Dynamic Studies of Catalyst Poisoning: Effect on Adsorption and Surface Reaction Rates for Hydrogenation of α-Methyl Styrene by Pd/Al_2O_3

Pulse-response data for the hydrogenation of α-methyl styrene were obtained as a function of poisoning of the Pd/Al_2O_3 catalyst. The reaction is a first-order, reversible adsorption of hydrogen followed by a first-order, irreversible surface reaction. The experiments, at 298 to 323 K and atmospheric pressure, were carried out in a three-phase slurry reactor for which mass transport effects could be accurately accounted.

Independent adsorption equilibrium data in cumene slurries showed that adsorption occurred to the same extent on both poisoned and unpoisoned sites with a heat of adsorption, $\Delta H_c = -16.3$ kJ/mol. Converted to styrene as the slurry liquid, $\Delta H_s = -20.9$ kJ/mol.

The zero and first moments of the response curves indicated that the rate constant for the surface reaction was independent of the extent of poisoning. The analysis required developing a new theory for interpreting dynamic data where reactant adsorption occurred on both poisoned and unpoisoned sites. The rate constant (per unit mass of catalyst) for adsorption decreased continuously to zero as the extent of poisoning increased.

The results are consistent with the concept that poisoning reduced the number of sites active for reaction, but that the activity per site for the surface reaction was constant. However, the activity per site for adsorption, while constant at poison levels up to 40%, appeared to decrease sharply at higher levels.

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Introduction

In studies of heterogeneous catalytic reactions, dynamic experiments provide the kind of data necessary to evaluate rate constants for the individual steps involved in the mechanism. With this information the usual assumption of one step controlling the rate is avoided. One of the simplest examples is for the two-step process of reversible adsorption followed by an irreversible surface reaction of adsorbed reactant. For this system dynamic data can be used to determine separate values for the rate constants for adsorption and surface reaction. Ahn et al. (1985a) applied this procedure for the catalytic oxidation of sulfur dioxide on activated carbon. The liquid phase hydrogenation of α-methyl styrene also fits the two-step mechanism, and Ahn et al. (1985b) have obtained dynamic data for this reaction. When both adsorption and surface reaction are first order, data interpretation is simplified and more well-defined because moments of response curves can be used.

A second advantage of obtaining dynamic data is that the effects of catalyst properties on the rate constants for the individual steps in the reaction mechanism can be investigated. Chen et al. (1985) studied the effect of catalyst reduction temperature on adsorption and surface reaction rates for the hydro-

genation of α-methyl styrene on Pd/Al_2O_3. The results showed that neither adsorption nor surface reaction completely controlled the overall rate although rate constants for both steps decreased with higher reduction temperatures.

Another important property of catalytic reactions is the influence of poisoning. One objective in the present research is to determine the effect of extent of poisoning on adsorption and surface reaction rates. Again the hydrogenation of α-methyl styrene was chosen as the reaction system. The procedure was to introduce pulses of hydrogen into a styrene slurry of Pd/Al_2O_3 catalyst particles and analyze the moments of the response curves. The extent of poisoning was varied by adding very small amounts of carbon disulfide, which is strongly and completely absorbed to the catalyst. Separate experiments for adsorption alone also are necessary. These were carried out using cumene as the slurry liquid in order to avoid reaction. A well-mixed slurry containing a large number of small catalyst particles is particularly well-suited for these studies since transport effects are either very small or determined simultaneously with the reaction experiments.

In the last two decades theories have been developed for analyzing dynamic experiments to evaluate rate constants for the individual steps in heterogeneous catalytic reactions (Bennett, 1967; Suzuki and Smith, 1971; Weng and Smith, 1984, among others). Individual rate constants cannot be extracted from steady state measurements, since in that case adsorbed concentrations on the catalytic surface are constant with time. One advantage of knowing individual rate constants is that the extent to which one or more steps control the overall rate of a catalytic reaction is known.

When adsorption and surface reaction both affect the rate, the best one can do with steady state data is to determine an overall rate constant. This rate constant is a combination of the rate constants for adsorption and surface reaction, and includes the equilibrium adsorption coefficient as well. A motivation for our research program of dynamic reaction investigations is to measure these individual parameters and relate them to properties of the catalyst.

Recently, dynamic experiments have been analyzed to obtain numerical values for adsorption and surface reaction rate constants for the oxidation of sulfur dioxide on activated carbon (Recasens et al., 1984; Ahn et al., 1985a), hydrogenation of α-methyl styrene (Ahn et al., 1985b), and dehydrogenation of cyclohexane over an industrial reforming catalyst and hydrogenolysis of thiophene over a $Co\text{-}Mo/Al_2O_3$ catalyst (Chen et al., 1984). Also, Ghosh and Agnew (1985) used a mass spectrometer for simultaneously measuring the concentration of several species, and determined rate constants for the three- and four-step mechanisms proposed for the hydrochlorination of acetylene. In several of these studies the results suggested that a single step did not control the overall rate.

The dynamic method also can be used to determine the effects of such aspects of catalysts as method of preparation, poisoning, additives, etc., on rates of individual steps. Chen et al. (1985) studied the effect of reduction temperature of $PdCl_2$ on the rate constants for hydrogenation of α-methyl styrene in a slurry reactor. The data were intepreted by a mechanism consisting of reversible adsorption of molecular hydrogen followed by an irreversible surface reaction, a condensation of the more descriptive mechanism proposed by Madon et al. (1978) for the liquid phase hydrogenation of cyclohexane. Increasing the reduction temperature resulted in decreased values for both the rate constant k_a for adsorption per unit mass of catalyst and for the adsorption equilibrium constant for hydrogen. These results are consistent with the finding of Boitiaux et al. (1983) that the number of active sites (dispersion) decreased with increasing reduction temperature.

In the present work the effects of poisoning on separate rate constants for adsorption and surface reaction were investigated. Again, the experiments were for the hydrogenation of α-methyl styrene with Pd/Al_2O_3 in a slurry reactor. Poisoning was accomplished by adding known amounts of carbon disulfide, which is strongly chemisorbed on the palladium sites (Hegedus, 1984). Yang and Pang (1982) and Gonzales-Tejuca et al. (1977) have used carbon disulfide poisoning for measuring dispersion and related properties of platinum catalysts. Steady state experiments were employed, so only overall rates could be measured.

The data given here are the first, to our knowledge, to be of the dynamic type so that rate constants could be evaluated for the separate processes of adsorption and surface reaction. The procedure was to introduce pulses of pure hydrogen into a stream of nitrogen entering the slurry of Pd/Al_2O_3 particles and measure the response curve in the effluent gas. Reaction data were obtained using α-methyl styrene as the slurry liquid, and adsorption equilibrium constants were determined using the product cumene as the liquid.

