Porosity	60–65 vol%
	Av pore diam	400 Å

Procedure. The sealed capsule containing the catalyst was placed in the reactor cell which was then evacuated to 150 μm Hg and tested for leaks. The adsorbate was then introduced into the cell and the cell was again evacuated; this procedure was repeated several times to reduce the residual air concentration. The cell was then brought to the desired temperature and adsorbate pressure. The capsule was then broken by striking the anvil and the cell pressure was recorded as a function of time.

DATA AND RESULTS

Preliminary Studies

Because of the exploratory nature of this work, preliminary experimentation was necessary in order to find the proper range of conditions. These exploratory studies were needed, for example, to determine the effects of particle size and catalyst treatment on the rate and quantity adsorbed.

Effect of particle size. If transport of the adsorbate to the interior of the particle is rate controlling, then it would be expected that the fine particles would exhibit a faster rate during the early part of the adsorption process. This was found to be the case for catalyst sizes ranging from 3/32 in. pellets down to 40/60 mesh. Further decreases in the particle sizes gave abnormally low rates during the first 1.5 sec. Beyond this time the quantity and the rates of adsorption were equal for all particle sizes investigated. This apparent abnormality was found to be caused by the smaller particles sticking together into a massive "ball" when the capsule was broken. Whereas, the larger particles fell freely and distributed

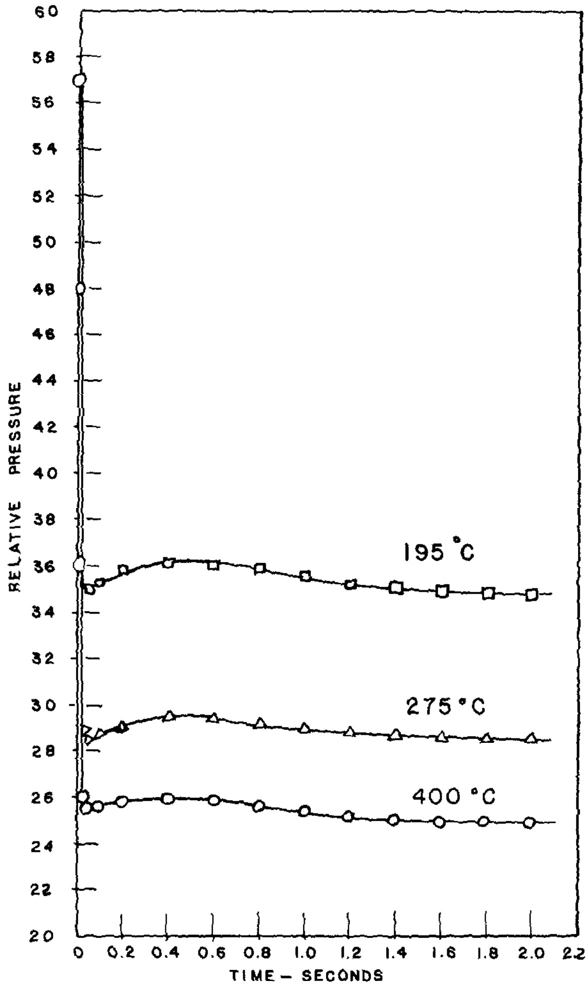

FIG. 3. Water adsorption at 195°C on untreated alumina as a function of catalyst activation temperature.

themselves uniformly on the support screen.

In view of these results, the 40/60 mesh size seemed to be optimum and was used for most of the work. In some of the runs, however, it was found necessary to use 10/20 mesh alumina because of partial disintegration of the alumina which occurred during desorption studies. Comparison of the adsorption characteristics of *t*-butyl alcohol and of water on the 10/20 mesh alumina with those observed on 40/60 mesh alumina showed negligible differences.

Influence of catalyst activation temperature. Figures 3 and 4 show the effect of catalyst activation temperature on the pressure–time relationship for water and *t*-butyl alcohol adsorbed at 195°C. The ordinate of these plots is the oscillograph scale reading which is directly proportional to the cell pressure (a reading of 51 is approximately equal to 760 mm Hg absolute). From Fig. 3 it can be seen that increasing the catalyst activation temperature results in a larger pressure drop which represents an increase in the quantity of water adsorbed.

As can be seen in Fig. 4, the fast initial pressure drop indicates that the quantity of alcohol adsorbed also increased when the catalyst activation temperature was in-

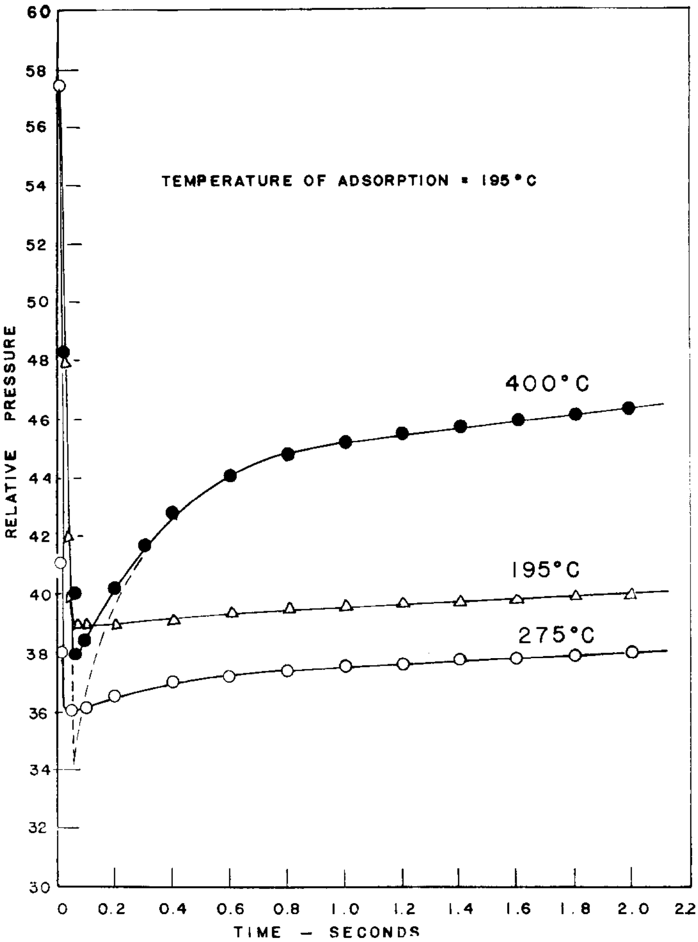

FIG. 4. *t*-Butyl alcohol adsorption on untreated alumina as a function of catalyst activation temperature.

creased from 195 to 275°C. Further increasing the temperature of activation to 400°C, results in an apparent decrease in the quantity adsorbed followed by a rapid increase in pressure resulting from the increasing number of moles in the system due to chemical reaction. Since for the system under study, the rate of pressure increase is a qualitative measure of the reaction rate, the initial reaction rate for the 400°C catalyst is several times faster than for either the 195 or 275°C catalysts. It is felt that the "minimum pressure" noted for the 400°C catalyst does not represent the true quantity of alcohol adsorbed because of the very fast simultaneous chemical reaction on this active catalyst. Thus, the results for *t*-butyl alcohol are qualitatively the same as for water, an increase in catalyst activation temperature causes an increase in the quantity adsorbed.

