Dynamic Hydrogenation Studies in a Catalytic Slurry Reactor

Hydrogenation of α-methyl styrene with Pd/Al_2O_3 catalyst was studied in a three-phase stirred slurry reactor. Responses to step inputs of H_2 in N_2 carrier gas provided temporal moments that allowed estimation of separate values for reversible adsorption and irreversible surface reaction rates for reactant H_2. Mass transfer resistances are either estimated from other sources and shown to be small, or are evaluated from the flow rate dependence of the moments. The adsorption equilibrium constant for H_2 on the catalyst was measured with reaction product cumene as the solvent. For temperatures between 290 and 322 K adsorption appears to have the dominant influence on the overall rate of hydrogenation. The energy of activation for the adsorption step was found to be 8 kcal/mol.

Bum-Jong Ahn
J. M. Smith
B. J. McCoy
University of California, Davis
Department of Chemical Engineering
Davis, CA 95616

SCOPE

Accurate prediction of transient behavior of catalytic systems where neither adsorption nor surface reaction controls is possible only if the separate rates are known. Furthermore, an understanding of the relative effects of adsorption and surface reaction for different reactions, different catalysts, catalysts prepared with different procedures, catalysts under the influence of different poisons or promoters, etc., could be helpful in providing a conceptual basis for developing improved catalysts.

In dynamic studies of fluid-solid catalytic reactions, the concentrations of adsorbed reactants as well as concentrations in the fluid change with time (Bell and Hegedus, 1982; Tamaru, 1978; Kobayashi and Kobayashi, 1974). For this reason dynamic experiments, in contrast to steady state measurements, provide information about separate values for adsorption rates and rates of the surface reaction. Bennett (1967, 1976) and Suzuki and Smith (1971) discussed methods for utilizing this characteristic of dynamic data to avoid the assumption that one step in a heterogeneous catalytic reaction controls the overall rate, an assumption that is usually invoked in interpreting steady state information. Most of the experimental studies have been for gas-solid systems.

Our objective in the present research was to extend the applicability of dynamic experiments for studying the importance of individual steps in liquid-solid catalytic reactions. A three-phase slurry reactor was used because the response period is long enough to use chromatographic analysis to establish the response curve to a step input of reactant gas. The reaction chosen was the hydrogenation of α-methyl styrene in a slurry of Pd/Al_2O_3 particles at atmospheric pressure and temperatures of 290 to 322 K. This irreversible hydrogenation produces only cumene as a product and is usually regarded as first-order in hydrogen at low pressures and temperatures (Babcock et al., 1957; Satterfield et al., 1968; Germain et al., 1974). Separate measurements of adsorption of hydrogen on the catalyst in a slurry of cumene indicated that the adsorption was reversible.

To evaluate rate constants for adsorption and reaction it is necessary to account for mass transfer retardations. An advantage of the slurry system is that by using a relatively large mass of very small particles

both liquid-to particle and intraparticle mass transfer have but a small effect on the overall rate. Mass transfer from gas bubbles to liquid is important, but it can be quantitatively evaluated from the dynamic measurements.

Zero and first moments of the response curves are sufficient to provide the relationships needed to evaluate the adsorption and surface rate constants. Since the adsorption step is reversible, the adsorption equilibrium constant for hydrogen is needed. This was obtained from separate dynamic experiments in the same reactor using cumene as the slurry liquid.

CONCLUSIONS AND SIGNIFICANCE

The results of applying the dynamic method to the hydrogenation of α-methyl styrene indicate that the rate of adsorption of hydrogen from the liquid α-methyl styrene has a pronounced effect on the overall rate. While difficulties in obtaining accurate values for the moments cause some scatter of the results, adsorption of hydrogen rather than the surface reaction has the major effect on the hydrogenation rate over the temperature range 290-322 K and at atmospheric pressure.

Mass transfer from gas bubbles to bulk liquid affected the global rate, but this resistance was accounted for experimentally by measurements at different gas flow rates. The adsorption and surface reaction rates were not sensitive to intraparticle diffusion and liquid-to-particle mass transfer resistances since very small (125.5 μm) catalyst particles were used.

The experimental estimates of the adsorption rate constant k_a were of the order 10^{-4} $m^3/s \cdot kg$ catalyst over the temperature range 290-322 K. The ratio of the surface reaction rate constant to the rate of desorption was of the order of unity over the temperature range. This ratio, $k_r/(k_a/K)$, is a measure of whether adsorbed hydrogen will react on the surface or desorb into the liquid. Its value suggests that neither adsorption nor surface reaction completely controls the overall reaction.

The first moments for adsorption of hydrogen (in the absence of reaction) showed little change with temperature. The decrease in the adsorption equilibrium constant, corresponding to a heat of adsorption of about 4.4 kcal/mol (18.4 kJ/mol), was nearly balanced by the solubility change with temperature of hydrogen in α-methyl styrene. The heat of solution of hydrogen in the styrene, estimated from solubility data (Herskowitz et al, 1978), is 2.4 kcal/mol (10.1 kJ/mol).

Earlier results (Ahn et al., 1985) for the oxidation of sulfur dioxide in an aqueous slurry indicated that neither adsorption of oxygen nor the subsequent surface reaction rate controlled the reaction. The current work suggests that while neither adsorption nor surface reaction totally dominates the hydrogenation of methyl styrene, adsorption has the stronger influence. These kinds of conclusions are important both for establishing reliable rate equations and for developing methods to improve catalysts.

Introduction

In studying rates of heterogeneous catalytic reactions at steady state conditions only the combined result of adsorption, surface reaction, and desorption can be measured. However, under dynamic conditions the net rates of adsorption and desorption are not equal to the rate of the surface reaction. This results in changes of adsorbed concentrations with time, and means that dynamic experiments can be used, in principle, to separate and evaluate rates of adsorption and surface reaction.