Our prior dynamic studies (Recasens et al., 1984; Ahn et al., 1985) have been based upon the assumption of one kind of site. The present poisoning experiments showed that the extent of hydrogen adsorption was independent of the extent of poisoning. Since the amount of reaction was dependent on the unpoisoned sites, it was necessary to consider two kinds of sites. Hence, a further objective of the research was to expand our analysis of dynamic experiments to treat catalytic surfaces containing both poisoned and unpoisoned sites.

Experimental

Experiments were conducted in a Pyrex cylindrical reactor about 0.15 m high and 0.10 m in diameter. It was equipped with eight stationary baffles and an eight-bladed impeller, all of stainless steel; the dimensions and locations of the baffles and impeller are the same as those described by Furusawa and Smith (1973).

Figure 1 is a diagram of the apparatus. Nitrogen carrier gas first flowed through an Oxiclear unit to remove traces of oxygen, then through a flow controller and six-way valve, with a 4.5×10^{-6} m^3 sample loop for hydrogen injection, and then dispersed into the bottom of the slurry. The continuous response curve was measured in a thermal conductivity cell maintained at 423 K in a Varian model 1400 gas chromatograph. The hydrogen in the sample loop was first passed through a Deoxo unit followed by a dryer containing anhydrous calcium sulfate.

The stated purities of the gas in the hydrogen and nitrogen cylinders were 99.996 and 99.99%. Technical grade cumene and α-methyl styrene (Eastman Kodak) were used. The 2% impurities of cumene and α-methyl styrene were primarily aromatic homologues.

Reagent grade palladium chloride (Aldrich Chemical Co.) and γ-alumina (T-126, Girdler Chemical Co.) were used to prepare the catalysts. Alumina particles were crushed and sieved and the fraction between 100 and 150 mesh screens (average

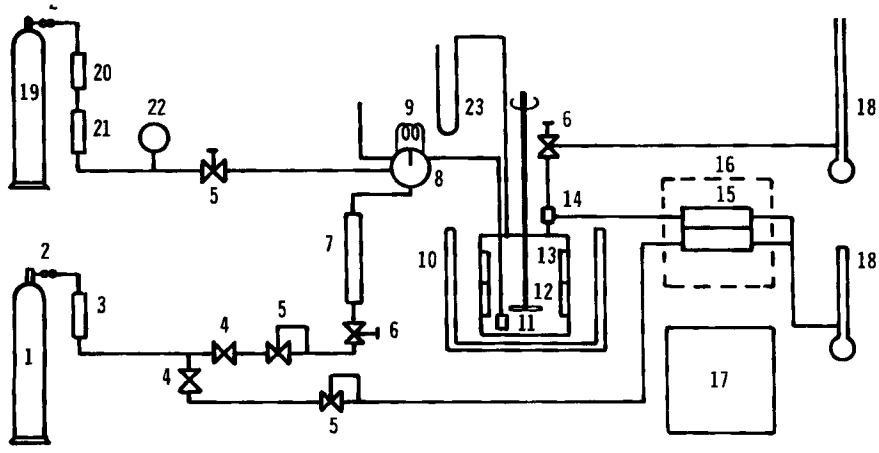

Figure 1. Experimental apparatus.

1. N_2 cylinder
2. Pressure regulator
3. Oxiclear gas purifier
4. Valve
5. Flow controller
6. Needle valve
7. Rotameter
8. Six-way valve
9. Sample loop
10. Constant-temp. water bath
11. Dispersion tube
12. Impeller
13. Stationary baffles
14. Tee
15. Thermal conductivity cell
16. Constant-temp. air bath
17. Recorder
18. Soap-bubble flow meter
19. H_2 cylinder
20. Deoxo unit
21. Dryer
22. Pressure gauge
23. Mercury manometer

opening 0.1255×10^{-3} m) retained. Properties of the alumina are given in Table 1. Carbon disulfide from Aldrich Chemical Co. (stated purity 99.9%) was dissolved in cumene and in styrene to prepare 0.3 vol % poisoning solutions.

Catalyst preparation

The 0.05 wt. % Pd catalyst was prepared by degassing the alumina particles and adding an aqueous $PdCl_2$ solution containing 5 wt. % HCl. After evaporating and drying at 393 K, the particles were reduced in a stream of hydrogen at 523 K. Reduction to Pd/Al_2O_3 was complete after about 110 h as ascertained by testing the effluent hydrogen from the furnace with $AgNO_3$ solution. The procedure is described in detail by Chen et al. (1985).

Procedure

Two batches of catalyst were reduced, one for the adsorption experiments, and a second batch for the reaction runs. The catalyst at 523 K in the reduction furnace was first cooled in place with a stream of hydrogen and then immediately added to the cumene or styrene in the reactor. Then about 20 pulses of hydrogen were successively introduced to stabilize the catalyst surface. Preliminary experiments changing the volume of the sample loop between 3.0 and 6.0×10^{-6} m^3 showed no change in retention times (first moments) at both 298 and 320 K when the slurry liquid was cumene. This indicated that hydrogen adsorption was linear. Also, it is known that the overall reaction is first-order and irreversible (Herskowitz et al., 1979).

Table 1. Properties of Al_2O_3 Catalyst Support*

Surface area (N_2 adsorption), m^2/kg	165×10^3
Pore volume, m^3/kg	0.33×10^{-3}
Solid density, kg/m^3	3.07×10^3
Particle density, ρ_p, kg/m^3	1.53×10^3
Particle radius, avg., m	6.27×10^{-5}
Particle porosity, β	0.503

*Ahn et al. (1985b)

Response curves were measured for both adsorption and reaction experiments at 298, 311, and 323 K and pressures near atmospheric. At each temperature and extent of poisoning, data were obtained at gas flow rates from 0.8 to 7.0×10^{-6} m^3/s (293 K, 101 kPa). The sequence of experiments for each level of poisoning was as follows:

1. Adsorption runs were made at the three temperatures in a cumene slurry.
2. liquid cumene was replaced with styrene by first allowing the catalyst particles to settle and carefully pumping out most of the cumene. Then liquid styrene was added, the mixture stirred, after which the catalyst particles were allowed to settle. This replacement procedure with styrene was repeated until the concentration of cumene in the slurry was reduced to less than 2%.
3. Reaction experiments were carried out at the three temperatures.

After sufficient CS_2 had been added to completely poison the reaction, adsorption experiments were also made in the styrene slurry. In this way adsorption on the poisoned catalyst could be compared with fresh and partially poisoned catalyst. Addition of enough of the 0.3 vol. % solution to provide approximately 1.5×10^{-9} m^3 of pure CS_2 was sufficient to poison completely the catalyst, as determined from the reaction experiments. Data were obtained at six levels of poisoning, corresponding to the addition of 0, 0.15, 0.45, 0.75, 1.05, and 1.5×10^{-9} m^3 of pure CS_2.