Note from Figs. 3 and 4 that the time required for the "minimum pressure" to be reached is apparently not a function of the quantity adsorbed over the range investigated. Comparison of these data also shows that this time is the same for both adsorbates. Both of these observations are further evidence that transport is not a controlling mechanism during the adsorption process under the conditions studied here.

Isobutylene adsorption. Preliminary studies to determine the extent to which isobutylene was adsorbed on alumina at 195°C showed that the quantity adsorbed was small compared to the values for water and alcohol on the same adsorbant. For an activation temperature of 400°C only 0.084 mg mole/g was adsorbed at 640 mm Hg while for alumina activated at 195°C only 0.075 mg mole/g was adsorbed at 650 mm Hg. The initial adsorption of isobutylene was quite rapid, on the order of 0.02 sec or less and accounted for about 65% of the total amount observed. Because the amount of isobutylene adsorbed was relatively small compared to the quantities of the other components, further studies were not deemed necessary for the purpose of this work.

Adsorption of Water on Alumina

Water sorption on untreated alumina. Adsorption of water on alumina was found to occur in two very distinct rate periods; an initial, extremely fast adsorption which occurred in less than 0.1 sec followed by a period of much slower adsorption which was essentially complete in 10 to 15 min, depending upon the pressure level. Figure 5 illustrates this behavior where 82% of the total adsorption occurred in less than 1 sec, less than 0.1% of the time required for the entire adsorptive process. It is believed that two distinct processes are occurring. In this work, the term "fast adsorption" refers to the quantity adsorbed up to the point where the pressure response curve shows a definite break as shown in Fig. 5.

The quantity of water adsorbed on untreated catalyst by the fast process is shown as curve 1 on Fig. 6 and the total amount adsorbed is shown as curve 2. The fast adsorption amounts to about 65% of the total adsorption; the difference between the total amount and the quantity of fast adsorption at the same pressure has been termed "slow adsorption" and is shown as curve 3 on Fig. 6. It should be recognized that the water isotherms reported here are relative isotherms and that the quantity adsorbed is in addition to the amount of water remaining on the surface following the activation procedure and which can be totally removed only by heating to very high temperatures.

After the cell pressure had reached a steady value and remained constant for approximately 30 min, a series of stepwise desorptions was carried out. The desorption data are represented as curves A through

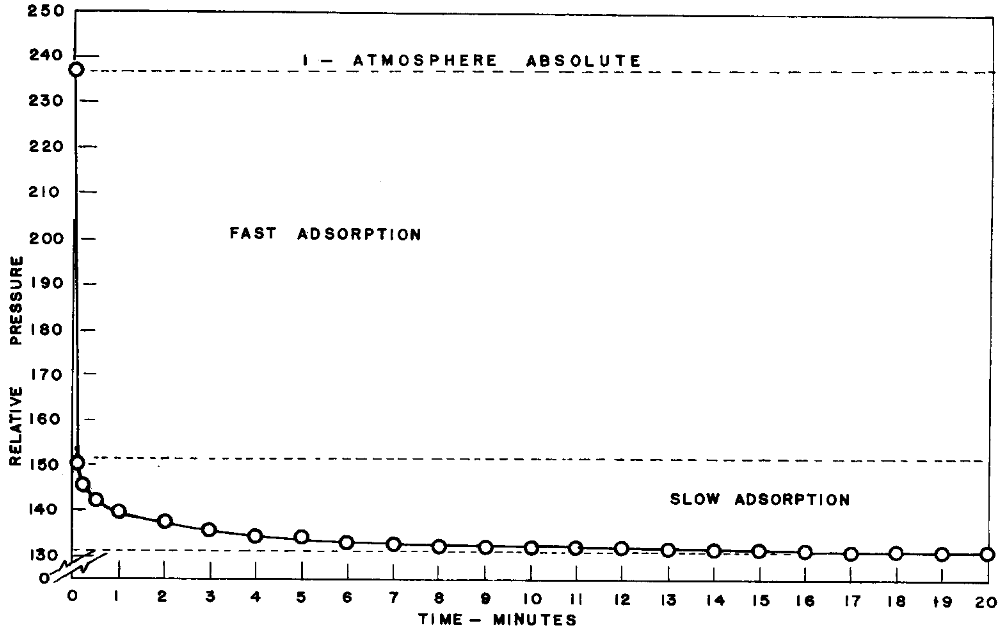

FIG. 5. Adsorption of water on alumina at 195°C.

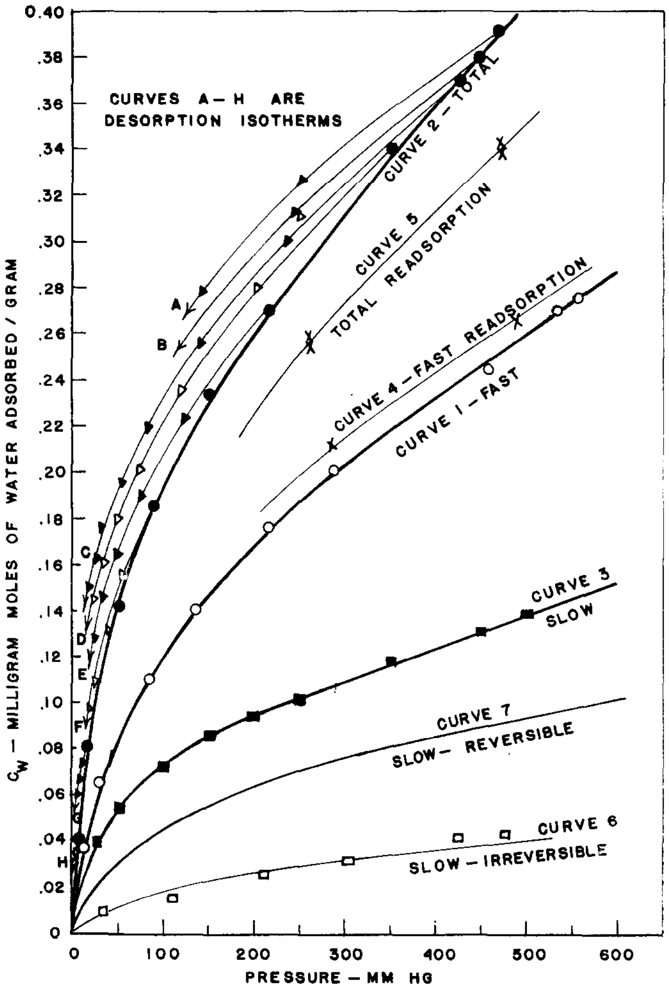

FIG. 6. Water isotherms at 195°C on untreated alumina activated at 195°C.