A common method of generating dynamic reaction data is to introduce a step change in reactant concentration in the feed to an isothermal reactor and then measure the response curve of reactant concentration in the reactor effluent. Various methods (Wakao and Kaguei, 1982) can be used to extract rate constants from the response curves. If the governing differential equations describing the dynamic behavior of the reactor are linear, the method of moments, based upon solution in the Laplace domain, can be used. This approach gives analytic relations between the moments and the rate constants for adsorption, surface reaction, desorption, and any significant mass transfer processes. If the reaction is irreversible, the desorption step is not involved. Using moments avoids the necessity of numerical solution and multivariable optimization that would be required by solution in the real-time domain. To satisfy the linearity requirement both the adsorption step and subsequent surface reaction must be first-order in the reactant.

Ahn et al. (1985) carried out dynamic studies for the oxidation of sulfur dioxide in an aqueous slurry of activated carbon particles. This system, at 298 K and 101.3 kPa for concentrations of sulfur dioxide as low as 1.8% in the gas feed, exhibited reversible first-order adsorption for oxygen and an irreversible surface reaction, first-order in oxygen and zero-order in sulfur dioxide. The results suggested that both the adsorption and surface reaction steps affected the overall rate. Recasens et al. (1984) extended the results to other temperatures and calculated energies of activation for the adsorption and surface reaction steps.

Slurry reactors provide an attractive method of studying liquid-solid heterogeneous catalytic reactions under dynamic conditions. This is because the response time following a change in input reactant concentrations is long enough to use conventional analysis methods to obtain the response curve. If all the rate processes are linear, moments of the response curve can be explicitly related to the rate parameters, that is, to the pertinent mass transfer coefficients and the rate constants for the adsorption and surface reaction. Ahn et al. and Weng and Smith (1984) have derived equations for the zero and first moments for reversible first-order adsorption and irreversible first-order reaction in a slurry reactor. Further, Ahn et al. applied the equations to their experimental data for the oxidation of sulfur dioxide in an aqueous slurry of a catalyst of activated carbon particles. With proper choice of operating conditions, mass transfer effects were accounted for accurately so that numerical values could be obtained for the adsorption and surface reaction rate constants. For the irreversible oxidation reaction, both adsorption and surface reaction steps influenced the overall rate; the assumption of a single step controlling the rate was not valid.

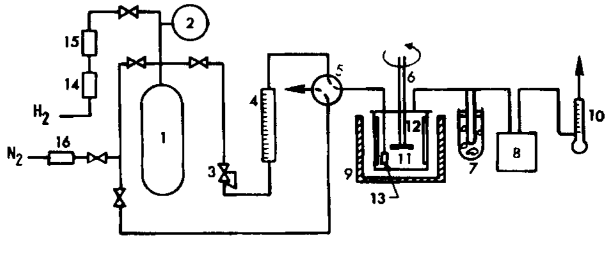
In the present work we studied the hydrogenation of α-methyl styrene in the same slurry reactor with Pd/Al_2O_3 catalyst. This reaction at low pressures appears to be first-order in hydrogen, and separate experiments showed that hydrogen adsorption was reversible on the catalyst particles in a slurry with liquid cumene. This system thus satisfied the requirement of reversible adsorption followed by irreversible surface reaction.

The reaction experiments were carried out by introducing a step change of hydrogen in the nitrogen feed gas bubbled into the slurry of catalyst particles in liquid α-methyl styrene at near atmospheric pressure and temperatures from 290 to 322 K. The reactor shell, baffles, and impeller were the same as used by Furusawa and Smith (1973) to obtain liquid-to-particle mass transfer coefficients (k_s). Hence, their correlation was employed to obtain k_s for our work. Also available were solubility data for hydrogen in α-methyl styrene (Herskowitz et al., 1978) and intraparticle diffusivities of hydrogen in α-methyl styrene-filled pores of Pd/Al_2O_3 catalyst particles (Herskowitz et al., 1979).

Adsorption experiments consisted of introducing a step change of hydrogen into a slurry of the catalyst particles in cumene.

Experimental

A schematic drawing of the apparatus is shown in Figure 1. The Pyrex reactor is about 0.15 m high and 0.1 m in diameter. It is equipped with an eight-bladed impeller and eight stationary baffles, all of stainless steel. Details of the dimensions, including location of the baffles and impeller blades are given by Furusawa and Smith. The reactor was located in a constant-temperature bath; temperatures in the reactor were held to ± 1K. The total volume of the reactor assembly, between the four-way valve and the sample injection valve of the chromatograph, was 1.32×10^{-3} m^3. The measured retention time of the sample passing through the chromatograph and to the detector was constant and equal to 9 s. The measured first moments were corrected for this retention time.



1. Feed Tank
2. Pressure Gauge
3. Regulator
4. Rotameter
5. Four-Way Valve
6. Reactor
7. Dry-Ice Trap
8. Gas Chromatograph
9. Constant-Temperature Bath
10. Soap-Bubble Flow Meter
11. Impeller
12. Stationary Baffles
13. Dispersion Tube
14. Deoxo Unit
15. Water Dryer
16. Oxiclear Gas Purifier

Figure 1. Diagram of apparatus.

Nitrogen was used as a carrier gas both for the feed to the reactor and for the chromatograph. A Deoxo unit (Engelhard) and water dryer containing anhydrous $CaSO_4$ were used to eliminate oxygen and water from the hydrogen stream. An Oxiclear gas purifier (Diamond Tool and Die) unit was used for nitrogen stream. A mixture of 10% hydrogen in nitrogen was prepared in the feed tank, Figure 1, and used as the step input for the reaction experiments. Stated purities of the hydrogen and nitrogen before elimination of oxygen and drying were 99.99 and 99.996%, respectively. The technical grade α-methyl styrene and cumene (Eastman Kodak) both had purities of 98% with the contaminants being primarily aromatic homologues. Reagent grade palladium chloride (Aldrich Chemical Co.) and γ-alumina (T-126, Girdler Chemical Co.) were used to prepare the catalyst. The alumina particles were crushed and sieved, retaining the fraction between 100 and 150 mesh screens (the midsize of screen openings is 125.5 μm). Physical properties of the alumina support are given in Table 1.

