Mass Transport and Reaction in Sulfonic Acid Resin Catalyst: the Dehydration of *t*-Butyl Alcohol

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Kinetics of the dehydration of *t*-butyl alcohol to isobutylene were measured with a semibatch reactor containing liquid reactant and suspended particles of cation exchange resin catalyst [sulfonated copolymer of styrene and divinylbenzene (DVB)]. Effects on rate were determined for variations in temperature (58 to 76°C.), reactant water mole fraction (0.0005 to 0.10), and catalyst particle diameter (77 to 620 μ) and crosslinking (2 to 12% DVB).

Nearly anhydrous *t*-butyl alcohol failed to penetrate the shrunken network of the polymer. Reaction began only on particle peripheries, and product water penetrated the gel network and swelled it to allow penetration of the alcohol. Rate consequently increased to a maximum (about 0.5 moles/min. equivalent of catalyst $-SO_3H$ groups at 76°C.) and then decreased as water competed with reactant for catalytic sites. A spherical catalyst particle is modeled as a shrinking central core, free of reactant and water, and a swollen shell in which concentrations are independent of position and time. The model fits reaction rate and separate particle swelling data for 80 μ particles of catalyst containing 12% DVB, but it is increasingly inadequate for larger particles and catalysts of lower DVB contents.

A review of the literature of ion-exchange resin catalysis (*1*) indicates that intraparticle mass transfer often influences reaction rates, and a review of experimental diffusion-reaction studies (*2*) shows that the Thiele model is generally applicable to hydrated (swollen) resin catalysts. However several studies show unusual transport effects which are not consistent with the simple theory. Gupta and Douglas (*3*) measured rates of isobutylene hydration catalyzed by a sulfonated copolymer of styrene and divinylbenzene and calculated effective diffusivities of isobutylene having an unusual negative temperature coefficient. The result indicates that transport in the polymer matrix may be strongly dependent on the degree of hydration and therefore not entirely comparable to transport in the rigid pores of inorganic solid catalysts. Gruber and Noller (*4*) used beads of the sulfonic acid resin to catalyze hydrolysis of diazoacetic ester, concluding that product nitrogen collected in the gel matrix and hindered transport of reactant. Helfferich (*5*) noted that catalysis by resins in contact with nonaqueous solutions is often impractical because the gel structure is not swollen as it would be in water, and the interior is not accessible to reactants. Equilibria and rates of swelling in acetone are strongly affected by the presence of even small amounts of water, which may be formed, for example, by reaction of dissolved base with acidic functional groups in the resin (*5*). Macroporous resins are of practical advantage in use with nonaqueous solvents (*6*).

The research described here was an experimental study of the effects of resin structure and degree of hydration on rates of reaction in sulfonic acid resin catalyst. The reaction was the dehydration of *t*-butyl alcohol to isobutylene, which evidenced a product-induced acceleration as water swelled the polymer network to allow transport of reactant to the particle interior. The reaction was also inhibited by product water, which competed with reactant for catalytic sites, as was previously reported by Frilette et al. (*7*).

Rates of many biological reaction sequences are regulated by products competing with reactants for enzyme sites and by effectors (inhibitors and activators), which combine with enzymes to change their conformations and thereby their activities. We suggest that mass transport-reaction phenomena encountered in ion-exchange resin catalysis might have relevance not only to catalysis by enzymes supported in synthetic resins, but perhaps even to biological catalysis, since many cellular enzymes are bound within membranes which may have highly selective transport properties regulated by inhibitors and activators.

EXPERIMENTAL PROCEDURE

Catalyst Preparation

Beads of crosslinked polystyrenesulfonic acid resin catalyst (Dowex 50W, Bio Rad Laboratories, and Amberlyst 15, Rohm and Haas) were preconditioned by twice converting them to the sodium, then back to the hydrogen form, and then washing in distilled water and drying for at least 72 hr. under vacuum at 65°C. Samples were stored in sealed vials over P_2O_5 in a desiccator. Dowex 50W was supplied as nearly spherical beads, 200-400 mesh. Samples containing nominally 2, 4, 8, and 12 mole % divinylbenzene crosslinking agent (DVB) were obtained in this size range, and the 8% crosslinked resin was also obtained as 100-200 and 50-100 mesh particles. Fractions of these batches were obtained by sieving air-dried particles through standard screens. Particle diameters were determined by microscopic measurement of water swollen beads. Ion exchange capacities were determined by titration with standard base; values ranged from 4 to 5 meq./g. vacuum-dried resin.