The pulses of pure H_2 in the N_2 carrier gas were of volume 4.5×10^{-6} m^3. The responses were of the shape expected for a well-mixed unit: the front of the curve rose steeply to a maximum and then declined with an exponential-shaped tail. The baseline was steady and the data scatter very small. The time for recording the entire response varied from 15 min at high flow

rates to 45 min at low flow rates. The long tail makes difficult an accurate calculations of second moments. The zero and first moments of these response curves constitute the rate data for this investigation. The zero moment is the unconverted fraction of reactant, which can be obtained by a steady state experiment. The first moment contains information that can only be obtained by a transient experiment.

Operating conditions are summarized in Table 2.

Theory

The carbon disulfide is irreversibly and completely adsorbed on the sites formed by palladium atoms, as demonstrated experimentally by the constant activity with time for any degree of poisoning.

Our reaction data showed that addition of a sufficient amount of CS_2 reduced the hydrogenation rate to zero, while the adsorption data indicated that hydrogen was adsorbed on both poisoned and unpoisoned sites. For these conditions the mass balance of hydrogen for first-order reversible adsorption on the poisoned (p) sites is,

$$\frac{dn_p}{dt} = k_p N_p (C_i - n_p/N_p K_p), \tag{1}$$

and for adsorption and irreversible, first-order reaction on the unpoisoned (a) sites,

$$\frac{dn_a}{dt} = k_a N_a \left(C_i - \frac{n_a}{N_a K_a}\right) - k_r n_a \tag{2}$$

The adsorption and surface reaction rate constants k_a and k_r and equilibrium constants K_a and K_p refer to a single site, and N_a and N_p are the number of sites per unit mass of catalyst. Mass conservation equations for the reaction case, for hydrogen in the bubbles, in the well-mixed liquid, and in the pores of the catalyst particles are:

$$V_B V_L \frac{dC_g}{dt} = Q(C_{g_o} - C_g) - k_L a_B V_L \left(\frac{C_g}{H} - C_L\right) \tag{3}$$

$$\left(1 - \frac{m_s \beta}{\rho_p}\right)\frac{dC_L}{dt} = k_L a_B \left(\frac{C_g}{H} - C_L\right) - k_s a_s [C_L - (C_i)_{r=R}] \tag{4}$$

$$\beta \frac{dC_i}{dt} = D_e \left(\frac{d^2 C_i}{dr^2} + \frac{2}{r}\frac{dC_i}{dr}\right) - \rho_p k_a N_a \cdot \left(C_i - \frac{n_a}{N_a K_a}\right) - \rho_p k_p N_p \left(C_i - \frac{n_p}{N_p K_p}\right) \tag{5}$$

Ahn et al. (1985a) have shown that there is little difference for the case of slightly soluble hydrogen between results based upon assuming a well-mixed residence time distribution (RTD) or plug flow for the gas bubbles. Equation 3 is written for the simpler form corresponding to the well-mixed RTD. By using a large mass (large a_s) of very small particles, liquid-to-particle and intraparticle mass transfer have but small effects on the observed data. Hence, highly accurate values of k_s and D_e are not required in Eqs. 4 and 5. These rate coefficients have been determined in the same slurry reactor and for the same catalyst by Ahn et al. (1985b) and are given in Table 4.

Table 2. Operating Conditions

Reactor vol., including lines	1.285×10^{-3}m^3
Vol. of H_2 (pure) pulse	4.5×10^{-6}m^3
Flow rate of carrier gas N_2 (1 atm, 293K)	0.8 to 7.0 $\times 10^{-6}$m^3/s
Impeller speed	15.3 rev/s
Reactor Pressure	atmospheric
Temp. for reaction and adsorption runs	298, 311, 323 K
Catalyst reduction temp., time	523 K, 110 h
Vol. of pure CS_2 poison added to slurry	0.0, 0.15, 0.45, 0.75, 1.05, 1.5 $\times 10^{-9}$m^3
Mass of catalyst in slurry	0.125 kg
A. Reaction runs	
Vol. of α-methyl styrene	1.10×10^{-3}m^3
B. Adsorption runs	
Vol. of cumene	1.16×10^{-3}m^3

The pulse input, initial, and boundary conditions are:

$$C_{g_o} = C_o(t) \tag{6}$$

$$C_g(t=0) = C_L(t=0) = C_i(t=0, r) = n_a(t=0) = n_p(t=0) = 0 \tag{7}$$

$$(dC_i/dr)_{r=0} = 0 \tag{8}$$

$$D_e \left(\frac{dC_i}{dr}\right)_{r=R} = k_s[C_i - (C_i)_{r=R}] \tag{9}$$

Linear equations 1–5 can be solved in the Laplace domain for $C_g(s)$ and theoretical equations for the moments determined from the Laplace solutions. The zero and first moment equations are:

$$m_o = \left(1 + K_L - \frac{K_L}{1 + B_o}\right)^{-1} \tag{10}$$

$$m_1 = \frac{\tau_g (1 + B_o)^2 + K_L(B_s + \epsilon)}{(1 + B_o + K_L B_o)^2} \tag{11}$$

where

$$B_o = \frac{k_s a_s}{k_L a_B}\left(1 - \frac{Bi}{Bi + \phi \coth \phi - 1}\right) \tag{12}$$

$$K_L = \frac{k_L a_B V_L}{HQ} \tag{13}$$

$$\tau_g = \frac{V_B V_L}{Q} \tag{14}$$

$$\epsilon = k_L a_B \left(1 - \frac{m_{s\beta}}{\rho_p}\right) \tag{15}$$

$$B_s = \frac{R a_s}{2 k_L a_B}\left[\rho_p N_p K_p + \frac{\rho_p N_a K_a (k_a N_a)^2}{(K_a N_a + k_r K_a N_a)^2} + \beta\right] \cdot \frac{\coth \phi - \phi \operatorname{csch}^2 \phi}{\phi \left(1 + \dfrac{\phi \coth \phi - 1}{Bi}\right)^2} \tag{16}$$

$$\phi^2 = \frac{\rho_p R^2}{D_e}\left[\frac{1}{k_a N_a} + \frac{1}{(N_a K_a)k_r}\right]^{-1} = \frac{\rho_p R^2}{D_e}\left(\frac{1}{k_o N_a}\right)^{-1} \quad (17)$$

$$Bi = \frac{RK_s}{D_e} \quad (18)$$

$$a_s = \frac{3m_s}{R\rho_p}; \quad \text{(spherical particles)} \quad (19)$$

For adsorption only, where cumene is the slurry liquid, the preceding equations are applicable with $k_r = 0$. Then the zero moment expression, analogous to Eq. 10, is:

$$m_o = 1 \quad (20)$$

since the adsorption is reversible. The reduced first moment expression, μ_1, using Eq. 11 and the first equation in Eq. 21, becomes:

$$\mu_1 = \frac{m_1}{m_o} = \tau_g + V_L[1 + m_s(N_a K_a + N_p K_p)]\frac{1}{HQ} \quad (21)$$

Here K_p and K_a are adsorption equilibrium constants for hydrogen in liquid in equilibrium with the catalyst. For our operating conditions, τ_g is negligible with respect to the second term and can be neglected in Eq. 21. The rate constants k_a and k_p do not appear in Eq. 21, only the total equilibrium adsorption on both poisoned and nonpoisoned sites.