The catalyst was prepared by first dissolving palladium chloride in a 5% aqueous HCl solution. After evacuation for 2 h, the alumina particles were soaked in the solution overnight at 333 K, and the wet catalyst was dried at 393 K for 24 h. Then the particles were placed in a Pyrex tube and reduced at 693 K in a pure hydrogen stream for 72 h. To check for complete reduction of palladium, the effluent stream of hydrogen was passed through distilled water. A few drops of aqueous silver nitrate solution were added to detect chloride ion dissolved in the water. Reduction was complete when a fresh solution showed no precipitate. After purging with nitrogen the reduced catalyst was added immediately to the reactor containing either α-methyl styrene or cumene. The particles contained 0.05 wt. % palladium.

The effluent gas from the reactor was analyzed periodically for hydrogen using a Varian model 1400 chromatograph equipped with a thermal conductivity detector and a 0.6 m long column of Porapak R held at 423 K.

Operating procedure

The operating conditions for the reaction and adsorption runs are given in Table 2. All the catalyst employed was prepared in one batch, and divided into three smaller batches. Each of these

Table 1. Properties of Alumina Particles (Catalyst Support)*

Surface area (N_2 adsorption), m^2/kg	1.65×10^5
Pore volume, m^3/kg	0.33×10^{-3}
Average pore radius, nm	6.0
Solid density, kg/m^3	3.07×10^3
Particle density, ρ_p, kg/m^3	1.53×10^3
Bulk density kg/m^3	0.79×10^3
Particle diameter, m	125.5×10^{-6}
Porosity of particle, β	0.503

*Morita and Smith (1978)

Table 2. Operating Conditions

Reactor volume, incl. tubing and dry-ice trap	$1.32 \times 10^{-3} m^3$
Feed gas composition, step input	10% H_2 and 90% N_2
Gas flow rate (1 atm [101.3 hPa], 298 K)	1.5×10^{-6} to $8 \times 10^{-6} m^3/s$
Impeller speed	14.3 rps
Pressure	≈ atmospheric
Temperature	290.5, 302, 311.5, and 322 K
Reaction Runs	
Catalyst loading, m_s	0.217×10^3 kg/m3
Volume of α-methyl styrene, V_L	$1.06 \times 10^{-3} m^3$
Dead volume, V_o	$0.185 \times 10^{-3} m^3$
Adsorption Runs	
Catalyst loading, m_s	$0.112 \times 10^3 kg/m^3$
Volume of cumene, V_L	$1.11 \times 10^{-3} m^3$
Additional Adsorption Runs	
Catalyst loading, m_s	0.164×10^3 and $0.077 \times 10^3 kg/m^3$
Volume of cumene, V_L	1.08×10^{-3} and $1.1 \times 10^{-3} m^3$
Temperature	290.5 K

was reduced by the same procedure immediately prior to use. The first sub-batch of 0.23 kg was used for the reaction runs. After an initial period of changing activity, response curves were made over a range of gas flow rates at each of the four operating temperatures. After all reaction runs, the accumulation of the product cumene was estimated at less than 4%. Next the methyl styrene was replaced, by settling and decanting, with cumene until the concentration of α-methyl styrene was less than 1.5%. Finally adsorption runs were carried out at one temperature, 290.5 K, to evaluate the adsorption equilibrium constant, K, for hydrogen.

The main adsorption runs at the four temperatures were carried out with the second sub-batch of catalyst (0.124 kg). These runs were made with cumene as the slurry liquid. Comparison of the values of K from these runs with that determined using the first sub-batch served as a reproducibility check. There was some concern that potential exposure to air in the decanting operation with the first sub-batch might cause a change in adsorption capacity. As a check on the reproducibility of the reduction process, adsorption runs at 290.5 K were made using the third catalyst sub-batch added immediately to cumene after reduction.

In the adsorption runs with freshly reduced catalyst, the first two response curves gave evidence of some irreversible adsorption. The third and subsequent response curves were reproducible.

Flow rates were measured at atmospheric pressure and 298 K at the exit of the apparatus, Figure 1, with a precision soap-film meter. The pressure was slightly higher in the reactor (maximum pressure = 116.5 kPa). Flow rates were corrected for these differences in pressure.

Method of Analysis

Ahn et al. in the earlier work on separation of adsorption and reaction rates in a three-phase slurry system presented the derivation of zero and first temporal moment expressions for effluent gas concentration. They showed that modeling the gas bubble concentration with either plug flow or well-mixed bubbles, the two extreme assumptions, did not significantly affect the estimation of the parameters. Therefore, in the present work we assume well-mixed bubbles in the conservation equation for reactant in the gas. The value of K_L, bubble-to-liquid mass transfer coefficient, would vary with different models for the flow pattern in the gas phase. It would not, however, affect further estimation of kinetic constants. We consider that adsorption is first-order and reversible, and that surface reaction is first-order and irreversible. We also assume that catalyst-particle distribution and liquid concentration are uniform in the stirred slurry. Mass conservation equations for reactant H_2 in the gas bubbles, in the liquid, in the liquid-filled pores of spherical particles of radius R, and on the catalyst surfaces are as follows:

$$V_B V_L \frac{dCg}{dt} = Q\,(C_{g_o} - C_g) - k_L a_B V_L \left(\frac{C_g}{H} - C_L\right) \qquad (1)$$

$$\left(1 - \frac{\beta m_s}{\rho_p}\right)\frac{dC_L}{dt} = k_L a_B \left(\frac{C_g}{H} - C_L\right) - k_s a_s [C_L - (C_i)_{r=R}] \qquad (2)$$

$$\beta \frac{\partial C_i}{\partial t} = D_e \frac{l}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_i}{\partial r}\right) - \rho_p k_a \left(C_i - \frac{n}{K}\right) \qquad (3)$$

$$\frac{dn}{dt} = k_a \left(C_i - \frac{n}{K}\right) - k_r n \qquad (4)$$

The initial and boundary conditions are

$$C_g = C_L = C_i = n = 0 \text{ for } t = 0 \qquad (5)$$

$$\left(\frac{\partial C_i}{\partial r}\right)_{r=0} = 0 \text{ for all } t \qquad (6)$$

$$k_s[C_L - (C_i)_{r=R}] = D_e \left(\frac{\partial C_i}{\partial r}\right)_{r=R} \text{ for all } t \qquad (7)$$