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Reaction Rate Measurement

A schematic diagram of the apparatus is shown in Figure 1. Liquid reactant contacted suspended beads of catalyst in a stirred 500-ml. flask held in a thermostat bath at 76°C. Reaction rate was measured as the rate of isobutylene evolution which was determined with a wet-test meter. In a typical run a charge of about 250 g. of Chromatoquality *t*-butyl alcohol (Matheson, Coleman, and Bell), containing 0.011 wt. % water by the manufacturer's Karl Fischer analysis, was brought to reaction temperature and contacted with isobutylene flowing through a sparger until the solution was saturated with 1.2 wt. % isobutylene. Water in measured amounts was occasionally added before saturation with isobutylene. A timer was started as catalyst (typically 1.3 g.) was charged to the reactor, and off-gas flow was metered until approximately 10% of the *t*-butyl alcohol had reacted, equivalent to about 50 moles alcohol reacted per equivalent of sulfonic acid groups in the catalyst.

Results were obtained at 58° and 65°C. with a modified procedure. The *t*-butyl alcohol was not presaturated with isobutylene; conversions were determined by gas chromatographic analysis of liquid samples periodically drawn from the reactor until the liquid was saturated with isobutylene. Subsequent measurements relied on the off-gas metering as before. The gas chromatograph was a Hewlett-Packard Model 700 equipped with thermal conductivity detectors. The column was a ⅛-in. diam. tube, 6 ft. in length, packed with Porapak N, 80-100 mesh beads of polystyrene. The column was maintained at 185°C. and helium carrier gas flow rate was 50 ml./min. The column resolved water, isobutylene, and *t*-butyl alcohol and was calibrated with weighed standards of water in alcohol and isobutylene in alcohol.

Particle Swelling Measurement

Samples of a few resin beads in the cavity of a microscope slide were dried in the vacuum oven. The cavity was quickly filled with *t*-butyl alcohol and a greased cover glass tightly applied. After a delay of several minutes during which the sample cooled, it was placed on a heated microscope stage held at one of the previously investigated reaction temperatures. Particle diameters were measured periodically until swelling stopped. Bubbles of isobutylene were occasionally seen in contact with the particles.

RESULTS AND DISCUSSION

Preliminary Results

Neither side reaction nor uncatalyzed reaction was observed. Stoichiometry was demonstrated for the *t*-butyl alcohol dehydration reaction at 65°C. by gas chromatographic determination of isobutylene and water in the reactor. Reaction rates were independent of stirring rate and the ratio of reactant to catalyst mass, indicating effects of liquid-phase mass transfer were negligible.

Typical conversion data obtained with the semibatch reactor operating at 75.6 ± 0.3°C. are shown in Figure 2. Observations were made more frequently than is shown to provide rate data with differential conversion increments of 0.2 to 2.0 moles per equivalent $-SO_3H$ groups, corresponding to off-gas evolution increments of 0.03 to 0.30 liter. Conversion increments were smallest when rate was changing most rapidly. Repeated experiments indicated scatter in rate data within ± 15% of mean values.

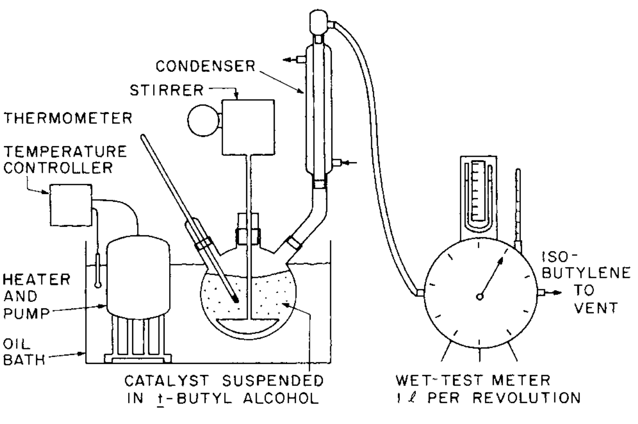

Fig. 1. Semi-batch reactor system.