H on Fig. 6. The desorption process was also observed to occur at two different rates, a rapid desorption which occurred in 1 sec or less followed by a slower process which in some cases continued up to 1 hr. The points shown on curves A–H of Fig. 6 represent the quantity remaining on the surface after desorption had been occurring for a period of 10 to 15 min, the time when the recorded cell pressure had become essentially constant. In one experiment the desorption was continued for 2 hr and it can be seen from the data of Table 2 that about 89% of the quantity which could be desorbed in 2 hr is released almost instantaneously, that an additional 8% comes off over the next 10 min period, leaving only 3% which is removed over the last 110 min period. Based on these data, it is concluded that the desorption data shown in curves A through H in Fig. 6 are for the purposes of this work, a close approximation to equilibrium desorption values for untreated alumina.

From Fig. 6 it can be noted that the adsorption–desorption isotherms are not entirely reversible and the desorption isotherms are a function of the level of adsorption reached prior to the start of desorption. This hysteresis effect is believed to be the result of an irreversible adsorption which occurs on the untreated alumina.

TABLE 2
DESORPTION OF WATER AT 195°C

	Surface concn (mg mole/g)	Quantity desorbed in increment (mg mole/g)	Total quantity desorbed (mg mole/g)
At end of 15 min adsorption	0.380	—	—
Immediate desorption (less than 1 sec)	0.318	0.062	0.062
After 10 min desorption	0.312	0.006	0.068
After 120 min desorption	0.310	0.002	0.070

In one of the experiments shown on Fig. 6 (curve A) after allowing desorption to proceed for a period of 2 hr, water was readsorbed on the catalyst. Following this readsorption the total surface concentration was calculated to be 0.392 mg mole H_2O/g of alumina compared with data taken on untreated catalyst which gave a value of 0.390 mg mole/g at the same pressure. These results show that only the portion of the adsorbant removed by desorption is reversible.

In another of the experiments following the adsorption–desorption cycle discussed above, the alumina in the reactor cell was subjected to the same activation conditions used for the untreated alumina. Following this *in situ* activation, the adsorption procedure was repeated; the data obtained are shown as curves 4 and 5 on Fig. 6. Here, the total quantity readsorbed is less than the concentrations observed on untreated catalyst. The difference between curves 2 and 5 represents the amount of irreversible adsorption that has occurred. Data for the amount of irreversible water obtained in this manner agrees very favorably with the data from the desorption studies. Curve 6 was constructed with data from both sources and is a representation of the amount of irreversible water. The pressure dependence is evident from this plot.

A comparison of the amount of water desorbed in 1 sec or less with the amount of fast adsorption noted on "untreated catalyst" between the same pressure levels showed that these quantities were nearly equal, indicating that the water which goes on quickly is also easily removed. Curve 4 is the amount of fast water noted on reactivated alumina which compares fairly well with the quantity found for "untreated catalyst." Because of the experimental technique involved in carrying out the readsorption studies, it is felt that curve 4 is probably too high and should be nearer curve 1.

Based on the above, it is concluded that most of the irreversible adsorption involves a portion of the slowly adsorbed material on untreated catalyst. Curve 7 of Fig. 6 is the difference between the amount of slow adsorption observed and the quantity of irreversible adsorption and represents an estimate of the amount of slow adsorption which is reversible.

Water sorption on treated alumina. In view of the complications arising from irreversible adsorption on untreated alumina, it was decided to examine the reversibility of adsorption of water on catalyst which had been previously treated with water. Studies were made on alumina which had been exposed to a water vapor pressure of 760 mm Hg at 195°C. Following this treatment, the alumina was evacuated at 195°C and a pressure of 150 μm Hg for a period of 4 hr. Catalyst prepared in this manner has been termed "treated alumina." This procedure is essentially the same treatment used by Dague (*18*) and Cutlip (*19*) in their fixed-bed studies of dehydration of *t*-butyl alcohol.

The adsorption on "treated catalyst" was found to be similar to the adsorption on "untreated alumina" except that the quantity adsorbed was less and no irreversible adsorption was noted. Data for this material are shown in Fig. 7. Correlation of the data was attempted by using several of the well-known adsorption isotherms; only the Freundlich equation gave a reasonable fit and the correlation is illustrated in Fig. 8.

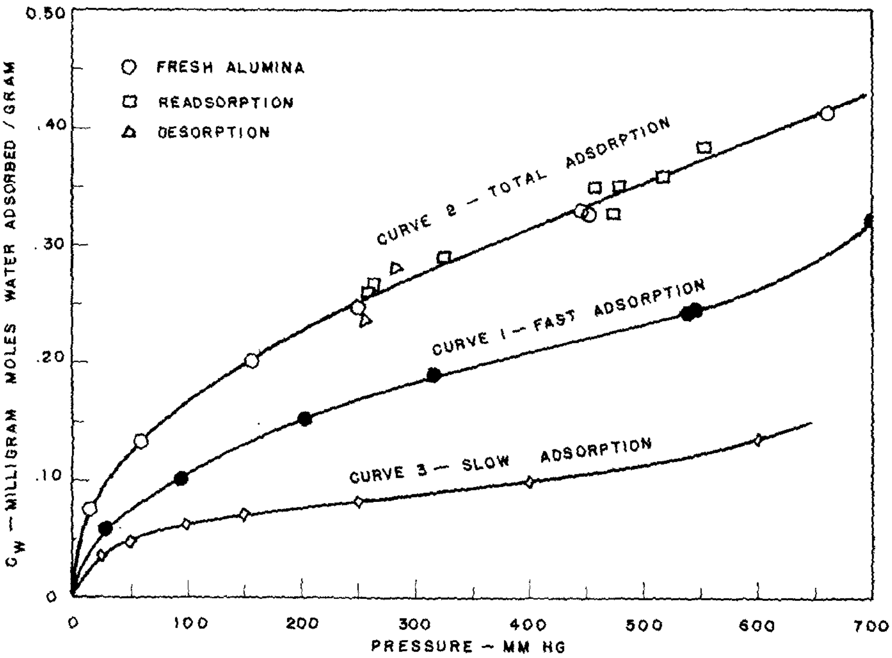

FIG. 7. Water isotherm at 195°C on treated alumina.