Equations 1–7 are transformed into the Laplace domain, and zero and first moment expressions are calculated from limits of derivatives of the transformed gas concentration. The zero and first moment expressions can be rearranged into the following forms:

$$\frac{1}{1 - m_o} = \left[\frac{3 m_s k_s}{H R \rho_p}\left(1 - \frac{Bi}{Bi + \phi_o \coth \phi_o - 1}\right)\right]^{-1} \frac{Q}{V_L} + 1 + 1/K_L \qquad (8)$$

$$\mu_1^0 Q/V_L + V_B(1 - m_o) = \frac{1}{H}\left[\frac{3 m_s}{2}\left\{\frac{\beta}{\rho_p} + \frac{K}{\left(1 + \frac{k_r}{k_a/K}\right)^2}\right\}\left\{\frac{\coth \phi_o - \phi_o \operatorname{csch}^2 \phi_o}{\phi_o\left(1 + \frac{\phi_o \coth \phi_o - 1}{Bi}\right)^2}\right\} + (1 - m_s\beta/\rho_p)\right]$$
$$[m_o(1 + 1/K_L - 1/K_L m_o)^2] + V_o/V_L \qquad (9)$$

The dimensionless groups are defined as

$$K_L = k_L a_B V_L / HQ \tag{10}$$

$$Bi = RK_s / D_e \tag{11}$$

$$\phi_o^2 = \frac{\rho_p R^2}{D_e}\left[\frac{1}{K}\left(\frac{1}{k_a/K} + \frac{1}{k_r}\right)\right]^{-1} \tag{12}$$

As implied by Eq. 8, a plot of $1/(1 - m_o)$, the inverse of conversion, v. Q/V_L will yield a straight line if the model suitably describes the experimental process. The Thiele modulus ϕ_o, and hence the combined rate $1/(1/k_a + 1/Kk_r)$, can be evaluated from the slope of the plot. The dimensionless gas-to-liquid mass transfer coefficient, K_L, can be obtained from the intercept. The zero moment is not affected by the dead volume, i.e., the gas volume other than bubbles in the slurry, but the observed first moment μ^o includes the dead volume residence time. The term $V_B(1 - m_o)$ at the lefthand side of Eq. 9 can be neglected, due to the small gas holdup V_B. A straight line is expected if the left side of Eq. 9 is plotted v. $m_o(1 + 1/K_L - 1/K_L m_o)^2$. The slope of this line provides the value for $K/(1 + Kk_r/k_a)^2$, from which the ratio between k_r and k_a can be evaluated if K is known. The intercept of the line yields the ratio of volumes, V_o/V_L, which can be compared to the known geometry of the reactor system.

The value of the equilibrium adsorption constant K must be known to evaluate k_a and k_r from the moments of the experimental data. If the second moment could be evaluated from the data with enough precision, it would provide a relationship for estimating K under reaction conditions. In the Appendix we present the relevant equations.

In the present case second moments were not sufficiently accurate to allow a quantitative estimate for K. Alternatively, the adsorption equilibrium constant K for H_2 on Pd/Al_2O_3 catalyst particles can be determined for reversible adsorption in a solvent that will not react with H_2. Because cumene is the product of the hydrogenation of α-methyl styrene, and has properties nearly the same as α-methyl styrene, we used cumene as the solvent for the adsorption experiments. Equilibrium thermodynamics specifies that the gas-solid adsorption constant, K_g, for H_2 on Pd/A_2O_3 is related to the liquid-solid adsorption constant, K, for H_2 in solvent by means of the solubility of H_2 in the solvent,

$$K_g = K/H. \tag{13}$$

Therefore, the ratio K/H is constant for the two solvents and permits the value of K determined in cumene to be corrected to its value in α-methyl styrene, given the solubility H of hydrogen in the two solvents. The Henry's law solubility constants for H_2 in cumene and α-methyl styrene are obtained from Satterfield et al. and Herskowitz et al., respectively, and are listed in Table 3.

Equation 9 reduces to the following expression, with $V_B(1 - m_o)$ neglected, for reversible adsorption:

$$\mu_1^o = \left[\frac{(m_s K + 1)}{H} + \frac{V_o}{V_L}\right]\frac{V_L}{Q} \tag{14}$$

Equation 14 shows that the slope of a plot of μ_1^o v. V_L/Q yields a value of K when H and V_o are known.

Results from adsorption experiments

The moments of measured response curves are computed from data as follows for the step function input,

$$m_o = C_{g\infty}/C_{g_o} \tag{15}$$

$$m_1 = \int_o^\infty (C_{g\infty} - C_g)\,\mathrm{d}t/C_{go} \tag{16}$$

All the zero moments for the reversible adsorption experiments were unchanged between gas inlet and outlet, confirming the absence of reaction of H_2 with the cumene solvent and Pd/Al_2O_3 catalyst.