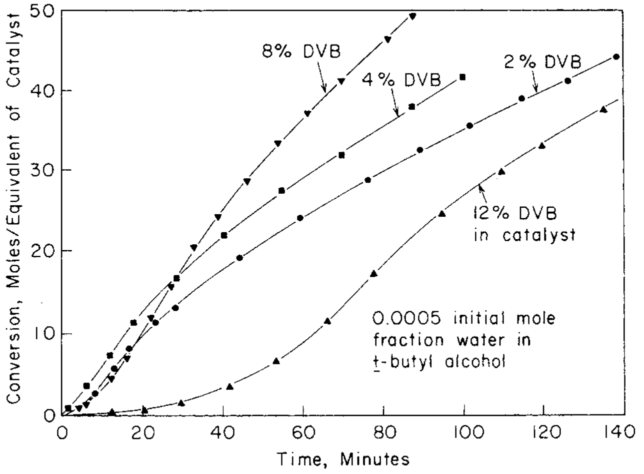

Fig. 2. Conversion of t-butyl alcohol at 75.6°C. in 200-400 mesh catalyst particles.

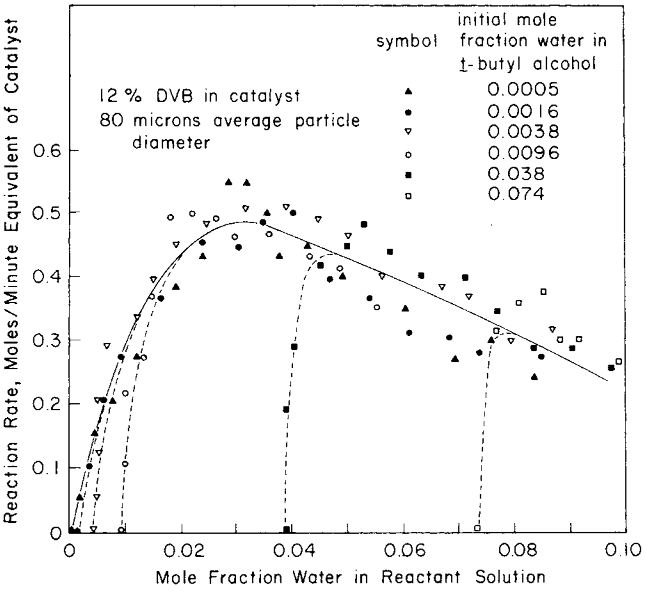

Fig. 3. Dependence of rate on water concentration at 75.6°C.

Effect of Catalyst Crosslinking

Conversion data for dehydration of nearly anhydrous *t*-butyl alcohol catalyzed by approximately 80 μ diameter particles show the effects of catalyst divinylbenzene content. The S-shaped curves of Figure 2 suggest a phenomenon akin to autocatalysis. The induction period (defined as the time to maximum reaction rate) increased from about 5 min. for resin containing 2% DVB to about 80 min. for resin containing 12% DVB; the latter catalyst has a tighter gel network and a much reduced tendency to swell.

Effects of Water

The data of Figure 3 are reaction rates for 12% crosslinked catalyst (200 to 400 mesh) with a series of initial reactant water concentrations between 0.0005 and 0.074 mole fraction. These and other data (*8*) demonstrate that for all resins water addition reduced the induction time. The effect was greatest with the 12% crosslinked resin, for which a fourfold reduction was observed. Water not only accelerated reaction initially, it also inhibited reaction as shown by the results of Figure 3; the rate data for the several initial water concentrations are represented by a single curve after the induction time is exceeded.

