Significance of Adsorption Equilibrium Constants of Rate Equations Involving Solid Catalysts

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It has been well established that the adsorption of one or more reacting component gases on a solid surface is essential and responsible for the catalysis of gaseous reactions. Mathematical models for expressing surface reaction rates have usually been based on measurements of the overall changes in a differential flow reactor, which come from terminal conditions by assuming equilibrium adsorption or no adsorption of the individual components with values of adsorption constants obtained indirectly from such data (*1*, *2*). The many phenomena associated with reactions catalyzed by solids, such as resistances imposed by mass and heat transfer within catalyst pellets, and in the ambient gas stream as well as changes in catalyst activity make model building based upon overall reaction rates alone unsatisfactory. Several different experimental procedures should be used to establish these separate effects. It is also well recognized that the many phenomena associated with reactions catalyzed by solids become so complex that mathematical equations arrived at empirically, with the range of experimental variables, are used in process design rather than mathematical models based upon rate-controlling steps.

In developing mathematical models for surface reaction rates catalyzed by solids, rarely have separate experiments been made on rates of adsorption and equilibrium adsorption constants and surface coverage of the separate components. Two exceptions are reported herewith.

Kabel and Johanson (*3*, *4*) studied the catalytic vapor phase dehydration of ethanol over an ion exchange resin. They performed both kinetic and separate adsorption experiments. In this system they found that the adsorption equilibrium constants of ethanol and water, obtained indirectly from overall reaction rates, agreed with those obtained from static adsorption experiments of the separate components. For the catalytic dehydration of isopropylether with an alumina catalyst, Inoue and co-workers (*5*) found a region of experimental conditions wherein the equilibrium constants for the adsorption of water showed good agreement in the two methods.

It may also be important that a distinction should be made between surface coverage obtained at equilibrium conditions and at steady state conditions. Where the relative resistance to adsorption of a component is high, compared with the resistance of the overall surface reaction, some time will elapse in obtaining a steady state and the extent of surface coverage of the component in question is less than the coverage at equilibrium adsorption.

Thus it is the purpose of this paper to establish the relationship between the equilibrium surface coverage and the surface coverage at the steady state and to discuss the important variables which influence these two quantities.

FORMULATION OF THE RELATIONSHIP

To develop the above relationship, the data presented by Kabel and Johanson (*3*, *4*) were employed. They reported that in the vapor phase catalytic dehydration of ethanol with an ion exchange resin in a flow reactor, a surface reaction is the rate-controlling step. They also reported that the adsorption equilibrium constants of ethanol obtained from kinetic experiments and from adsorption experiments were in a good agreement. In continuation of these studies Yurchak (*6*) measured the rate of adsorption of ethanol on the same catalyst. On the basis of these data the correlation of adsorption rates, equilibrium adsorption and surface reaction rate was developed.

The catalytic dehydration of ethanol to ether and water is given by the relation

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O$$

It has been well established that the surface reaction proceeds between two ethanol molecules adsorbed on adjacent active sites to produce adsorbed water and feebly adsorbed ether, both continuously desorbed to produce gaseous water vapor and ether. For a differential flow reactor with pure ethanol feed, the rates of adsorption and desorption of ethanol and the surface reaction rate may be described by the following relationships:

$$r_A = k_A p_A \frac{C_l}{L} \tag{1}$$

$$r_A' = k_A' \frac{C_A}{L} \tag{2}$$

$$r_s = k \frac{S}{L^2} C_A^2 = k_s \frac{C_A^2}{L^2} \tag{3}$$

The net rate of adsorption of ethanol during the reaction is

$$\frac{dC_A}{dt} = k_A p_A \frac{C_l}{L} - k_A' \frac{C_A}{L} - k_s \frac{C_A^2}{L^2} \tag{4}$$