For fresh catalyst, $N_p = 0$ and Eqs. 10, 11, and 22 are reduced to these presented by Chen et al. (1985) for a single type of site.

Method of Analysis

Experimental values for the zero and first reduced moments were calculated from the measured response curves $C_g(t)$ using the equations

$$m_o = \frac{\int_0^\infty C_g(t)\,dt}{\int_0^\infty C_{g_o}(t)\,dt} \quad (22)$$

$$\mu_1 = \frac{m_1}{m_o} = \frac{\int_0^\infty tC_g(t)\,dt}{\int_0^\infty C_g(t)\,dt} \quad (23)$$

Moments from Eqs. 22 and 23 for the reaction runs were then equated to the theoretical moment expressions, Eqs. 10 and 11, for reaction data, and Eq. 21 for the adsorption data. Also included in the first moment expression are the quantities $N_a K_a$ and $N_p K_p$. These quantities are obtained from the independent adsorption data, as described later.

Reaction case

Substituting Eqs. 12 and 13 into Eqs. 10 gives the following zero moment expression for the reaction case

$$\frac{1}{1 - m_o} = \frac{Q}{V_L} \cdot \left[\frac{3m_s k_s}{HR\rho_p}\left(1 - \frac{Bi}{Bi + \phi\coth\phi - 1}\right)\right]^{-1} + \frac{1}{K_L} + 1 \quad (24)$$

K_L is independent of Q since both a_B and V_B in Eq. 13 are proportional to Q. Hence, Eq. 24 shows that plotting $1/(1 - m_o)$ vs. Q/V_L should give a straight line whose slope depends upon $k_a N_a$ and k_r, and the intercept is a function of $k_L a_B$ via Eq. 13. Equation 24 gives results equivalent to those obtainable from steady state experiments ($1 - m_o$ = conversion). This is the function of $(k_a N_a)$ and k_r determined by the bracketed quantity in Eq. 17. Thus the overall rate constant $k_o N_a$, determinable from steady state data or from the steady state form of Eq. 2, is given by

$$\frac{1}{k_o N_a} = \frac{1}{k_a N_a} + \frac{1}{(N_a K_a)k_r} \quad (25)$$

While the zero moment is unaffected by the dead volumes between the pulse injection valve and dispersion tube, and between the liquid level in the reactor and the tee (*14* in Figure 1), the measured first moment must be corrected for these volumes. If the total dead volume is V_o, the observed first moment

Table 3. Total Adsorption Equilibrium Constants: Values of $(N_a K_a + N_p K_p) \times 10^3$, m³/kg

	Vol. × 10^9m³ of CS_2 Added to Slurry				
Temp. K	0	0.75	1.05	1.50*	1.50**
A. In Cumene					
298	12.2	12.3	12.3	12.6	—
311	8.4	8.5	8.4	8.9	—
323	6.4	6.5	6.6	6.7	—
B. In Styrene					
298	14.6	14.8	14.8	15.2 (15.2)†	15.0
311	11.1	11.2	11.1	11.8 (10.9)	12.2
323	8.7	8.8	9.0	9.1 (9.3)	9.7

*1.50 × 10^{-9}m³ of CS_2 (completely poisoned catalyst).
**Results from experiments on completely poisoned catalyst in styrene.
†Reproducibility test with different batch of catalyst.

μ_1 is related to m_1/m_o by

$$\mu_1 = \frac{m_1}{m_o} + \frac{V_o}{Q} \tag{26}$$

Combining this expression with Eqs. 10 and 11 and rearranging yields:

$$\mu_1\left(\frac{Q}{V_L}\right) + V_B(1 - m_o) = \frac{1}{H} \cdot \left\{\frac{3m_s}{2}\left(\frac{\beta}{\rho_p} + K_pN_p + \frac{K_aN_a\,k_aN_a^2}{k_aN_a + k_rK_aN_a^2}\right)\left[\frac{\coth\phi - \phi\,\mathrm{csch}^2\phi}{\phi\left(1 + \frac{\phi\coth\phi - 1}{Bi}\right)^2}\right] + 1 - \frac{m_s\beta}{\rho_p}\right\} \cdot \left[m_o\left(1 + \frac{1}{K_L} - \frac{1}{m_oK_L}\right)^2\right] + \frac{V_o}{V_L} \tag{27}$$

The term $V_B(1 - m_o)$ can be neglected because the gas holdup V_B is small.

Hence, plotting

$$\mu_1(Q/V_L) \text{ vs. } m_o[1 + (1/K_L) - (1/m_oK_L)]^2$$

should give a straight line whose slope provides a second relationship between k_aN_a and k_r. The intercept, V_o/V_L determines a value of the total dead volume which may be compared with that estimated from the size of the apparatus. This geometric V_o was found to be 0.175×10^{-3} m^3 by subtracting the volumes of the bubble-free slurry and the connecting lines from the total system volume of 1.285×10^{-3} m^3.

Adsorption case

At high enough pressures and low enough temperatures, palladium reacts with hydrogen to produce the hydride, but at 303 K the hydride does not begin to form until the partial pressure of H_2 is greater than 2 kPa. A conservative estimate of the H_2 concentration in the liquid comes from the steady state form of Eq. 4, i.e., $C_L \sim C_g/\mathrm{H}(1 + k_sa_s/k_La_B) \sim 10^{-3}\,C_g$. Thus, due to the low solubility and the gas-to-liquid mass transfer resistance, the hydrogen concentration is well below that required to form the hydride at the temperature and pressure of our experiments.

Equation 21 shows that the slope of the first moments, corrected for the dead volume by Eq. 26 and plotted vs. V_L/Q, should give a straight line whose slope is a function of the total adsorption $(N_aK_a + N_pK_p)$. This method, with experimental adsorption data for different levels of poisoning, was used to evaluate separately N_aK_a and N_pK_p as described in the next section.

Adsorption results

Values for $(N_aK_a) + (N_pK_p)$ in cumene from Eq. 21 for fresh catalyst ($CS_2 = 0$) and completely poisoned catalyst ($CS_2 = 1.5 \times 10^{-9}$ m^3 of CS_2) are given in part A of Table 3. Complete poisoning was obtained when the area of the response peaks did not change with gas flow rate. This result requires that the zero moment, or conversion, be independent of flow rate and can be true only when there is no reaction. By adding increasing amounts of CS_2, it was found that 1.5×10^{-9} m^3 was sufficient for complete poisoning. The results in Table 3 were obtained with cumene as the slurry liquid. The first moment data at 298 K are shown in Figure 2, where two different amounts of catalyst were used for adsorption on fresh (unpoisoned) and on completely poisoned catalyst. Within the accuracy of the experiments the values of $N_aK_a + N_pK_p$ are the same for the two cases. Hence, for the fresh catalyst, at 298 K

$$(N_aK_a)_f + 0 = 12.4 \times 10^{-3}\ \mathrm{m^3/kg}$$

and for the completely poisoned catalyst

$$0 + (N_pK_p)_{cp} = 12.4 \times 10^{-3}\ \mathrm{m^3/kg}$$

or

$$(K_aN_a)_f = (N_pK_p)_{cp} = 12.4 \times 10^{-3}\ \mathrm{m^3/kg} \tag{28}$$

where the subscripts f and cp denote fresh and completely poisoned catalyst.

