Dynamic Response and Poisoning Studies of a Liquid–Solid Catalytic Reaction: Effects of Metal Content on Adsorption and Surface Reaction Rates

S.-Y. CHEN, J. M. SMITH, AND B. J. McCOY

Department of Chemical Engineering, University of California, Davis, California 95616

Individual adsorption equilibrium, adsorption rate, and surface reaction rate coefficients were determined for three supported-metal (Pd/Al$_2$O$_3$) catalysts of 0.050, 0.150, and 0.450 wt% palladium content. The data were obtained by a hydrogen-gas, pulse response technique in a well-mixed, three-phase slurry reactor at 25, 38, and 50°C and atmospheric pressure. The reaction, hydrogenation of α-methyl styrene to cumene in pure methyl styrene, is first-order in H$_2$ and zero-order in methyl styrene. Adsorption equilibrium coefficients for hydrogen on Pd increased with Pd content. The heat of adsorption, 13.7 kJ/mole, was the same for the three catalysts. Adsorption and surface reaction rate coefficients based on mass of catalyst also increase, while those based on mass of Pd decrease with Pd content. The energy of activation increases for adsorption and decreases for the surface reaction rate as Pd content increases, but remains constant for the overall rate constant. The number of active sites on the catalyst surface for these metal loadings was estimated from experimental data of CS$_2$ poisoning. The number of active sites per gram of catalyst increases, and the number per gram of Pd decreases with Pd content. Adsorption equilibrium, adsorption rate, and surface reaction coefficients increase with number of active sites for unpoisoned catalyst. The results suggest that the dynamic response technique combined with poisoning studies is a useful tool in the study of heterogeneous catalysis. © 1986 Academic Press, Inc.

INTRODUCTION

Elucidation of the essential features of catalytic activity requires identification and determination of active sites. Gonzalez-Tejuca *et al.* (*1*) proposed that the number of active sites for supported platinum catalyst could be determined by a poisoning method. Both they (*1*) and Yang and Pang (*2*) used carbon disulfide as the poison for catalytic reactions at the gas–solid interface.

Recently a dynamic response technique has been applied to determine separate rate coefficients for adsorption and surface reaction on catalysts. The kinetic steps for the oxidation and hydrogenation reactions studied were interpreted as first-order, reversible adsorption followed by first-order, irreversible surface reaction. Ahn *et al.* (*3*) and Recasens *et al.* (*4*) measured separate adsorption and surface reaction rate coefficients for the oxidation of sulfur dioxide in

an aqueous slurry of activated carbon catalyst. Ahn *et al.* (*5*) determined the individual rate coefficients of adsorption and surface reaction for hydrogenation of methyl styrene in a slurry of Pd/Al$_2$O$_3$ catalyst. These experiments showed that the traditional assumption of a single step controlling the rate was not valid, or at best only an approximation.
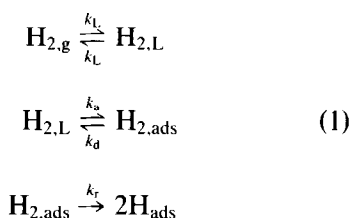
By the dynamic technique, Chen *et al.* (*6*) studied the effect of Pd/Al$_2$O$_3$ catalyst reduction temperature on individual adsorption and reaction rates of hydrogenation of methyl styrene. Due to decreased Pd dispersion, the rate coefficients decreased with increasing reduction temperature.

Recently, Chen *et al.* (*7*) applied a new model for reactive and unreactive sites to experimental data for CS$_2$ poisoning of the hydrogenation catalyst. The rate constant (per mass of catalyst) for adsorption decreased continuously to zero as the extent of poisoning increased; the rate constant

for the surface reaction and the adsorption equilibrium constant did not change. The major finding of (7) was that the number of sites decreased for catalyst poisoning, but the surface reactivity per site was unchanged.

In a study of catalytic liquid-phase hydrogenation of cyclohexene on supported platinum, Madon et al. (8) measured overall rate constants, but did not evaluate the separate rate constants of adsorption and surface reaction. They ascertained that the rate of hydrogenation was zero-order with respect to cyclohexene and first-order with respect to the concentration (not thermodynamic activity) of dissolved H_2. The overall rate was independent of the nature of the solvent if cyclohexene concentrations were greater than about 20%.

The mechanism they proposed for the hydrogenation (8) is compatible with the kinetic expressions used in our past work (5–7) for dissolution, adsorption, and surface reaction of hydrogen:

$$H_{2,g} \underset{k_L}{\overset{k_L}{\rightleftharpoons}} H_{2,L}$$

$$H_{2,L} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} H_{2,ads} \qquad (1)$$

$$H_{2,ads} \xrightarrow{k_r} 2H_{ads}$$

Madon et al. (8) refer to the nondissociated, adsorbed hydrogen molecule as being in a physically adsorbed state. Chen et al. (6) measured an activation energy of 4 kcal/mole for the reversible adsorption of H_2 on Pd/Al_2O_3 in cumene solvent, placing the adsorption step in the category of weakly activated, nondissociative adsorption. The kinetics of hydrogen adsorption and dissociation given in Eq. (1) will not be directly influenced by subsequent steps of the hydrogenation process since the third reaction step is irreversible. It is presumed that hydrogenation of unsaturated carbon–carbon bonds occurs when an alkene is in the vicinity of the chemisorbed hydrogen atoms.

The salient feature of the dynamic technique (3–7) is that it allows the separate determination of adsorption and surface reaction sites. The poisoning technique enables the measurement of the number and strength of active sites. By combining the dynamic response and poisoning methods, one can study the dependence of adsorption and reaction on the nature of active sites. The objective of the present work is to examine the effect of metal content on these processes. For a supported metal catalyst, metal content is an important parameter because of its potential effect on activity, selectivity, and life of the catalyst, and thus on the economics of the catalytic process.