The observed first moments, μ_1^o, which include the residence time in the dead volume, are plotted in Figure 2 at a catalyst loading 0.112 kg/L (the second sub-batch) for temperatures of 290.5, 302, 311.5, and 322 K. The dead volume V_o was estimated by subtracting the volume of liquid cumene and the particles from the total volume of 1.32×10^{-3} m^3, which was measured by water displacement. Knowing V_o, V_L, m_s, and H, we can compute K from the slope of Figure 2 by means of Eq. 14. The first moment plots in Figure 2 show no significant temperature dependence of the slopes. The Henry's law constants, H, for hydrogen in cumene were taken from the work of Satterfield et al. (1968) and are listed in Table 3. The values of K obtained from the slopes of Figure 2 are given in Table 4; these are for adsorption of H_2 on Pd/Al_2O_3 in cumene. Published data are meager for the adsorption of hydrogen from liquid phase. The heat of adsorption, however, calculated as the slope of ln K v. $1/T$, is 4.4 kcal/mol (18.4 kJ/mol). In a similar manner the heat of solution for H_2 in cumene is found to be 2.4 kcal/mol (10.1 kJ/mol). From Eq. 13 the heat of adsorption for the gas would be 2.0 kcal/mol (8.4 kJ/mol). Adsorption heat for the gas phase has been shown to depend on the concentration of adsorbed hydrogen on palladium catalyst supported by silica-alumina (Uehara et al., 1970). Extrapolated to small concentration, this adsorption heat is 3.5 kcal/mol (14.7 kJ/mol), consistent with our value based on data for liquid-phase adsorption.

The catalyst particles used in the present work were reduced

Table 3. Values of Parameters Used in Calculations

	Temp., K				
	290.5	302	311.5	322	Ref.
H H_2-cumene	14.0	12.0	10.5	9.53	Satterfield et al. (1968)
H H_2-methyl styrene	16.8	15.1	13.9	12.7	Herskowitz et al. (1978)
k_s, m/s	1.20×10^{-3}	1.33×10^{-3}	1.41×10^{-3}	1.56×10^{-3}	Furusawa and Smith (1973)
D_e, m^2/s	1.17×10^{-8}	1.28×10^{-8}	1.38×10^{-8}	1.49×10^{-8}	Herskowitz et al. (1979)

Table 4. Results for Equilibrium and Kinetic Constants

	Temp., K			
	290.5	302	311.5	322
K,m^3/kg {H$_2$-cumene	11.6×10^{-3}	8.64×10^{-3}	6.92×10^{-3}	5.37×10^{-3}
H$_2$-methyl styrene	13.9×10^{-3}	10.9×10^{-3}	9.16×10^{-3}	7.16×10^{-3}
$(1/k_a + 1)/Kk_r)^{-1}$m^3/kg · s	2.2×10^{-5}	3.7×10^{-5}	6.5×10^{-5}	10×10^{-5}
k_r, s^{-1}	0.01	0.02	0.04	0.2
K_L	1.1	1.1	1.4	2.7

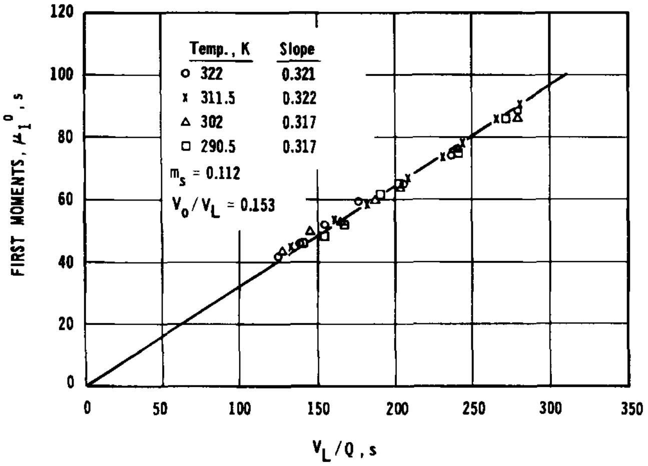


Figure 2. First moments for hydrogen adsorption.

in three separate batches. To check for possible differences in adsorption capacity, K was measured at 290.5 K for each batch. For the catalyst used in the reaction runs, (first sub-batch) α-methyl styrene in the slurry was carefully replaced by cumene by repeated decantation. The upper line in Figure 3 shows the first moments measured at various flow rates with this catalyst batch. From the slope, the value of K was found to be 9.52×10^{-3} m^3/kg. The same adsorption experiments were performed with a third fresh catalyst sub-batch that had not been used in reaction experiments. The results, plotted as the lower line in Figure 3, gave a value of 11.4×10^{-3} m^3/kg for K. The slopes are different for the two runs due to different amounts of catalyst in the slurry. The adsorption equilibrium constant does not vary greatly for different catalyst batches: at 290.5 K three values of K were measured, 11.6, 9.52, and 11.4×10^{-3} m^3/kg, and are in reasonably good agreement.

Results of reaction experiments

Reaction runs for the hydrogenation of α-methyl styrene were done at the same four temperatures for which adsorption equilibrium constants were determined. The zero moment values are plotted as a function of gas flow rate in Figure 4. According to Eq. 8 the intercepts of the straight lines provide the gas-to-liquid mass transfer coefficient. Values of K_L, determined by linear regression, are listed in Table 4. The combined rate constants of adsorption and surface reaction, $1/(1/k_a + 1/Kk_r)$, are obtained from the slopes of the lines in Figure 4, and are listed in Table 4. An Arrhenius plot of this rate constant, Figure 6, yields an activation energy of 8 kcal/mol (33.5 kJ/mol). This is in reasonable accord with the value, 7 kcal/mol (29.3 kJ/mol), found by Germain et al. (1974). The intercepts on the expanded ordinate scale of Figure 5 represent the ratio, V_o/V_L, since $V_B(1 - m_o)$ is negligible (see Eq. 9). The values of V_o/V_L determined from the plot range between 0.196 and 0.206, and are in general agreement with the value 0.18, determined from the geometry of the experimental reactor.