The two separate effects of water suggest the following interpretation. The acceleration in reaction results as water swells the resin network, reduces intraparticle resistance to mass transport, and makes an increasing fraction of the catalytic sites accessible to reactant; the inhibition by water as previously defined by Frilette et al. (7) indicates a competition between water and alcohol for the catalytic sites.

The substantial effect of initial catalyst water content was confirmed by experimental results (8) when 12% crosslinked resin containing about 20 wt. % water was charged to the reactor containing nearly anhydrous reactant; the induction time was about 20 min., compared to 80 min. for the vacuum-dried catalyst. No substantial change was observed when the vacuum drying temperature was increased from 65 to 105°C., suggesting that nearly anhydrous catalyst was normally obtained.

Effect of Particle Size

The influence of intraparticle mass transport on the period of accelerating reaction is verified by results shown in Figure 4. As average particle diameter of 8% crosslinked catalyst was increased from 77 to 620 μ, induction time increased from 20 to about 100 min. Results, at times clearly greater than the induction period, are included for the 77 and 360 μ diam. particles. Comparison of rates for these two catalysts at each of several liquid-phase water concentrations between 0.05 and 0.10 mole fraction, with the assumption of pseudo first-order reaction, yields approximate effectiveness factors of 1.0 for the 77 μ and 0.6 for the 360 μ particles, respectively.

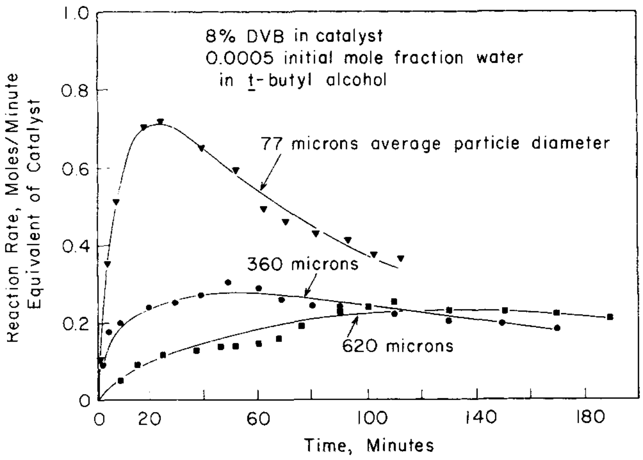

Fig. 4. Dependence of rate on catalyst particle size at 75.6°C.

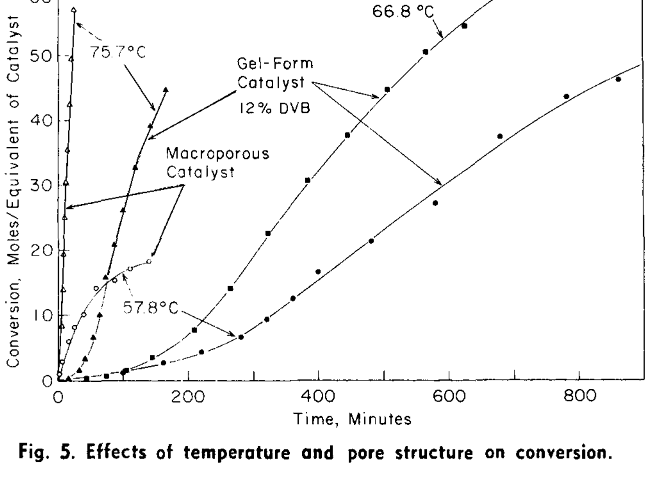

Fig. 5. Effects of temperature and pore structure on conversion.

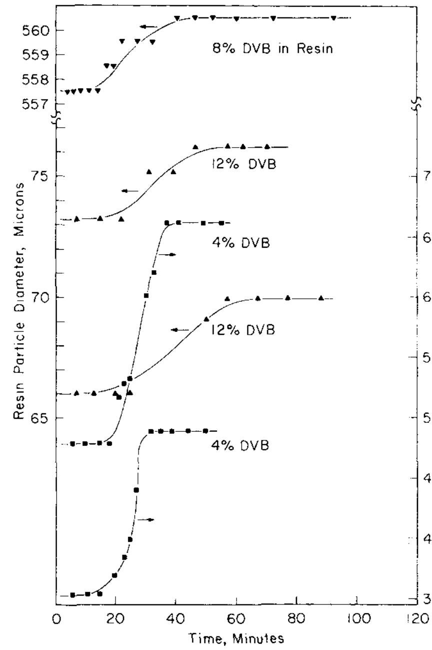

Fig. 6. Swelling of single resin particles in t-butyl alcohol at 76°C.