It is reasonable to assume that N_pK_p is proportional to the fraction of CS_2 necessary to poison completely all the sites, that is

$$N_pK_p = (N_pK_p)_{cp}\frac{N_p}{N_{cp}} \tag{29}$$

or

$$N_pK_p = (N_pK_p)_{cp}\frac{V_{cs_2}}{(V_{CS_2})_{cp}} = 12.4 \times 10^{-3}\frac{V_{cs_2}}{(V_{CS_2})_{cp}} \tag{30}$$

For the nonpoisoned sites

$$N_aK_a = (N_aK_a)_f\left[1 - \frac{V_{CS_2}}{(V_{CS_2})_{cp}}\right] \tag{31}$$

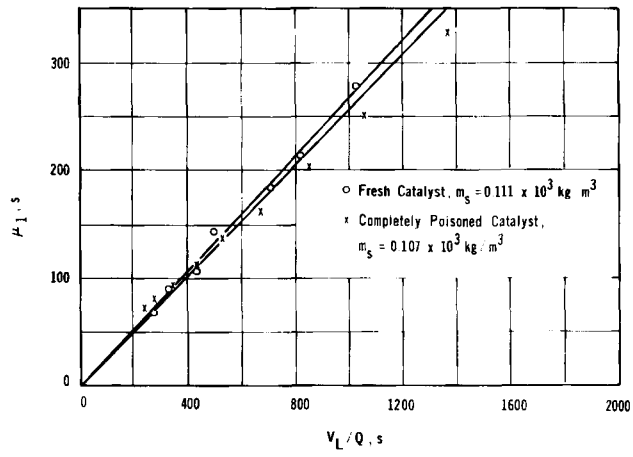

Figure 2. First moments from adsorption runs at 298 K for fresh and completely poisoned catalyst in cumene.

or, in view of Eq. 25,

$$N_aK_a = 12.4 \times 10^{-3}\left[1 - \frac{V_{CS_2}}{(V_{CS_2})_{cp}}\right] \tag{32}$$

From Eqs. 30 and 32, the sum $(N_aK_a + N_pK_p)$ for any level of poison is a constant value

$$N_aK_a + N_pK_p = \alpha(\alpha = 12.4 \times 10^{-3}\ \text{m}^3/\text{kg for cumene at 298 K}) \tag{33}$$

Equation 33 states that the total equilibrium adsorption should be independent of the amount of CS_2 added. The values in Table 3 for the intermediate volumes of CS_2 of 0.75 and 1.05 $\times 10^{-3}$ m^3 show that this is indeed the case at all three temperatures. This means that numerical values of N_aK_a and N_pK_p for any level of poisoning can be calculated from Eqs. 30 and 32. With these quantities known, k_aN_a and k_r can be obtained from Eqs. *10* and *11* as described in the previous section.

The constant value of the total equilibrium adsorption shown in part A of Table 3 for any poison level suggests that adsorption occurs to the same extent on poisoned and unpoisoned sites. Madon et al. (1978), from studies on the hydrogenation of cyclohexene on platinum catalyst, hypothesized that the first step was a reversible adsorption of hydrogen on sites on which the hydrocarbon is already preferentially adsorbed. Our results do not disagree with this concept if the hydrocarbon is adsorbed on both poisoned and unpoisoned sites.

The required values for N_aK_a and N_pK_p are for the styrene slurry. Since

$$K = HK_g \tag{34}$$

where K_g is the adsorption equilibrium constant between gas and catalyst surface, K for styrene can be calculated from the cumene results and the ratio of Henry's law constants:

$$(K)_{\text{styrene}} = (K)_{\text{cumene}}\frac{H_s}{H_c} \tag{35}$$

Values of $K_aN_a + K_pN_p$ obtained from Eq. 35 and the data in part A of Table 3 are given in part B of Table 3. Henry's law constants were taken from the measurements of Satterfield et al. (1968) and Herskowitz et al. (1979) and are given in Table 4.

Also, the adsorption equilibrium constant can be obtained with styrene as the slurry liquid, provided that the catalyst is completely poisoned. The last column for styrene in Table 3 shows such values. They agree reasonably well with the results calculated from the cumene measurements. The form of Eq. 32 to use for evaluating k_aN_a for use with the reaction data is:

$$N_aK_a = \alpha\left[1 - \frac{V_{CS_2}}{(V_{CS_2})_{cp}}\right] \tag{36}$$

where average values of α are 15.0 at 298 K, 11.4 at 311 K, and 9.2 $\times 10^{-3}$ m^3/kg at 323 K.

Values of N_aK_a for the three temperatures and various levels of poison are shown in Figure 3. According to the van't Hoff equation the shape of the straight line is related to the heat of adsorption by

$$\text{Slope} = \frac{d\ln(N_aK_a)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R_g} \tag{37}$$

Figure 3 shows that ΔH_s for adsorption of dissolved hydrogen on the catalyst is independent of the poison level and equal to about -20.9 kJ/mol.

Reaction results

Zero moment results plotted according to Eq. 24 are illustrated in Figure 4 for data at 311 K. Similar results were obtained at 298 and 313 K. The slopes of the lines increased with poison level, corresponding to a decrease in conversion and in k_o. The intercepts were nearly the same, as they should be since the intercept is determined by mass transfer from gas bubble to liquid via K_L. The values of K_L agree with values determined by Ahn et al. (1986).