The empirical correlations shown must be considered only approximations since from the definition of the three types of water adsorption it is evident that mathematically the Freundlich equation cannot be used to represent all three types except in the limited case when the power terms are equal, which is not the case here.

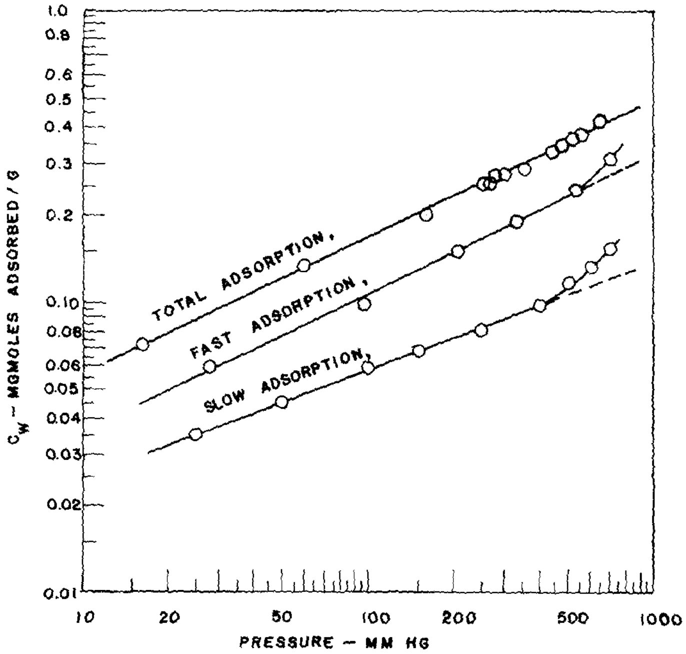

FIG. 8. Correlation of water isotherms at 195°C on treated alumina.

t-Butyl Alcohol Adsorption

Alcohol adsorption studies were made on alumina at 195°C and pressure up to 600 mm Hg. The studies can be divided into three areas depending upon the prior treatment of the alumina. The data are summarized in Fig. 9.

When alumina activated at 195°C and 150 μm Hg was exposed to *t*-butyl alcohol vapor at 195°C, a rapid adsorption was observed to occur in less than 0.3 sec. Following this initial adsorption, the cell pressure was observed to increase as would be expected due to the chemical reaction. The quantity adsorbed on untreated catalyst is shown in Fig. 9. It should be noted that only fast adsorption could be observed for alcohol as measured by this method. While the existence of a slower process similar to that observed in the case of water might be expected, it could not be detected here if the chemical reaction rate was comparable to the slow adsorption rate. As discussed below, it seems unlikely that slow adsorption is present in this case.

Because of the observed dependence of the amount of water adsorbed on alumina on the method of pretreatment, alcohol adsorption studies were also made on treated alumina; the results are also shown in Fig. 9. As before, the prior exposure of the alumina to water vapor has reduced the quantity of alcohol adsorbed.

In order to obtain a quantitative measure of the effect of adsorbed water on the adsorption of *t*-butyl alcohol, several experiments were made with treated alumina, which after activation, had been exposed to and maintained at known water vapor pressures. To minimize the effect of further

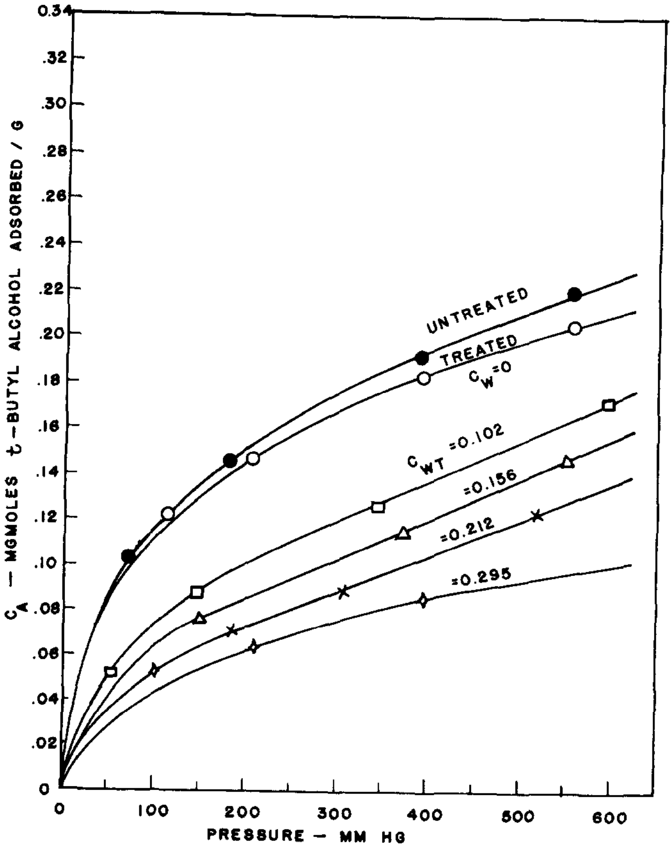

FIG. 9. *t*-Butyl alcohol isotherms at 195°C.

water desorption or adsorption upon contact with the alcohol vapor, the vapor composition in the adsorption cell prior to breaking the capsule was adjusted so that the partial pressure of water in the cell was equal to the pressure in the catalyst capsule. It was assumed then, that with no gradient for water vapor pressure, that the drop in total pressure was a measure of the amount of alcohol adsorbed. The results of these studies are also shown on Fig. 9. The quantity of preadsorbed water is shown as a parameter of the curves. As in the case of water, the Freundlich equation was found to represent the alcohol data as shown in Fig. 10.

One of the significant results of these experiments was that the rate of adsorption of alcohol in these studies was just as fast as the adsorption noted for evacuated capsules containing catalyst. The fact that the presence of water vapor in the capsule (up to 343 mm Hg pressure) did not affect the rate of alcohol adsorption presents significant evidence that transport of the adsorbate is not rate controlling under the conditions used in this work.

In an attempt to determine the quantitative effect that the adsorbed water had on the quantity of alcohol adsorbed, plots of concentration of adsorbed alcohol versus the concentration of water were prepared. Three such plots are possible depending upon which water isotherm is used. An example plot for total water is shown in Fig. 11. Similar curves were obtained for slow and fast water. It was hoped that these plots would help to distinguish which type of water affected the alcohol adsorption the most, but because of the relationship that exists between the water isotherms, i.e., $C_{ws} = 1/3C_{wt} = 1/2C_{wf}$ no clear distinction could be made. It can be noted from Fig. 11 that at the higher alcohol pressures the concentration of alcohol seems to be a linear function of the concentration of water. At the lower pressures this relationship becomes quite nonlinear.