Effect of Temperature

Conversion data for 200 to 400 mesh particles of 12% crosslinked catalyst are shown in Figure 5. The induction time increased fivefold as temperature was decreased from 76° to 58°C. This strong temperature dependence indicates that the initial mass transfer-induced acceleration is dependent on the occurrence of chemical reaction and is further evidence that the acceleration is caused by swelling of the catalyst by water produced in the reaction. Rate data for times beyond the induction period at any water concentration between 0.03 and 0.07 mole fraction yield approximately linear Arrhenius plots (8) and an apparent activation energy of about 23 kcal./mole.

Resin Swelling

Representative data for particle swelling during reaction are presented in Figure 6. Swelling was accompanied by increasing reaction rate over roughly the same period (Figures 2 and 4). For the smallest particles (80 μ average diameter) of the most highly crosslinked catalyst (12%), the maximum reaction rate occurred at nearly the same time the particles were completely swollen. As degree of crosslinking and particle size were increased and temperature decreased, the time for particle swelling became greater, very roughly paralleling the induction time in reaction. The maximum swelling decreased strongly with increased crosslinking: volume increase was 2.6-fold for 4% crosslinked resin and only 1.1-fold for 12% crosslinked resin.

Effect of Macropores

Amberlyst 15, which presumably contains about 20% divinylbenzene, differs from the other resins in containing macropores within the gel network. The pores are of the order of 300Å in diameter, and the internal surface area is about 40 sq. meter/g. (9). Many of the interior sulfonic acid groups of a macroporous particle are initially accessible to anhydrous *t*-butyl alcohol, which according to the preceding results does not swell the gel network. This accessibility is evidenced by the catalyst performance (Figure 5): there is virtually no induction period. The macroporous catalyst is clearly of practical advantage in reactions such as alkylations, since reactants fail to swell the network and since water, which would cause swelling, simutaneously would inhibit reaction (*6*, *10*). The macroporous resin has been used to measure initial reaction rates in the absence of transport effects and reaction-inhibiting water; results are given with discussion of the bonding of *t*-butyl alcohol and water to sulfonic acid groups and the mechanism of the dehydration reaction (*11*).

SHRINKING CORE MODEL

The preceding interpretation of catalyst swelling and inhibition by product water suggests a simplified mathematical representation. The following is a statement of the model, restricted by simplifying assumptions to only the smallest particles of the most highly crosslinked resin studied.

Anhydrous *t*-butyl alcohol in contact with anhydrous sulfonic acid resin catalyst does not by itself swell the resin, and reaction begins with only the sulfonic acid groups on the periphery of a catalyst particle being effective. At low conversions a constant fraction of the water formed by reaction is assumed to be transferred to the liquid phase; the remaining water is combined by strong hydrogen bonds into the network of hydrogen-bonded anhydrous sulfonic acid groups (*12*). This process swells the sieve-like matrix and allows transport of alcohol between the polymer chains. There is assumed to be a distinct boundary between completely swollen and unswollen matrix in a spherical particle, with the rate of decrease of the unswollen central core volume proportional to the rate of water generation in the surounding shell. The assumption thus implies that the concentrations of *t*-butyl alcohol and water in the shell are independent of time and position as the swelling occurs. This description accounts for the initial acceleration of reaction but not for the subsequent deceleration; the latter is accounted for by the postulate that after the particle is swollen, part of the water produced in the catalyst remains weakly bonded in the hydrated network without further swelling it. Water concentration then increases with time and increasing inhibition results from the competition between water and alcohol for catalytic sites.