Table 4. Solubility and Mass Transfer Parameters

	Temp. K		
	298	311	323
H_c*	12.6	10.5	9.16
H_s**	15.2	13.9	12.5
D_e† $\times 10^8$, m^2/s	1.26	1.38	1.49
k_s† $\times 10^2$, m/s	0.128	0.141	0.156

*Satterfield et al. (1968)
**Herskowitz et al. (1979)
†Ahn et al. (1985b)

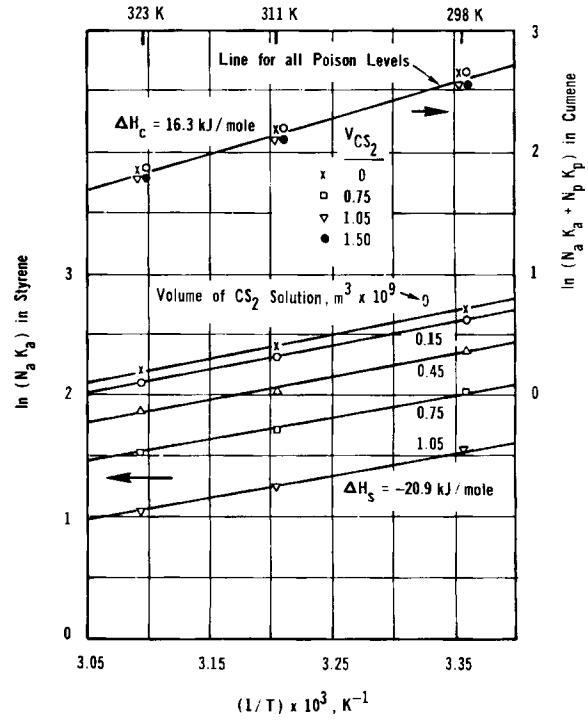

Figure 3. Adsorption equilibrium constants N_aK_a in styrene and $(N_aK_a + N_pK_p)$ in cumene.

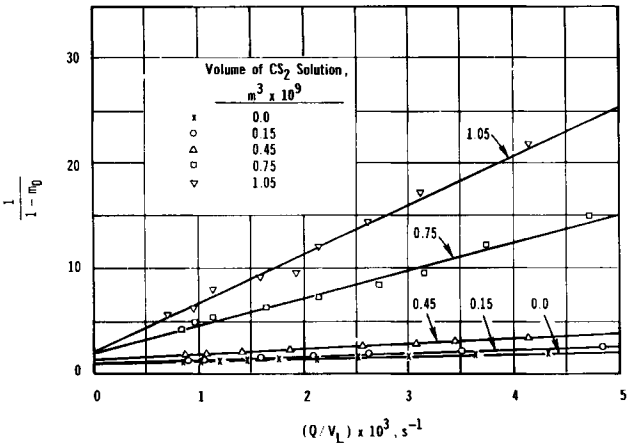

Figure 4. Zero moments for reaction data at 311 K.

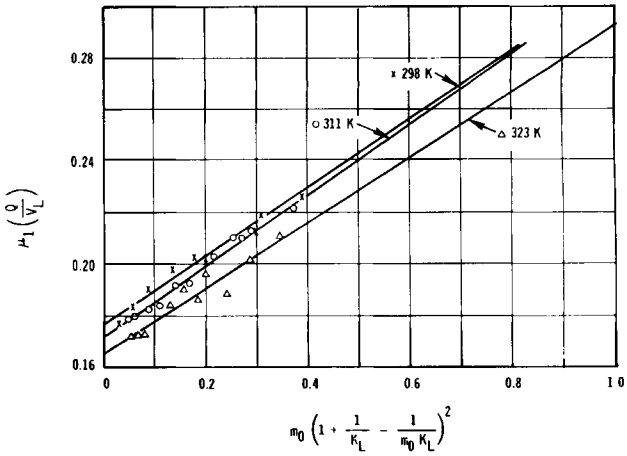

Figure 6. First moment data for reaction on fresh (unpoisoned) catalyst.

Liquid-to-particle and intraparticle mass transfer resistances in the slurry reactor were very small. Hence, the values of k_s and D_e need not be particularly accurate. We used values estimated by Ahn et al. (1985b) in the same reactor operated at about the same stirrer speed and catalyst loading. With these quantities known, ϕ and hence $k_o N_a$ can be evaluated from the slopes of the lines in Figure 4.

Figure 5, is an Arrhenius plot of $k_o N_a$ for all the data. Overall activation energies determined from the slopes of the lines do not change significantly with poison level; the average value is about 30 kJ/mol. Germain et al. (1974) and Ahn et al. (1985b), for unpoisoned Pd/Al_2O_3 catalysts reduced at 693 K, reported 29.3 and 33.4 kJ/mol. Our earlier research (Chen et al., 1985) with another batch of unpoisoned catalyst reduced at 523 K gave 28 kJ/mol.

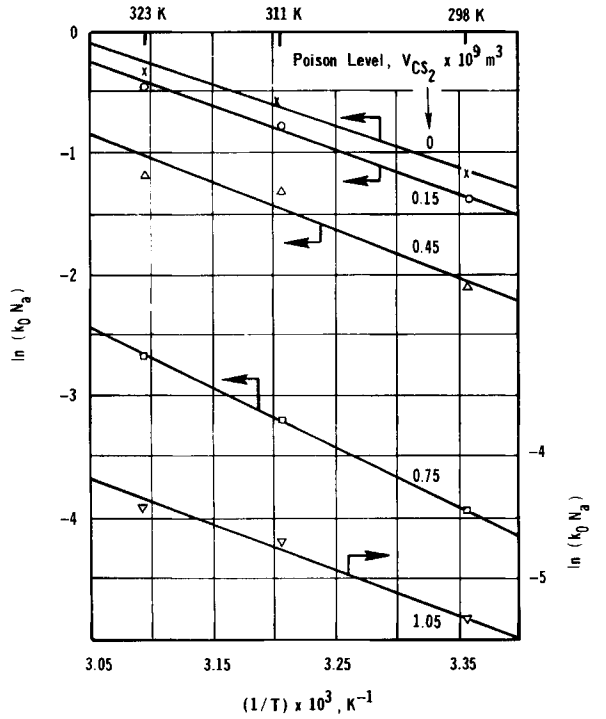

Figure 5. Overall rate constants, $k_o N_a$.

The first moment data plotted according to Eq. 27 are shown in Figures 6–8 for fresh catalyst and two levels of poison. The intercepts, which are equal to V_o/V_L, according to Eq. 27 decrease with an increase in temperature. This is due to the volume expansion of the liquid. From the geometrically determined V_o, the ratio V_o/V_L at 298 K is 0.159, which agrees reasonably well with the average values at this temperature from Figures 6–8.

The slopes of the regression lines in Figures 6–8 provide the second relationship between $k_a N_a$ and k_r. The necessary adsorption equilibrium constants $N_a K_a$ and $N_p K_p$ are those given by Eqs. 33 and 36. All other quantities in Eq. 27 are known. Hence, $k_a N_a$ and k_r can be evaluated from the slopes in Figures 6–8 and the k_o results in Figure 5. These rate constants for all poison levels and temperatures, as well as values of $k_o N_a$, $K_a N_a$, and $(K_a N_a + K_p N_p)$, are given in Tables 5–7. These tables show that k_r does not change significantly with poison level, while $k_a N_a$ decreases with increasing poison. Both rate constants increase with temperature. The ratio $k_r/(k_a N_a/K_a N_a)$, or $k_r K_a/k_a$, is a measure of the relative rates of desorption and surface reaction. This ratio is low at low poison levels, indicating that the surface rate is dominant in determining the overall hydrogenation rate