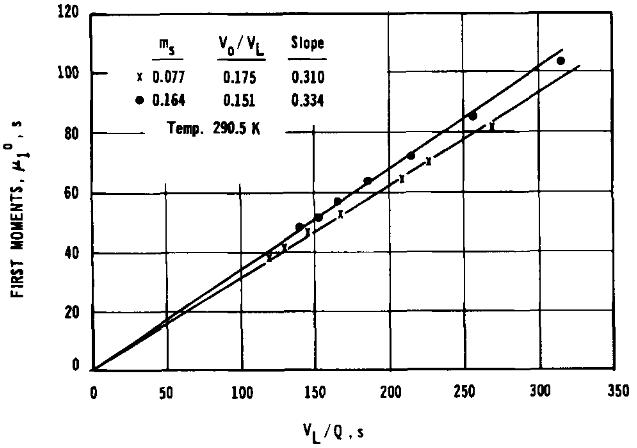


Figure 3. First moments for H_2 adsorption with two batches of fresh catalyst.

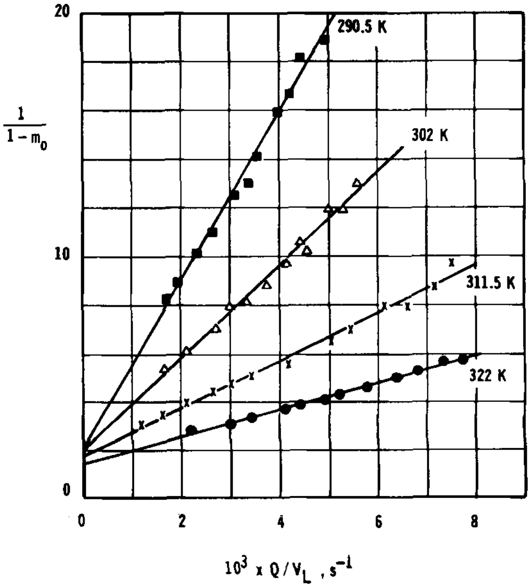


Figure 4. Zero moments for reaction runs.

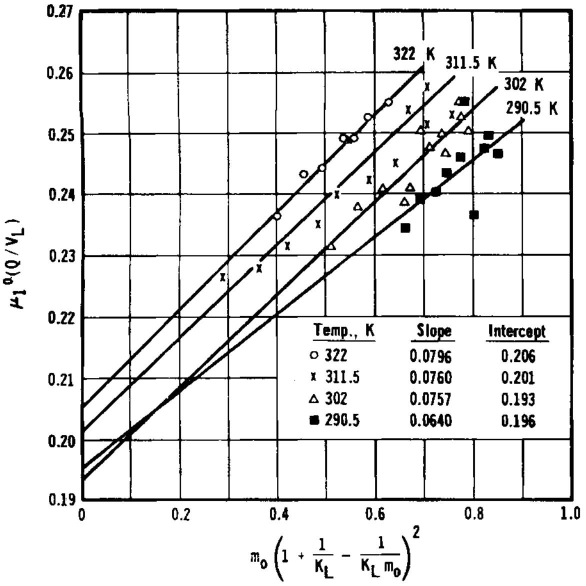


Figure 5. First moments for reaction runs.

To evaluate the individual rate constants k_a and k_r requires values of the effective intraparticle diffusion coefficient, D_e, and the liquid-to-particle mass transfer coefficient, k_s. Because of the very small particle size and relatively high diffusivity of H_2, the results are not highly sensitive to D_e and k_s. We estimated D_e using the work of Herskowitz et al. (1979) for similar conditions. The molecular diffusivity was estimated from the correlation with liquid viscosity proposed by Sporka et al. (1971). The viscosity of α-methyl styrene was extrapolated by Thomas's method reported by Reid et al. (1977), and the density was found by the Goldhammer correlation reported by Perry et al. (1973). The reference viscosity and density were 0.940 × 10^{-3} kg/m · s at 293 K, and 0.906 × 10^3 kg/m^3 at 298 K, respectively. The liquid-to-particle mass transfer coefficient, k_s, was evaluated by the correlation reported by Furusawa and Smith (1973), since the dimensions of the apparatus were the same as in our work. Calculated values of k_s and D_e for the four temperatures of the experiments are given in Table 3.

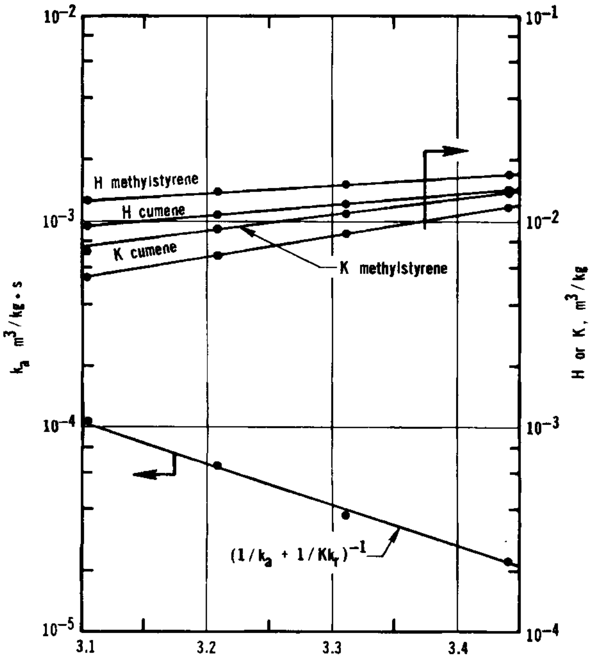


Figure 6. Temperature dependence of equilibrium and kinetic constants.