The assumption of uniform concentration in the shell during swelling is clearly not applicable to the larger particles of 8 and 12% crosslinked catalyst, but the approximate effectiveness factor of unity for the swollen 77 μ particles of 8% crosslinked catalyst suggests the assumption is applicable to the smallest particles studied. The assumption of a sharp moving boundary may have broad applicability in swelling of polymers according to Helfferich, who summarized the brief literature (5). The assumption may become less realistic as resin crosslinking is decreased since the degree of maximum swelling increases considerably with decreasing crosslinking, and there would be increased competition between the unswollen core and the only partly swollen shell for water produced in the shell.

The model is formulated for spherical catalyst particles of one size (Figure 7). During the swelling regime ($t \leq t_s$) the rate of reaction is proportional to the fraction of sulfonic acid groups on particle peripheries plus the fraction in the swollen shells

$$\mathbf{r}N_c = \mathbf{r}_{\text{shell}} N_c \left[1 - (1-\gamma)\left(\frac{r_c}{r_{p0}}\right)^3 \right] \tag{1}$$

The reaction rate determines the rate of shrinking of the internal core.

$$-4\pi N_p r_c^2 \frac{dr_c}{dt} = \frac{\alpha N_c \mathbf{r}_{\text{shell}}}{\rho w} \left[1 - (1-\gamma)\left(\frac{r_c}{r_{p0}}\right)^3 \right] \tag{2}$$

This equation is integrated with the condition that the core radius is initially equal to the particle radius:

$$\frac{4}{3} N_p \frac{\pi r_{p0}^3}{(1-\gamma)} \ln \frac{1-(1-\gamma)\left(\frac{r_c}{r_{p0}}\right)^3}{\gamma} = \frac{\alpha N_c \mathbf{r}_{\text{shell}} t}{\rho w} \tag{3}$$

When this result is combined with Equation (1) the reaction rate is determined as

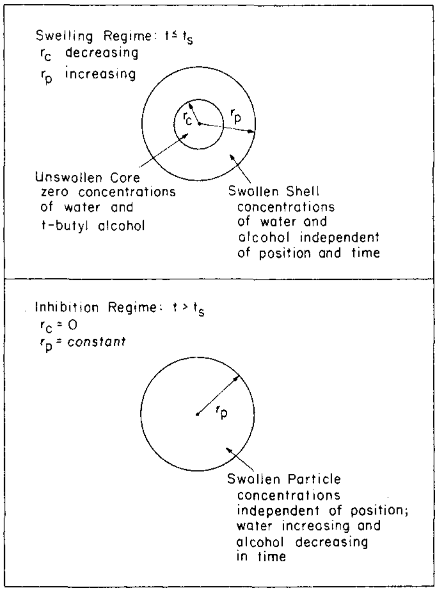

Fig. 7. Depiction of shrinking-core model.

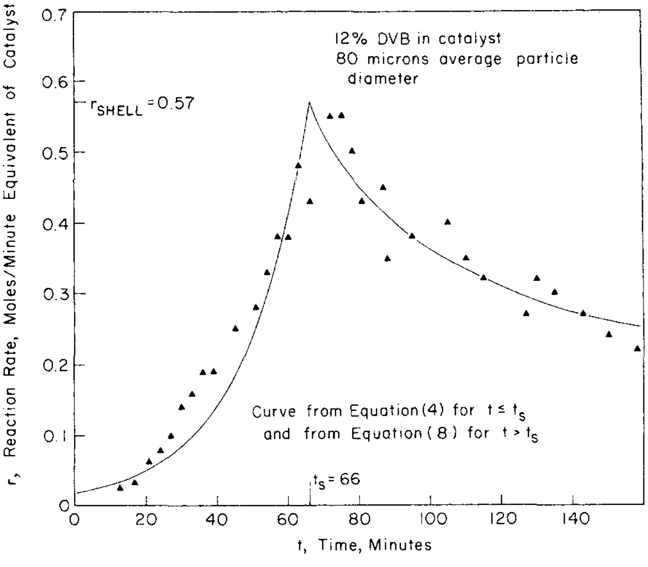

Fig. 8. Comparison of model with reaction rate data at 75.6°C.