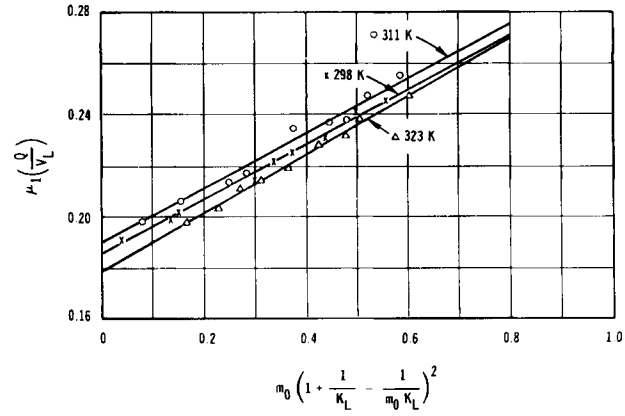

Figure 7. First moment data for reaction on partially poisoned catalyst.
$V_{CS_2} = 0.45 \times 10^{-9}$ m³

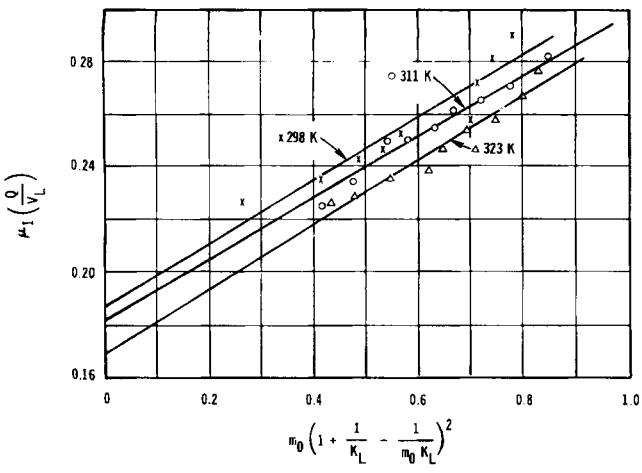

Figure 8. First moment data for reaction on partially poisoned catalyst.
$V_{CS_2} = 0.75 \times 10^{-9}$ m³

for a fresh catalyst. For highly poisoned catalysts the ratio is high, indicating that adsorption of hydrogen is the step of major resistance. These results suggest that the major effect of poisoning is to reduce the number (N_a) of sites available for reaction.

Figure 9 is a plot of k_aN_a vs. $1 - (V/V_{cp})_{CS_2}$. The abscissa is proportional to the fraction of unpoisoned sites, Eq. 31. The linear decrease in k_aN_a up to a poison level of about 40% corresponds to a decrease in number of sites with a constant rate constant k_a. At higher poison levels k_aN_a is less and decreases much more slowly. This suggests that there may be two kinds of active sites, with the more active type poisoned first. Hydrogen absorbs, but does not react, on poisoned sites. Many years ago Babcock et al. (1957) proposed two types of palladium-hydrogen phases, one with a much higher activity than the other, for the hydrogenation of α-methyl styrene. It should be noted that the amount of reaction is low when only a small number of sites is left unpoisoned (high poison levels) so that these results are not of high accuracy. Also, the values of k_aN_a are sensitive to the slope of the lines in Figures 6–8. Hence, the results for k_a are not

Table 5. Equilibrium Adsorption and Rate Constants at 298 K

$V_{CS_2} \times 10^9$m³	$k_oN_a \times 10^3$ m³/kg · s	$(K_aN_a + K_pN_p) \times 10^3$ m³/kg	k_r s⁻¹	$k_aN_a \times 10^3$ m³/kg · s	K_ak_r/k_a	$K_aN_a \times 10^3$ m³/kg
0.0	0.304	15.0	0.0266	1.88	0.212	15.0
0.15	0.250	15.0	0.0254	1.43	0.266	13.5
0.45	0.121	15.0	0.0283	0.34	1.26	10.5
0.75	0.0184	15.0	0.0289	0.053	8.14	7.5
1.05	0.00464	15.0	0.0222	0.089	3.73	4.5
1.5	0.00	15.0	0.0263	0.0	∞	0

Table 6. Equilibrium Adsorption and Rate Constants at 311 K

$V_{CS_2} \times 10^9$m³	$k_oN_a \times 10^3$ m³/kg · s	$(K_aN_a + K_pN_p) \times 10^3$ m³/kg	k_r s⁻¹	$k_aN_a \times 10^3$ m³/kg · s	K_ak_r/k_a	$K_aN_a \times 10^3$ m³/kg
0.0	0.582	11.4	0.0621	5.22	0.136	11.4
0.15	0.467	11.4	0.0620	2.77	0.255	10.3
0.45	0.263	11.4	0.0682	0.72	1.05	8.0
0.75	0.0409	11.4	0.0580	0.11	6.09	5.7
1.05	0.00902	11.4	0.0607	0.10	7.17	3.4
1.5	0.00	11.4	0.0622	0.0	∞	0

Table 7. Equilibrium Adsorption and Rate Constants at 323 K

$V_{CS_2} \times 10^9$m³	$k_oN_a \times 10^3$ m³/kg · s	$(K_aN_a + K_pN_p) \times 10^3$ m³/kg	k_r s⁻¹	$k_aN_a \times 10^3$ m³/kg · s	K_ak_r/k_a	$K_aN_a \times 10^3$ m³/kg
0.0	0.738	9.2	0.114	4.02	0.264	9.2
0.15	0.621	9.2	0.105	3.86	0.228	8.4
0.45	0.306	9.2	0.108	0.83	0.85	6.5
0.75	0.0696	9.2	0.115	0.13	4.28	4.7
1.05	0.0115	9.2	0.111	0.08	4.15	2.8
1.5	0	9.2	0.111	0	∞	0

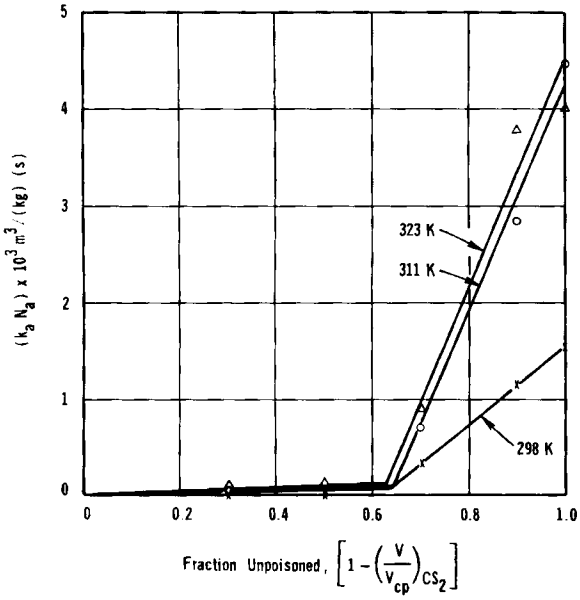

Figure 9. Effect of poisoning on adsorption rate constants.

as accurate as those for k_r, particularly for high poison levels. However, as indicated by results $m_o < 1$, nonzero reaction rates were definitely measured for the poison levels of Figure 9.