Similarly the net rate of adsorption of water is given by

$$\frac{dC_W}{dt} = k_W p_W \frac{C_l}{L} - k_W' \frac{C_W}{L} + \frac{1}{2} k_s \frac{C_A^2}{L^2} \tag{5}$$

The concentration of available sites becomes

$$C_l = L - C_A - C_W \tag{6}$$

To evaluate the surface coverage by ethanol, Equations (4), (5), and (6) are solved simultaneously. Equation (4) can be simplified for a flow type differential reactor with a pure ethanol feed at 1 atm. pressure. Otherwise the following formulation of the equations may be unwarranted. Under these specific conditions, Equation (5) may be neglected and the integration of Equation (4) yields

$$\int_0^t dt = -\frac{L}{k_A} \int_0^{C_A/L} \frac{d\left(\frac{C_A}{L}\right)}{\frac{k_s}{k_A} \cdot \left(\frac{C_A}{L}\right)^2 + \left[1 + \frac{k_A'}{k_A}\right]\left(\frac{C_A}{L}\right) - 1} \tag{7}$$

The following groups are introduced into Equation (7)

$$\frac{k_A}{k_s} = R \qquad \frac{k_A'}{k_A} = \kappa_A \tag{8}$$

to give

$$\int_0^t dt = -\frac{L}{k_A}\int_0^{C_A/L} \frac{d\left(\frac{C_A}{L}\right)}{\frac{1}{R}\left(\frac{C_A}{L}\right)^2 + (1+\kappa_A)\left(\frac{C_A}{L}\right) - 1} \tag{9}$$

Integration of Equation (9) gives

$$t = \frac{L}{k_A\sqrt{(1+\kappa_A)^2+\frac{4}{R}}} \times \ln \frac{\left[(1+\kappa_A)+\sqrt{(1+\kappa_A)^2+\frac{4}{R}}\right]\left[\frac{2}{R}\cdot\frac{C_A}{L}+(1+\kappa_A)-\sqrt{(1+\kappa_A)^2+\frac{4}{R}}\right]}{\left[(1+\kappa_A)-\sqrt{(1+\kappa_A)^2+\frac{4}{R}}\right]\left[\frac{2}{R}\cdot\frac{C_A}{L}+(1+\kappa_A)+\sqrt{(1+\kappa_A)^2+\frac{4}{R}}\right]} \tag{10}$$

From Equation (10), both the surface coverage at steady state C_{ss} and the equilibrium surface coverage C_{es} may be obtained. The surface coverage at steady state is given by the value of C_A/L when residence time approaches infinity. Accordingly

$$C_{ss} = \lim_{t\to\infty}\left(\frac{C_A}{L}\right)$$

$$= \frac{R}{2}\left[\sqrt{(1+\kappa_A)^2+\frac{4}{R}} - (1+\kappa_A)\right] \tag{11}$$

The equilibrium coverage becomes:

$$C_{es} = \lim_{\substack{t\to\infty \\ R\to\infty}}\left(\frac{C_A}{L}\right) = \frac{1}{1+\kappa_A} \tag{12}$$

CALCULATION OF C_{ss} AND C_{es}

The reaction and adsorption velocity constants for ethanol on an ion exchange resin catalyst at a temperature of 105.8°C. are reported (*6*) to be $k_s = 4.03 \times 10^{-5}$ g.-moles/(min.)(g. cat.) and $k_A = 2.83 \times 10^{-3}$ g.-moles/(min.)(g. cat.)(atm.) Hence $R = k_A/k_s = 70$. The static adsorption equilibrium constant was measured to be 8.9 at 100°C. On this basis, the values of the surface coverage C_A/L were evaluated at the various values of residence time for the different values of R and $\kappa_A = 1/9.0$ by employing Equation (10). The estimated values of C_{ss} at several values of R are tabulated in Table 1. For this system C_{es} at 1 atm. obtained from Equation (12) is equal to 0.9.