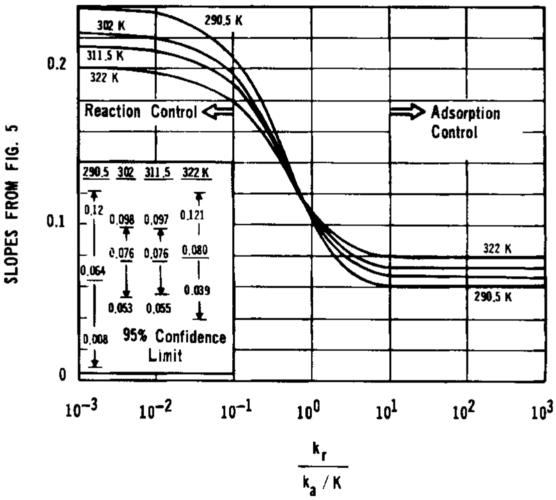


Figure 7. Sensitivity of slopes of first moment data (Fig. 5) to adsorption and reaction rate constants.

From the slopes of the lines in Figure 5 the ratios of rate constants, $k_r/(k_a/K)$, were computed and are of the order of unity. The statistical error associated with the slope presents some difficulty in establishing accurate estimates of k_r and especially k_a. The values of k_r are shown in Table 4 and k_a is estimated to be of the order of 10^{-4}m^3/kg · s. Figure 7 shows the sensitivity of $k_r/(k_a/K)$ to the slope. The 95% confidence limits, indicated as two standard deviations on either side of each value of the slope, are also given in Figure 7. Within the uncertainty of the data, adsorption exerts a strong influence on the overall rate. Approximate individual values of k_r are reported in Table 4.

Application of the dynamic technique to the oxidation of sulfur dioxide via similar slurry reactor studies (Ahn et al., 1985) showed that the rate was not controlled by either adsorption or surface reaction. In contrast, adsorption appears to influence more strongly the hydrogenation reaction reported here. These kinds of conclusions, which are possible from analysis of dynamic data, are valuable for increasing our understanding of the kinetics of heterogeneous catalytic reactions. Extensions of this method to gas-solid catalytic reactions, possibly in a single-pellet reactor, could be useful.

Acknowledgment

The financial assistance of National Science Foundation Grant CPE80-26101 is gratefully acknowledged. Also we thank Dow Chemical Company for supplying α-methyl styrene and cumene.

Notation

a_B = surface area of gas bubbles per unit volume of bubble- and particle-free liquid, m^2/m^3
a_s = surface area of catalyst particles per unit volume of bubble- and particle-free liquid, m^2/m^3
A_o = quantity, Eq. A6, s

A_1 = quantity, Eq. A7, s^2
Bi = Biot number, Rk_s/D_e
B_o = dimensionless quantity, Eq. A9
B_s = quantity, Eq. A3, s
C_g = hydrogen concentration in gas phase, $kmol/m^3$
C_{g_o} = concentration in feed
C_{g^∞} = steady state concentration in effluent gas
C_i = hydrogen concentration in liquid-filled pores of catalyst, $kmol/m^3$
C_L = hydrogen concentration in bulk liquid, $kmol/m^3$
D_e = effective diffusivity in the liquid-filled pores of catalyst particle, m^2/s
H = Henry's constant for solubility of hydrogen in solvent, C_g/C_L
k_a = adsorption rate constant, $m^3/kg \cdot s$
k_L = gas bubble-to-liquid mass transfer coefficient, m/s
k_r = surface reaction rate constant, s^{-1}
k_s = liquid-to-particle mass transfer coefficient, m/s
K = adsorption equilibrium constant for hydrogen in liquid phase, m^3/kg
K_g = adsorption equilibrium constant for hydrogen in gas phase, m^3/kg
K_L = dimensionless quantity, Eq. 11
m_o = zero moment
m_1 = first-order moment, s
m_s = mass of catalyst particles per unit volume of bubble- and particle-free liquid, kg/m^3
M_r = quantity, Eq. A10
n = concentration of hydrogen adsorbed on catalyst particles, kmol/kg
Q = volumetric gas flow rate, m^3/s
r = radial distance from center of spherical catalyst particle, m
R = radius of catalyst particle, m
t = time, s
V_B = bubble volume per unit volume of bubble- and particle-free liquid
V_L = volume of liquid in the slurry, m^3
V_o = dead volume with no gas flow, including gas space over slurry, in the tubing and trap, m^3

Greek letters

β = porosity of catalyst particle
ϵ = quantity, Eq. A4, s
μ_1^o = reduced first-order moment including dead volume, s
μ_1 = reduced first-order moment, m_1/m_o, s
μ_2 = reduced second-order moment, m_2/m_o, s^2
ϕ_o = Thiele-type modulus, Eq. 12
ρ_p = density of catalyst particle, kg/m^3
τ_g = residence time of gas in slurry, V_BV_L/Q, s

Appendix

If data were sufficiently accurate the second central moment could be used for parameter estimation. From the second derivative of the Laplace-transformed gas concentration the expression for the second moment can be derived:

$$\mu_2 = 2\mu_1^2 + 2m_oK_L(B_s+\epsilon)^2/(1+B_o)^3 + \frac{m_oK_L}{(Bi+\phi_o\coth\phi_o-1)(1+B_o)^2} \cdot \left(2B_sA_o + \frac{M_rBiA_1}{Bi+\phi_o\coth\phi_o-1}\right) \quad \text{(A1)}$$

where the dimensional groups are defined as

$$\mu_1 = m_o\left\{\tau_g + \frac{K_L(B_S+\epsilon)}{(1+B_o)^2}\right\} \quad \text{(A2)}$$

$$B_s = \frac{Ra_s}{2k_La_B}\left[\frac{\rho_pK}{\left(1+\frac{k_r}{k_a/K}\right)^2}+\beta\right]\frac{\coth\phi_o-\phi_o\operatorname{csch}^2\phi_o}{\phi_o\left(1+\frac{\phi_o\coth\phi_o-1}{Bi}\right)^2} \quad \text{(A3)}$$

$$\epsilon = \left(1-\frac{m_s\beta}{\rho_p}\right)\Big/k_La_B \quad \text{(A4)}$$