Figure 10 shows the effect of temperature on k_r and K_aN_a. The variation of surface rate constant is the same at all poison levels and the line in Figure 10 for k_r corresponds to an average

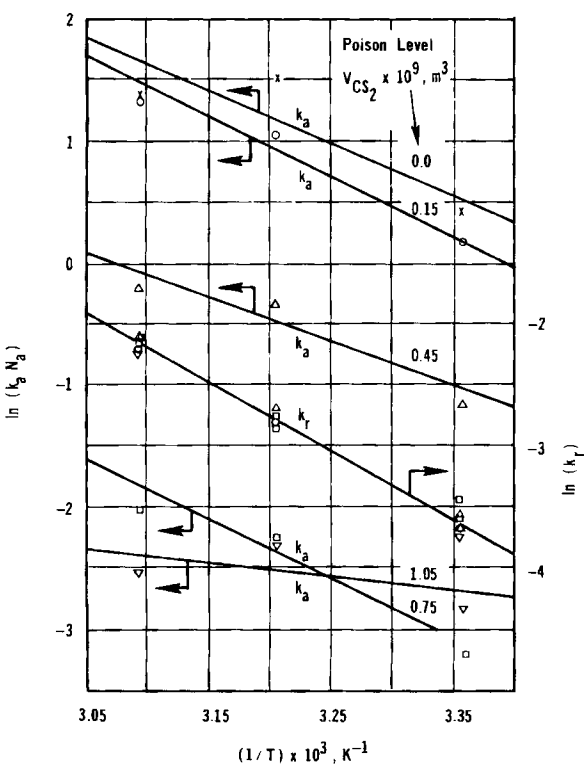

Figure 10. Adsorption and surface reaction rate constants.

activation energy of about 47 kJ/mol. The uniform value of k_r for different degrees of poisoning supplements the conclusion that the site activity for the surface reaction is independent of the amount of poison. The data for the effect of temperature on k_a are less accurate. At all but the highest poison level the activation energy for adsorption is about 35 kJ/mol. The flatter line in Figure 10, for the highest poison level (1.05), corresponds to an activation energy of about 10 kJ/mol, but this value is uncertain because of the small amount of reaction.

Conclusions

One of the major conclusions from this work is that dynamic experiments can provide information about the effect of poisoning on the individual rate constants for the adsorption and surface reaction steps in a heterogeneous catalytic reaction.

The adsorption results showed that the adsorption equilibrium constant was essentially the same for fresh, partially poisoned, and completely poisoned catalyst. This showed that hydrogen was adsorbed on the same catalyst sites as the poison. Accordingly, a model was developed for two kinds of sites: poisoned sites on which adsorption but no reaction occurred, and unpoisoned sites on which both adsorption and surface reaction took place.

From the reaction experiments the rate constant per site for the surface reaction did not change with poisoning. Hence, poisoning did not change the activity of the remaining active sites. This was confirmed by the constant activation energy (47 kJ/mol) regardless of the extent of poisoning.

The adsorption equilibrium constant K_aN_a and adsorption rate constant k_aN_a per unit mass of catalyst both decreased with addition of poison. Up to about 40% poisoning the change in k_aN_a was proportional to the number of active sites, suggesting that k_a and the activity per site were constant. At higher poison levels the activity per site was much less. The reason for this is not clear. Perhaps there are two kinds of active sites and the more active kind is poisoned first. However, the accuracy of the data is somewhat uncertain at the low rates of reaction observed at high poison levels.

Acknowledgment

A grant from Academia Sinica, People's Republic of China, to Song-Ying Chen is gratefully acknowledged. We also appreciate the financial assistance of the National Science Foundation, Grant No. CPE-80-26101. Dow Chemical Company kindly provided chemicals for this work.

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
Bi = Biot number, Rk_r/D_e
B_o = dimensionless quantity, Eq. 12
B_s = quantity, Eq. 16, s
C_g = hydrogen concentration in gas phase, mol/m^3
C_{g_o} = concentration in feed pulse, mol/m^3
C_i = hydrogen concentration in liquid-filled pores of catalyst, mol/m^3
C_L = hydrogen concentration in bulk liquid, mol/m^3
D_e = effective diffusivity in liquid-filled pores of catalyst particle, m^2/s
H = Henry's law constant
H_s, H_c = Henry's law constants for solubility of hydrogen in styrene and cumene, $(C_g/C_L)_{equil.}$

k_a = adsorption rate constant on unpoisoned sites, m^3/site · s
k_aN_a = adsorption rate constant on unpoisoned sites, m^3/s · kg catalyst
k_L = gas bubble-to-liquid mass transfer coefficient, m/s
k_oN_a = overall reaction rate constant, Eq. 25, m^3/s · kg catalyst
k_p = adsorption rate constant on poisoned sites, m^3/sites · s
k_pN_p = adsorption rate constant on poisoned sites, m^3/kg catalyst · s
k_r = surface reaction rate constant on unpoisoned sites, s^{-1}
k_s = liquid-to-particle mass transfer coefficient, m/s
K_a = adsorption equilibrium constant for hydrogen on unpoisoned sites, m^3/site
K_p = adsorption equilibrium constant for hydrogen on poisoned sites, m^3/site
K_L = dimensionless quantity, Eq. 13
m_o = zero moment, Eq. 22
m_1 = first moment, Eq. 23, s
m_s = mass of catalyst particles per unit volume of bubble- and particle-free liquid, kg/m^3
n_a = concentration of hydrogen adsorbed on unpoisoned sites, mol/kg
n_p = concentration of hydrogen adsorbed on poisoned sites, mol/kg
N_a = unpoisoned site concentration, sites/kg catalyst
N_p = poisoned site concentration, sites/kg catalyst
Q = volumetric gas flow rate, m^3/s
r = radial distance from center of spherical catalyst particle, m
R = radius of catalyst particle, m
R_g = gas constant, J/mol · K
t = time, s
V_B = bubble volume per unit volume of bubble- and particle-free liquid
V_o = dead volume with no gas flow, including gas space over slurry, in sample loop and in tubing, m^3
V_L = volume of liquid in slurry, m^3
V_{CS_2} = volume of pure CS_2

Greek letters

α = constant total adsorption capacity of catalyst, Eq. 33, m^3/kg catalyst
β = porosity of catalyst particle
ϵ = quantity, Eq. 15, s^{-1}
μ_1 = reduced first moment, including dead volume, s
ϕ = Thiele-type modulus, Eq. 17
ρ_p = density of catalyst particle, kg/m^3
τ_g = residence time of gas in slurry, V_BV_L/Q, s

Subscripts

a = active sites
c = cumene
cp = completely poisoned sites
f = unpoisoned sites
p = poisoned sites
s = styrene

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Manuscript received Dec. 19, 1985, and revision received Apr. 3, 1986.