Attempts to correlate the mixed adsorption data using various theoretical equations did not give satisfactory results. The data were found to fit a semiempirical representation based in part on Glueckauf's work (*20*). As can be seen in Fig. 12, the data can be represented very well by single

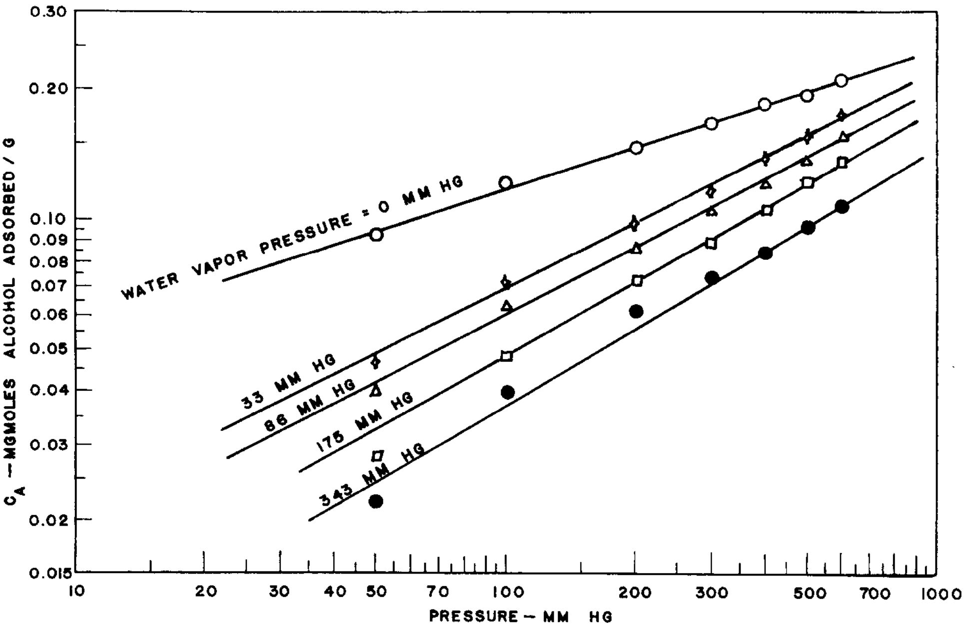

FIG. 10. Correlation of *t*-butyl alcohol isotherms at 195°C on treated alumina.

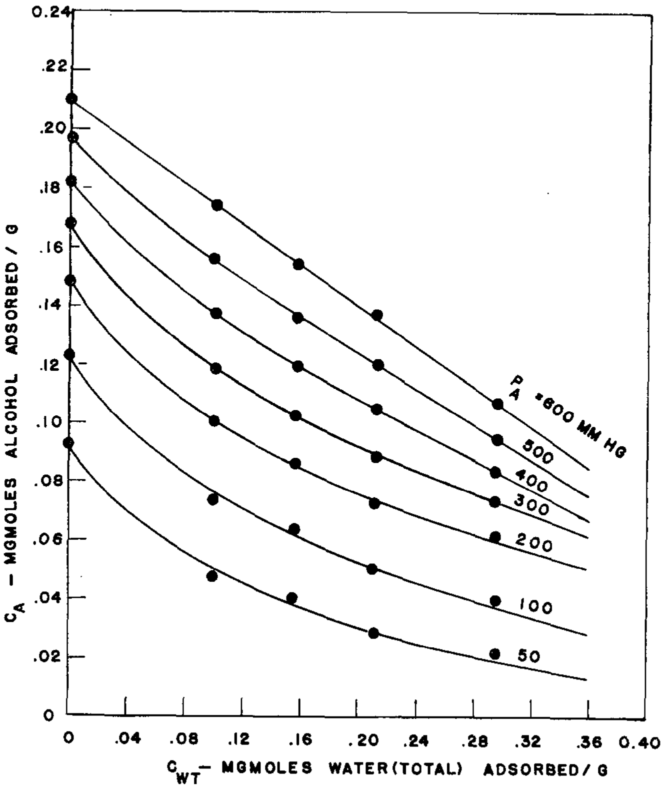

FIG. 11. Effect of total water adsorbed on the quantity of *t*-butyl alcohol adsorbed at 195°C.

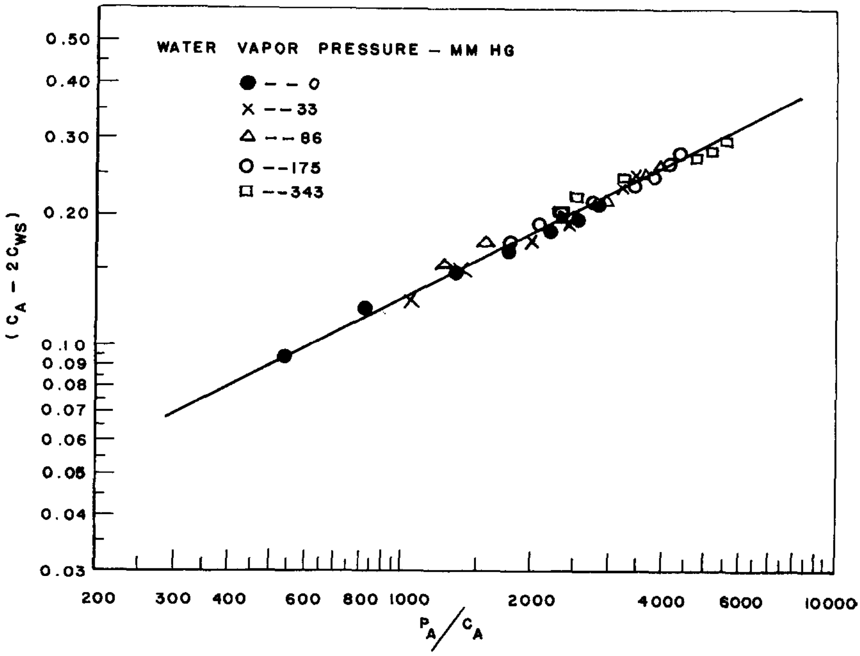

FIG. 12. Correlation of mixed isotherms with modified form of Glueckauf's equation.

equation. The meaning of this representation is not clear at this time and since it is not germane to the major message of this paper, further discussion is not given here.

Kinetic Rate Equation and Correlation Based on Adsorption Data

Although several models were envisioned to describe the kinetics of the dehydration of *t*-butyl alcohol, it was found that the simplest of these models correlated the data best. This correlation is based on the following premises or assumptions.