$$\mathbf{r}N_c = \mathbf{r}_{\text{shell}} N_c \gamma e^{\theta} \tag{4}$$

where the dimensionless time θ is defined as follows:

$$\theta = \frac{3\alpha N_c (1-\gamma)\mathbf{r}_{\text{shell}} t}{4\pi r^3_{p0} \rho_W N_p} \tag{5}$$

The particle radius during the swelling period is then

$$r_p = r_{ps} - r_{p0}\left(\frac{r_{ps}}{r_{p0}} - 1\right)\left(\frac{1-\gamma e^{\theta}}{1-\gamma}\right)^{1/3} \tag{6}$$

For times greater than the swelling period t_s the particle radius is r_{ps} and the reaction rate is expressed by the Langmuir-Hinshelwood equation suggested by Frilette et al. (7) to account for water inhibition

$$\mathbf{r}N_c = N_c \frac{kK_A c_A}{1 + K_A c_A + K_W c_W} \tag{7}$$

For conditions of the experiments the concentration of the alcohol was nearly constant, and to a good approximation we may write

$$\mathbf{r}N_c = \frac{N_c \mathbf{r}_{\text{shell}}}{a + bc_W} \tag{8}$$

The model has been tested against the data for 80 μ particles of catalyst containing 12% DVB. Rate was established from the data at the end of the induction (swelling) period and γ and a and b were determined from linearized plots of log rate versus time and reciprocal of rate versus concentration of water, respectively. As shown in Figure 8, a satisfactory fit to the data is obtained with parameter values given in Table 1.

The value of $\gamma = 0.03$ corresponds to initial penetration of reactant to a depth of 1% of a particle radius, equal to about 4,000 Å, or roughly 10^3 times the spacing between parallel strands in the polymer matrix. Thus γ is many times larger than would be expected for a smooth, initially impermeable sphere. The result is interpreted as an indication of rapid partial swelling by impurity water, present to the extent of about 0.2 moles per equivalent of sulfonic acid groups. The large value of γ may further indicate the presence of regions of low crosslinking, which are known to surround islands of high crosslinking in ion exchange resins (*13*); these regions could be rapidly swollen as shown by the results of Figure 2.

The value of α, the fraction of water generated in the resin shell remaining to swell the particle, is not uniquely determined by the results. A rough estimate is obtained from an approximate value of ρ_W: If a hydration number of 3 moles water/equivalent sulfonic acid groups is assumed (the result of Reichenberg and Wall (*14*) for resins equilibrated with solutions of *n*-butanol in water at 25°C.), then ρ_W is about 10^{-2} moles/cu. cm. resin volume, and α is about 0.2.

The results are not sufficient to determine the distribution of water and *t*-butyl alcohol between the resin and solution phases, nor are they sufficient to determine K_A and K_W, which establish the distribution of the two compounds in combination with catalytic sites.

The particle swelling data for the 12% crosslinked resin are compared to model predictions in Figure 9. Values of r_{p0} and r_{ps} were established from the data for each particle, and curves were calculated from Equation (6) with parameter values determined from the reaction rate data (Table 1). The comparison confirms that the model is descriptive of the swelling-reaction process and not just an arbitrary fit of the reaction rate data. The lack of fit to the data for the largest particle (Figure 9) may be evidence of an unusually high water impurity level in *t*-butyl alcohol.

The model was found to deviate increasingly from the data as crosslinking was reduced (8). It is evidently appropriate for resins containing more than about 12% DVB in particles less than roughly 100 μ in diameter. In resins of lower DVB content the assumption of a sharp moving boundary becomes inapplicable, while for the larger particles the assumption of flat concentration profiles in the swollen shell is invalid.