TABLE 1. ESTIMATED VALUES OF STEADY STATE SURFACE COVERAGE

R	C_{ss}
∞	0.90
70	0.89
1.0	0.59
0.1	0.27
0.01	0.09

DISCUSSION

Calculations were made to validate the assumption which was imposed on the surface concentration of water vapor. With the different values of the ratio, R, the concentration of adsorbed water was computed by solving the simultaneous partial differential equations which were obtained from the material balances of the three reaction components (ethanol, ether, and water) in the vapor phase and on the solid phase. The solution of these equations indicated the following. Even when the adsorption rate constant of ethanol is small, comparing the surface reaction rate constant, the steady state surface concentration of water is small and does not tend to build up on the surface. Of course, this is valid only for a differential reactor with a pure ethanol feed. Moreover, the surface concentration of water depends on the values of both adsorption and desorption rate constants of water. According to the reports of Kabel and Yurchak (*4*, *6*) the values of k_w and k_w' are, respectively, 2.48×10^{-2} g.-moles/(min.)(g. cat.)(atm.) and 1.82×10^{-3} g.-moles/(min.)(g.cat.) for this system. On these grounds, the use of Equation (5) is discarded.

From Equation (11) and Table 1 it is evident that the value of C_{ss} increases with the ratio of k_A to k_s. When this ratio, R, approaches infinity, the value of C_{ss} approaches the equilibrium surface coverage. The equilibrium surface coverage is obtained experimentally by independent static adsorption of the gaseous component. In this case, equilibrium and steady state surface coverage are equivalent at a surface coverage of 0.89. Consequently, the adsorption equilibrium constant obtained from kinetic data is in good agreement with the constant obtained by static experiment. The agreement may be caused by the nature of ion exchange resin catalyst used. For this special case it may be true that adsorption sites play the role of active sites for the chemical reaction. When the ratio, R, is large, equilibrium surface coverage will be readily attained in the relatively short period of residence time. On the contrary, if R is small, the equilibrium surface coverage may be unattainable.

Except for the particular studies of Kabel, Johanson, and Yurchak the significance of the so-called "adsorption equilibrium constants" in conventional rate equations (*2*) for gaseous reactions catalyzed by solids has not been well established experimentally. Such constants have usually been obtained indirectly in the correlation of experimental data on reaction rates under steady state conditions. Constants thus obtained are restricted to those sites actually participating in the reaction and may or may not correspond to sites engaged in total adsorption of the separate components in the absence of any catalytic reaction.

Kinetic studies of reactions catalyzed by solids based only upon overall reaction rates are usually not sensitive enough to establish a reliable model, or to permit discrimination among different plausible models. Reaction rate experiments should be supplemented by experiments on adsorption rates and adsorption equilibrium constants of the individual components in the absence of chemical reaction. Such supplementary experiments would establish whether or not individual components are adsorbed. If not adsorbed, adsorption constants for such components are zero and need not be further considered.

If the values of adsorption velocity constants are extremely high compared with surface reaction velocity constant, for example $k_A/k_s > 100$, the resistance to adsorption becomes negligible. In case the two velocity constants are of equal magnitude, adsorption equilibrium for that component is not attained under steady state reactions and the assumption of a single rate controlling step is invalid; both adsorption and surface reaction become rate-controlling steps.

The information supplied by such experiments would also reveal whether or not all sites or only selective sites participate in the surface reaction. Adsorption equilibrium constants obtained from reaction rate data are independent of surface coverage or have been so assumed. This indicates that only a small fraction of surface coverage is involved or that only selective sites are involved. Equilibrium constants obtained from total adsorption experiments, on the other hand, decreases with surface coverage.