1. The reaction rate is proportional to the concentration of the adsorbed alcohol (which is influenced by the amount of water adsorbed).
2. The rate is also proportional to a reactive property of the surfaces, L, which is a measure of the reaction surface which is available.
3. The reactivity of the surface is decreased by the adsorption of water.

Mathematically these premises can be expressed as:

$$r = kC_aL, \tag{2}$$

$$L = (L_0 - C_w), \tag{3}$$

$$r = kC_a(L_0 - C_w). \tag{4}$$

Equation (4) has two constants, k and L_0, to be evaluated. There are two approaches, not wholly independent, which can be taken to evaluate these constants.

Extrapolations of the mixed adsorption isotherm correlations indicated, that under the conditions studied, that the quantity of adsorbed alcohol would become zero when the quantity of adsorbed water was between 0.40 to 0.60 mg mole/g. Based on the above model, this would indicate that the value of L_0 should lie between 0.40 to 0.60 mg mole/g.

In the second approach both k and L_0 are constants which can be evaluated from the fixed-bed rate data. Rearranging Eq. (4) results in:

$$\frac{r}{C_a} = kL_0 - kC_w, \tag{5}$$

indicating that a plot of the reaction rate divided by the concentration of adsorbed alcohol should be a linear function of the quantity of adsorbed water. A preliminary plot of the data in this manner indicated the value of L_0 is between 0.40 and 0.45 mg mole/g with corresponding values of k between 0.069 and 0.053 (g mole)(g)/(hr)(mg mole)^2.

Having approximate values for k and L_0, an iterative evaluation was performed to find the values of k and L_0 which gave the best fit of the fixed-bed data. Values for k and L_0 were assumed and the rate equation was evaluated at various conversion levels, using the adsorption data for water and alcohol from Fig. 11 to give values for C_a and C_w. Integral conversion data were then evaluated by the numerical integration of:

$$\frac{W}{F} = \int \frac{dx}{r}. \tag{6}$$

The results of the integration were compared to the fixed-bed data of Dague (*18*) and Cutlip (*19*). The best correlation was obtained with values of:

$$k = 0.0525 \frac{(\text{g mole})(\text{g})}{(\text{hr})(\text{mg mole})^2},$$

$$L_0 = 0.450 \text{ mg mole/g},$$

or

$$r = 0.0525C_a\,(0.450 - C_{\text{wt}}). \tag{7}$$

Comparison of the calculated conversion based on Eq. (7) and the fixed-bed data is given in Fig. 13. The solid curve is Eq. (7) while the points are from the fixed bed data. The broken lines labeled A and B represent the upper and lower limits of the values of k and L_0 investigated.

In the correlation above, the total water concentration C_{wt} was used. Equation (4) was also evaluated using both the fast water concentration, C_{wf}, and the slow water concentration, C_{ws}. The resulting correlations were equally good as illustrated by Fig. 14 which is based on the slow water equation:

$$r = 0.22C_a\,(0.13 - C_{\text{ws}}). \tag{8}$$

It was hoped that the results of the

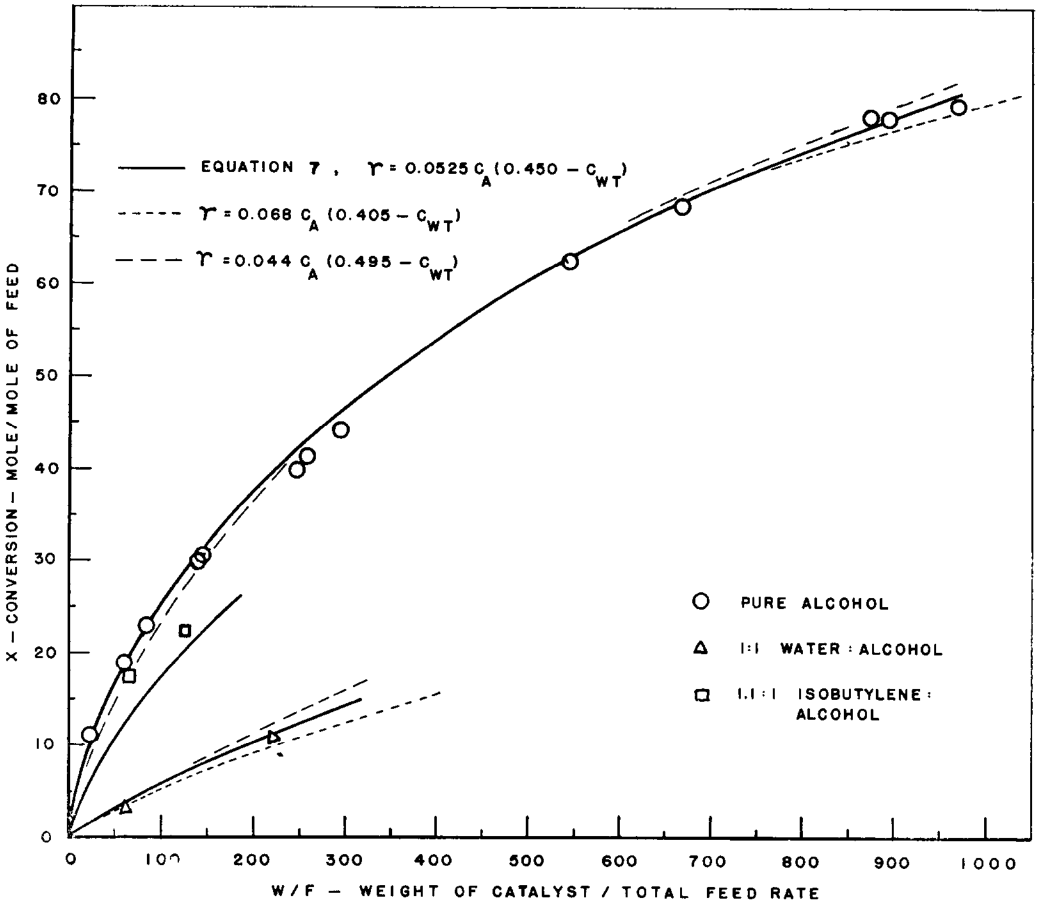

FIG. 13. Comparison of fixed-bed data (*18*, *19*) with Eq. (7).

kinetic correlation would shed some light upon which type of adsorbed water (fast or slow) was more important in the surface reaction. Unfortunately because of the mathematical relationships that exist between the three isotherms for adsorbed water, no clear distinction could be made as to which was more important to surface catalysis. This is discussed in greater detail below.