$$\tau_g = V_BV_L/Q \quad \text{(A5)}$$

$$A_o = \frac{R^2}{2\,D_e}\left\{\frac{\rho_pK}{\left(1+\frac{k_r}{k_a/K}\right)^2}+\beta\right\}\left\{\frac{\coth\phi_o}{\phi_o}-\operatorname{csch}^2\phi_o\right\} \quad \text{(A6)}$$

$$A_1 = \frac{R^2}{D_e}\frac{\rho_pK^2/k_a}{\left(1+\frac{k_r}{k_a/K}\right)^3}\left[\frac{\coth\phi_o}{\phi_o}-\operatorname{csch}^2\phi_o\right] + \left(\frac{R^2}{2D_e}\right)\left\{\frac{\rho_pK}{\left(1+\frac{k_r}{k_a/K}\right)^2}\right\} + \beta^2\left\{\frac{\coth\phi_o}{\phi_o^3}+\frac{\operatorname{csch}^2\phi_o}{\phi_o^2}-2\frac{\coth\phi_o}{\phi_o}\operatorname{csch}^2\phi_o\right\} \quad \text{(A7)}$$

The dimensionless groups are defined as

$$m_o = \left(1+K_L-\frac{K_L}{1+B_o}\right)^{-1} \quad \text{(A8)}$$

$$B_o = \frac{k_sa_s}{k_La_B}\left(1-\frac{Bi}{Bi+\phi_o\coth\phi_o-1}\right) \quad \text{(A9)}$$

$$M_r = \frac{k_sa_s}{k_La_B} \quad \text{(A10)}$$

In the absence of reaction, Eq. A1 for the second moment reduces to the simple adsorption case given by Niiyama and Smith (1976) for plug-flow bubbles and negligible τ_g. Although the present data are insufficiently accurate to estimate reliable values of second moments, future improved experimental methods may allow application of these expressions.

Literature Cited

Ahn, B. J., B. J. McCoy, and J. M. Smith, "Separation of Adsorption and Surface Reaction Rates—Dynamic Studies in a Catalytic Slurry Reactor," *AIChE J.*, **31**, 541 (1985).

Babcock, B. D., G. T. Mejdell, and O. A. Hougen, "Catalyzed Gas-Liquid Reactions in Trickling-Bed Reactors," *AIChE J.*, 3(3), 366 (1957).

Bell, A. T., and L. L. Hegedus, eds., "Catalysis Under Transient Conditions," *ACS Symp. Ser.* **178** (1982).

Bennett, C. O., "A Dynamic Method for the Study of Heterogeneous Catalytic Reactions," *AIChE J.*, **13**, 890 (1967).

Bennett, C. O., "The Transient Method and Elementary Steps in Heterogeneous Catalysis," *Catal. Rev. Sci. Eng.*, **13**, 2 (1976).

Furusawa, T., and J. M. Smith, "Fluid-Particle and Intraparticle Mass Transport Rates in Slurries," *Ind. Eng. Chem. Fund.*, **12** (2), 197 (1973).

Germain, A. H., A. G. Lefebvre, and G. A. L'Homme, "Experimental Study of a Catalytic Trickle-Bed Reactor," *Chem. Reac. Eng. II.*, *ACS Monog. Ser.* **133**, 164 (1974).

Herskowitz, M., S. Morita, and J. M. Smith, "Solubility of Hydrogen in α-Methyl Styrene," *J. Chem. Eng. Data*, **23**, 227 (1978).

Herskowitz, M., R. G. Carbonell, and J. M. Smith, "Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors," *AIChE J.*, **25** (2), 272 (1979).

Kobayashi, H., and M. Kobayashi, *Catal. Rev. Sci. Eng.*, **10**, 139 (1974).

Morita, S., and J. M. Smith, "Mass Transfer and Contacting Efficiency in a Trickle-Bed Reactor," *Ind. Eng. Chem. Fundam.*, **17** (2), 113 (1978).

Niiyama, H. and J. M. Smith, "Adsorption of Nitric Oxide in Aqueous Slurries of Activated Carbon: Transport Rates by Moment Analysis of Dynamic Data," *AIChE J.*, **22** (6), 961 (1976).

Perry, R. H., C. H. Chilton, and S. D. Kirkpatrick, *Chemical Engineer's Handbook*, McGraw-Hill, New York, 3–216 (1973).

Recasens, F., J. M. Smith, and B. J. McCoy, "Temperature Effects on Separate Values of Adsorption and Surface Reaction Rates by Dynamic Studies," *Chem. Eng. Sci.*, **39**, 1,469 (1984).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 441 (1977).

Satterfield, C. N., Y. H. Ma, and T. K. Sherwood, "The Effectiveness Factor in a Liquid-Filled Porous Catalyst," *ICE Symp. Ser.*, **28**, 22 (1968).

Sporka, K., et al., "Diffusion of Gases in Liquids. III: Diffusion Coefficients of Hydrogen in Organic Solvents," *Colln. Czechoslov. Chem. Commun.*, **36** (3), 2,130 (1971).

Suzuki, M., and J. M. Smith, "Kinetic Studies by Chromotography," *Chem. Eng. Sci.*, **26**, 221 (1971).

Tamaru, K., *Dynamic Heterogeneous Catalysis*, Academic Press, New York (1978).

Uehara, M., T. Yamabe, and S. Suzuki, "Fundamental Studies on Supported Palladium Catalysts," (title in Japanese) *Kogyo Kagaku Zasshi*, **73** (2), 252 (1970).

Wakao, N., and S. Kaguei, *Heat and Mass Transfer in Packed Beds*, Gordon and Breach, New York, 1–71 (1982).

Weng, Hung-Shan, and J. M. Smith, "Mass Transfer, Adsorption and Reaction in Slurry Reactors," *Chem. Eng. J.*, **28**, 115 (1984).

Manuscript received Sept. 25, 1984, and revision received May 17, 1985.