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NOTATION

C_A = concentration of adsorbed ethanol, g.-moles/g. cat.
C_{es} = equilibrium surface coverage of catalyst
C_l = concentration of empty active sites, g.-moles/g. cat.
C_{ss} = surface coverage at steady state
C_w = concentration of adsorbed water, g.-moles/g. cat.
k_A = adsorption velocity constant of ethanol, g.-moles/min. g. cat.
k'_A = desorption velocity constant of ethanol, g.-moles/min. g. cat.
k_s = kS = surface reaction velocity constant of dehydration reaction, g.-moles/min. g. cat.
k_w = adsorption velocity constant of water, g.-moles/min. g. cat. atm.
k'_w = desorption velocity constant of water, g.-moles/min. g. cat.
L = total adsorption sites on catalyst g.-moles of active sites, g.-moles/g. cat.
p_A = partial pressure of ethanol, atm.
p_w = partial pressure of water, atm.
R = k_A/k_s
r_A = adsorption velocity of ethanol, g.-moles/min. g. cat. atm.
r_A' = desorption velocity of ethanol, g.-moles/min. g. cat.
r_s = surface reaction velocity of dehydration reaction, g.-moles/min. g. cat.
S = number of equidistant active centers adjacent to each other
t = residence time, min.
κ_A = k_A'/k_A

LITERATURE CITED

1. Hougen, O. A., and K. M. Watson, *Ind. Eng. Chem.*, **53**, 529 (1943).
2. ———, "Chemical Process Principles, Part III," John Wiley, New York (1947).
3. Kabel, R. L., Ph.D. thesis, Univ. Washington, Seattle (1961).
4. ———, and L. N. Johanson, *AIChE J.*, **8**, 621 (1962).
5. Inoue, H., J. Goda, and S. Yagi, *Symp. of Chem. React. Eng.*, Preprint, Tokyo, Japan, (Sept., 1963).
6. Yurchak, S., B.S. thesis, Pennsylvania State Univ., University Park, (1964).

Mass Transfer Rates for Vaporization and Gas-Phase Controlled Desorption in a Short Wetted Wall Column

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In the experimental investigation of gas absorption in packed towers, investigators have studied the absorption or desorption of highly soluble gases, the vaporization of pure liquids into inert gas streams, and the absorption of gases which undergo a rapid chemical reaction with the absorbent liquid to determine individual gas phase absorption coefficients. Gas phase coefficients have also been reported based on studies of the absorption of moderately soluble gases in which allowance was made for the liquid phase resistance by simple additivity theory. It has long been recognized that unexplained discrepancies exist in the results obtained by the different systems.

In general, the mass transfer coefficients for vaporization are significantly higher than those for absorption of a highly soluble gas, although both processes would be expected to be essentially gas phase controlled. A comparison of the data of Fellinger (*5*) for the absorption of ammonia into water with the data of Sherwood and Holloway (*8*), and McAdams, et al. (*7*) for the vaporization of water into air shows the vaporization coefficients to be higher by factors of two to three. Gas phase coefficients estimated from data on the absorption of sulfur dioxide in water (*14*), a moderately soluble gas system, are also lower than the vaporization data and agree approximately with the ammonia data. The data on the absorption of chlorine into concentrated caustic solutions (*9*) agree approximately with the vaporization data. However, considering the general scatter of packed tower data when they are obtained by different investigators using different experimental equipment, the question of the significance of these discrepancies might well be raised.

In two recently reported studies, vaporization and absorption rates have been compared in the same apparatus. Yoshida and Koyanagi (*16*) studied methanol absorption and water vaporization in a single packed column under the same controlled operating conditions with careful allowance for end effects. After correcting for the difference in diffusivity, the methanol absorption data agree quite well with the ammonia data of Fellinger and the vaporization data agree quite well with the Sherwood and Pigford correlation of the data on vaporization and rapid chemical reaction (*9*). These data are shown in Figure 1 in which all data have been adjusted on the basis of the diffusivity of water vapor in air. The absorption data expressed as the height of a transfer unit, H_G, are shown by solid lines and the vaporization data by dotted lines. It is clear that the methanol absorption rates are substantially lower than the vaporization rates. Shulman, Savini,