DISCUSSION

Water adsorption. The observation that adsorption of water on alumina occurs at two distinct rates suggests that two types of adsorption are present, which is in agreement with the results obtained by others. While it is difficult to determine conclusively the nature of each of these types of adsorption, i.e., chemisorption or physisorption, some speculations can be made. Both DeBoer *et al.* (*21*) and Cornelius *et al.* (*22*) have reported that the adsorption of water occurs by three basic processes—formation of a chemisorbed layer, followed by a strongly physisorbed monolayer on top of the chemisorbed layer, followed by multilayer adsorption. Cornelius and co-workers reported the capacity of the chemisorbed layer on alumina to be 21 mg $H_2O/100\,m^2$ while DeBoer *et al.* indicated the capacity to be 25 mg/100 m^2. DeBoer *et al.* also showed that the physisorbed layer should have a capacity of about 25 mg/100 m^2. It is estimated, based on surface area, that the capacity of the chemisorbed layer is approximately 19 mg/g for the alumina used in these studies.

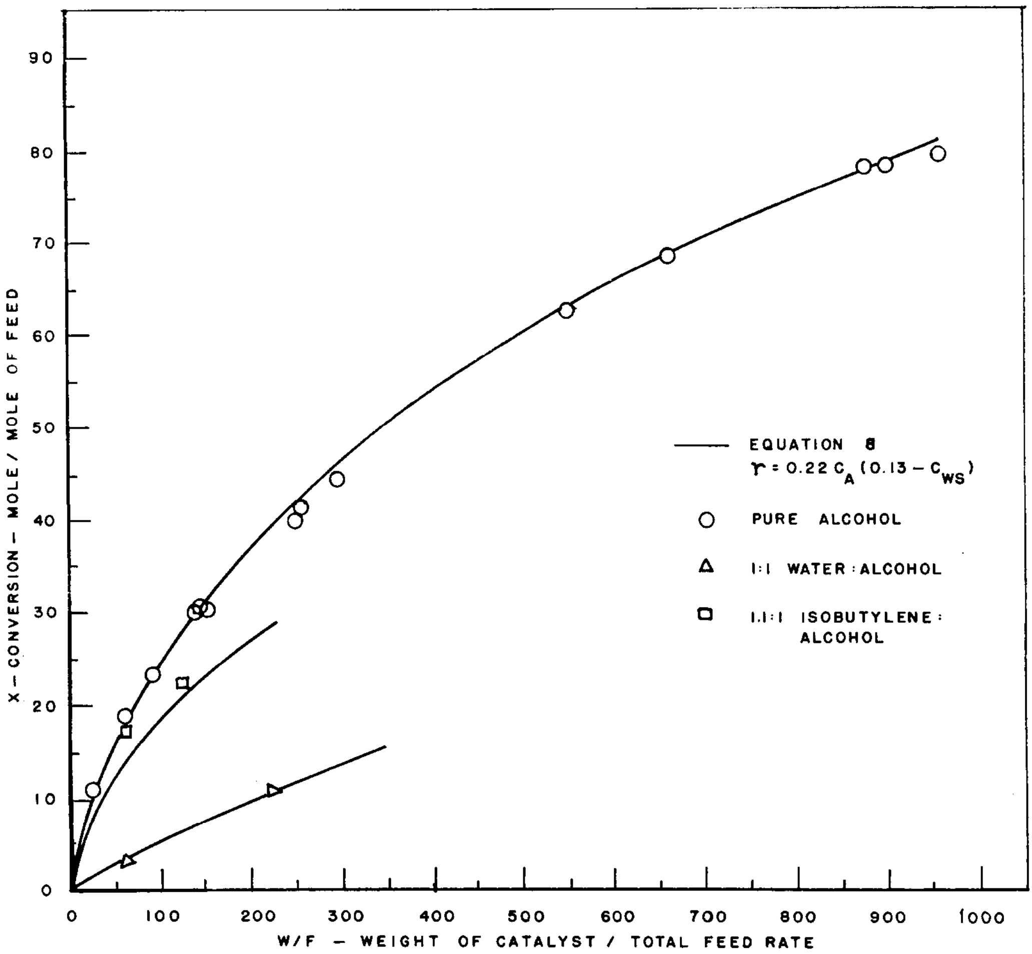

FIG. 14. Comparison of fixed-bed data (*18*, *19*) with Eq. (8).

From the data of Cornelius *et al.* it is estimated that the untreated catalyst has residual water content of about 16 mg/g. The difference represents about 0.16 mg mole/g which agrees well with the maximum amount of slow adsorption noted in this work which is estimated to be in the range of 0.16–0.18 mg mole/g.

Based on the data of DeBoer *et al.*, it is estimated that the total capacity of the chemisorbed and strongly physisorbed monolayer for the alumina used here is about 2.1 mg mole/g. Since the maximum amount adsorbed in these studies was 1.34 mg moles it is believed that only these two types of adsorption were observed. Probably the fast adsorption represents strong physical adsorption (a weak chemisorption) while the slower process represents chemisorption.

The adsorption of water based on the above can be pictured as taking place with the fast adsorption as physisorbed water on top of the residual chemisorbed water. This is followed by a slower process which represents the transition of part of the physisorbed water on to the unfilled chemisorption sites. The nature of the small amount of irreversible adsorption noted when the "untreated alumina" is treated in the presence of water vapor at 760 mm Hg is not clear. It seems unlikely that this irreversibility results from capillary condensation because of the low relative pressure P/P_0 of 0.035 or less used in these studies. A more probable cause is that some type of surface reaction, possibly formation of a hydrated complex, has occurred. Brey and Krieger (*25*) found that a crystallographic change occurred when alumina was heated in the presence of water vapor as evidenced by a sharpening of the alumina line on X-ray analysis. Cornelius *et al.* also observed some hysteresis in their studies which they attributed to the slow approach to equilibrium.

t-Butyl alcohol adsorption and reaction. In accordance with the previous discussion, it seems plausible that the adsorption of alcohol occurs as physisorption as the first step. The dehydration reaction then proceeds with the transition of the alcohol molecules from this state to the active sites which are located in the unfilled chemisorbed layer. The rate at which alcohol proceeds from the precursor state to the reactive sites would be proportional to the amount physisorbed or C_a. While the number of reactive sites would be given by $L_{0s} - C_{ws}$ so that the reaction rate would be:

$$r = kC_a(L_{0s} - C_{ws}) \tag{9}$$

which is identical to Eq. (8). As shown above, L_{0s} on the untreated catalyst can be estimated to be 0.16 mg mole/g or 0.12 mg mole/g for treated catalyst. The value obtained from the kinetic data based on slow water and which would, in effect, be treated catalyst was 0.13. The agreement is, indeed, very close.