Table 1. Model Parameter Values for 12% DVB Resin at 76°C.

t_s = 66 min.
$\mathbf{r}_{\text{shell}}$ = 0.57 moles/min. equivalent
N_c/N_p = 1.07×10^{-9} equivalent/particle
r_{p0} = 73 μ
α/ρ_W = 18.2 cu.cm./mole
γ = 0.03
a = 0.50
b = 1.97 l/mole

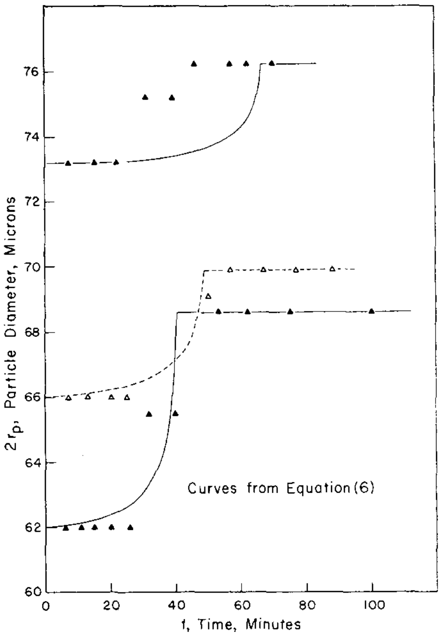

Fig. 9. Comparison of model with single particle swelling data at 76°C.

ACKNOWLEDGMENT

The particle swelling measurements were made by P. Fedkiw. S. B. Brown assisted in developing the kinetics experiments.

NOTATION

a = rate equation parameter, dimensionless
b = rate equation parameter, l/mole
c = liquid-phase concentration, moles/l
k = rate constant, moles/min. equivalent of catalyst sulfonic acid groups
K = adsorption equilibrium constant in Langmuir-Hinshelwood rate equation, l/mole
N_c = equivalents of catalyst sulfonic acid groups
N_p = number of catalyst particles
r_c = radius of unswollen core
r_p = radius of particle
$\mathbf{r}$ = reaction rate, moles/min. equivalent of total catalyst sulfonic acid groups

r_{shell} = reaction rate in shell, moles/min. equivalent of catalyst sulfonic acid groups in shell
t = time, min.

Greek Letters

α = fraction of water produced in swelling period which remains in particle
γ = fraction of catalytic sites located on particle peripheries
ρ_W = moles of water per unit volume in shell, moles/cu. cm.
θ = $\dfrac{3\alpha N_c(1-\gamma)r_{shell}t}{4\pi r_{p0}^3\rho_W N_p}$, dimensionless

Subscripts

A = alcohol
W = water
0 = value at $t = 0$
s = value at $r_c = 0$

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Dynamics of Diffusion and Adsorption in a Single Catalyst Pellet

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Exposing one face of a catalyst pellet to a pulse of tracer gas and analyzing the response at the opposite end provides a dynamic method for measuring the effective diffusivity of porous catalysts. The first and second moments of the response peak are shown to be a function of only D_e and the geometry of the pellet and detector chamber for a nonadsorbing, tracer-carrier system. Data obtained for alumina pellets of different densities illustrate the method.

For an adsorbing tracer, the first moment is a function of both D_e and the adsorption equilibrium constant. Measurements for an unconsolidated assembly of nickel/Kieselguhr particles, using the D_2-H_2 system, show that first-moment data are sufficient to calculate reasonably accurate values of the equilibrium adsorption. However, it appears to be difficult to obtain adsorption rate constants by this method.

Chromatographic measurements for beds of catalyst particles have been used [for example, (5, 8, 9)] to measure adsorption and intraparticle rate coefficients. This method relates the moments of the concentration peak at the exit of the bed to the various rate coefficients. Hence, the influence of all the transport effects, including axial dispersion, are measured. For studying only intraparticle effects it would be advantageous to eliminate the influence of axial dispersion. Chromatographic experiments with single pellets would accomplish this objective. In this paper a method is presented, and tested experimentally, for using single pellet chromatography to evaluate effective diffusivities and adsorption equilibrium data for porous catalysts. Isothermal operation and a first-order adsorption process are necessary. These restrictions are the same as required for bed chromatography. Isothermal conditions are approached by employing low concentrations of adsorbable component and pseudo first-order adsorption is achieved by the isotope technique (5, 9).

THEORY OF SINGLE-PELLET CHROMATOGRAPHY

Balder and Peterson (*1*) have developed the theory and experimental procedure for single pellet reactors operating

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