As shown above, the quantity of alcohol adsorbed was diminished when water vapor was present. The effect of water on the reaction rate, based on the above model would be due to two factors. The first is a reduction in the amount of alcohol adsorbed in the precursor state or C_a and then second by the elimination of active sites resulting from the adsorption of water. While the above picture is speculative, it does seem to be a reasonable model which is capable of explaining the experimental results and seems to be in agreement with the proposed mechanisms for the dehydration alcohols. However, the nature of this work does not provide any additional insight into whether the reaction proceeds via the alcoholate structure as favored by Notari (*10*) or by the concerted E 2 mechanism proposed by Knozinger (*9*). The reaction site in either mechanism is created by the desorption of water from the surface and they basically differ only in whether the alcohol interacts with the resulting anion or the oxygen ion.

Further evidence that the general mechanism developed above represents the processes occurring on the catalyst is provided by the pressure–time curves for the adsorption of alcohol in the presence of water. At the highest water pressures investigated, the pressure rise following the initial adsorption of the alcohol was very small, indicating that the reaction rate was very slow as would be predicted from the above considerations. An important observation that can be made from these studies is that there was no observable pressure drop following the initial, fast adsorption in any of these studies which would have been indicative that slow adsorption of alcohol was occurring. This lends support to the contention that the analog to slow water adsorption in the case of the alcohol is the mechanism by which the dehydration reaction occurs, i.e., the transition from the physisorbed state to the chemisorbed state.

Experimental technique. There are several possibilities for experimental errors involved in the technique employed in this study. It is felt that these effects have been minimized. As discussed above, the effect of the rate of mass transfer was not important under the conditions used. Evidence of this is given by the particle size studies. Further evidence is given by the fact that the time required for fast adsorption was independent of the quantity or type of adsorbate used as well as the fact that the time required was the same for the evacuated vials as for those with up to 340 mm Hg water pressure. Although not strictly applicable to these studies, it was estimated by the procedures outlined in Satterfield and Sherwood (*26*) that mass transfer would become important at reaction rates above 3.9×10^{-5} g mole/(sec) (g) while the maximum rate observed in these studies was 1.4×10^{-6} g mole/(sec)(g).

Thermal effects due to the heat of adsorption offer another possible source of error. This would have the greatest effect on the concentration of adsorbate which has been termed fast adsorption. It was estimated that for the adsorption of water the catalyst could experience a maximum temperature rise of about 15°C. This would cause the observed fast water isotherm to be about 7% low.

One of the major questions that can be raised concerning this work is whether or not the minimum pressure noted in the alcohol adsorption studies truly represent the quantity of alcohol adsorbed. If the reaction rate were sufficiently fast, then the pressure drop would be too small. This behavior was noted in the case of the 400°C catalyst but is not felt to be the case for the 195°C catalyst used in the bulk of these studies. From Eq. (7) the maximum rate of reaction can be found to be 0.00138 mg mole/(sec)(g), which would indicate that during the period of fast adsorption (0.1 sec) that 1.38×10^{-3} mg mole of alcohol at the maximum would react. Assuming that the corresponding quantity of isobutylene is released, this would represent an error of about 0.0001 mg mole/g in the observed alcohol adsorption or an error of less than 0.5%. Further evidence can be found if we compare the observed rate of adsorption with the kinetic rate. The average rate of adsorption was calculated to be about 2 mg mole/(g)(sec) compared to the maximum rate of 0.00138 mg mole/(g)(sec) or the rate of adsorption is about 1450 times as fast as the kinetic rate. It is interesting to note that the rate of slow adsorption of water is of the same order of magnitude as the reaction rate, which seems to support the picture of adsorption–reaction presented earlier.

TABLE 3
COMPARISON OF EXPERIMENTAL DATA WITH LITERATURE VALUES—WATER ADSORPTION ON ALUMINA

Pressure (mm Hg)	Total water adsorption (mg mole/g)			
	195°C		400°C	
	This study	Cornelius *et al.*	This study	Cornelius *et al.*
100	0.190	0.185	0.424	0.421
200	0.260	0.264	—	—

Another question which can be raised concerns the time required for adsorption. In these studies the adsorption was allowed to continue until there was no detectable change in the pressure level of the cell, usually 15 to 20 min. Other investigators have reported that the adsorption of water can continue up to several days. Comparison of the data of this study with the adsorption studies of Cornelius *et al.* (*22*), resulted in very good agreement as shown in Table 3. It is felt that the isotherms reported here are close to the final, equilibrium isotherms that would be obtained after extended periods of exposure.

Some error may have been introduced into the kinetic equation by the assumption that the isobutylene adsorption could be neglected. As shown above, the amount adsorbed was small compared to the quantity of water adsorbed. It was estimated that under the conditions studied here the maximum concentration of isobutylene would amount to only 0.01 mg mole/g and the effect on the terms C_a and $(L - C_w)$ of Eq. (4) would be negligible.

CONCLUSIONS

In order to gain a better understanding of the role of adsorption in catalysis, a new experimental technique and associated apparatus has been developed for measuring the adsorption of both the reactants and products of a chemical reaction at reaction conditions. The results of these studies led to the formulation of a simple kinetic rate equation which gave an excellent correlation of fixed-bed reactor data. Although the present experimental apparatus is limited to the study of fairly simple reactions, it is believed that the techniques can be extended to the study of more complicated reactions as well as to the study of other physical–chemical phenomena involved in the overall picture of catalysis.

Following is a summary of the conclusions:

1. Water exhibits two types of adsorption on alumina. The first is a fast adsorption which occurs in less than 1 sec and amounts to about two-thirds of the total and is reversible. A slow adsorption follows the fast type and is essentially complete in 20 min. Only a part of this is reversible. The quantity irreversibly adsorbed at a given temperature is a function of the vapor pressure of water to which the alumina has been exposed.
2. Isobutylene is only slightly adsorbed on alumina at 195°C.
3. *t*-Butyl alcohol exhibits a fast adsorption and the amount adsorbed depends upon the pressure and the quantity of water adsorbed.
4. The adsorption isotherms of both water and alcohol can be represented by a Freundlich equation over part of the range of conditions. A modified form of Glueckauf's equation was capable of correlating the mixed adsorption of alcohol and water.
5. A simple kinetic equation employing adsorption measurements gave an excellent correlation of fixed-bed kinetic data.
6. Based on these studies, a relatively simple model of adsorption and reaction was proposed.
7. The rapid response adsorption technique used in these studies can provide a better understanding of the various physical and chemical processes involved in catalysis. Adsorption data and improved models should result in better catalysts and improved reactor design and performance.

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