EXPERIMENT

The slurry reactor used in the present work is unchanged from that in our earlier papers (3–7), which provide details describing the cylindrical vessel with impeller and baffles. The experimental setup for injecting gas into the liquid and measuring its effluent composition is shown schematically in Refs. (5–7), and operating conditions are listed in Table 1.

The α-methyl styrene was technical grade (Eastman–Kodak). Carbon disulfide (Aldrich) was dissolved in methyl styrene to form a 0.3 vol% solution for poisoning.

The catalyst support consisted of γ-alumina particles (T-126, Girdler Chemical Co.) of average diameter 442 μm and porosity 0.503. Other properties of the support are given in Table 2. Palladium in the amounts 0.050, 0.150, and 0.450 wt% was deposited and reduced on the alumina as previously described (5–7).

To stabilize catalyst activity after addition to the reactor vessel, about 20 pulses of pure hydrogen were introduced with nitrogen carrier gas. Continuous pulse-response curves were recorded for each unpoisoned catalyst at gas flow rates from 0.8 to 7.0 ml/s. The reaction runs for each metal loading of catalyst provided data for determination

TABLE 1

Summary of Operating Conditions

Reactor volume, including lines	1285 cm³
Volume of sample loop containing pure H₂	4.5 cm³
Flow rate of N₂ carrier gas (1 atm, 20°C)	0.8 ~ 7 cm³/s
Impeller speed	920 rpm
Reactor pressure	Atmospheric
Palladium contents in catalysts	0.05, 0.15, 0.45 wt%
Temperatures for reaction and adsorption runs	25, 38, 50°C
Temperature for catalyst reduction	250°C
(A) Reaction runs:	
Weight of catalyst	125, 100, 95 g
Volume of α-methyl styrene	1100 cm³
(B) Poisoning runs:	
Weight of catalyst	125, 100, 95 g
Volume of α-methyl styrene	1120 or 1130 cm³
Temperature	25°C
(C) Adsorption runs:	
Weight of catalyst	125, 100, 95 g
Volume of α-methyl styrene	1120 or 1130 cm³

of k_0, k_a, and k_r at three temperatures, 25, 38, and 50°C.

After completion of reaction runs with fresh (unpoisoned) catalyst, poisoning experiments were conducted at 25°C. The 0.30 vol% CS_2 solution was added to the reactor in increments of 50 μl with a microliter syringe, and stirred for an hour before the hydrogen pulse runs. Each pulse response for the poisoned catalyst was repeated at least three times at one flow rate, 0.8 ml/s, and one temperature, 25°C. This data allowed determination of k_0 as a function of amount of added poison. The catalyst was considered completely poisoned when the heights of response peaks of H_2 at three levels of poison were unchanged.

Adsorption runs for determination of adsorption equilibrium coefficients of hydrogen on Pd/Al_2O_3 were carried out on completely poisoned catalyst. Since the

completely poisoned catalyst was unreactive, only adsorption occurs at the interface of the metal and the methyl styrene. Adsorption runs at 25, 38, and 50°C were performed at flow rates from 0.8 to 7.0 ml/s.

Values for metal dispersion (percentage metal exposed) were determined for the 0.05, 0.15, and 0.45% Pd/Al_2O_3 loadings by H_2 chemisorption in a Micromeritics Chemisorb 2500 instrument. The steps for the analysis technique were as follows: (a) the poisoned catalyst particles were dried and oxidized in air for 4 h at 250°C, (b) the oxidized catalyst was reduced in pure hydrogen for 8 h at 250°C, and (c) the H_2 adsorption uptake was measured at 35°C.

THEORY

Zero and first moments for pulse-response experiments are calculated by numerical integration of reactor effluent gas concentration readings as follows:

$$m_0 = \int_0^\infty c_g(t)dt \bigg/ \int_0^\infty c_{g0}(t)dt \qquad (2)$$

$$m_1 = \int_0^\infty c_g(t)t\,dt \bigg/ \int_0^\infty c_{g0}(t)dt. \qquad (3)$$

For a three-phase, well-stirred, isothermal slurry reactor Ahn et al. (5) presented the derivation of zero and first temporal moment expressions for concentration of reactant in effluent gas concentration. The mathematical model accounted for intraparticle diffusion, and mass transfer from gas bubble to liquid and from liquid to particle. The rate of conversion of adsorbed H_2 was described by the equation

$$dn/dt = k_a(c_i - n/K) - k_r n \qquad (4)$$

TABLE 2

Properties of Catalyst Support Al_2O_3

Surface area (N₂ adsorption), m²/g	165
Average pore radius, nm	6
Particle density, ρ_p, g/cm³	1.53
Average radius of particle, cm	0.0221
Porosity of particle, β	0.503

TABLE 3

Values of Parameters Used in k_r and k_a Calculations

	25°C	38°C	50°C
H^a	15.2	13.9	12.5
$D_e \times 10^4$ (cm^2/s)^b	1.26	1.38	1.49
k_s (cm/s)	0.130	0.141	0.156
Thiele modulus for			
0.05% Pd/Al$_2$O$_3$	0.32	1.77	1.98
0.15% Pd/Al$_2$O$_3$	1.77	2.07	2.56
0.45% Pd/Al$_2$O$_3$	2.07	2.55	2.89

[a] Herskowitz et al. (14).
[b] Ahn et al. (5).

in terms of the adsorption rate constant, k_a, the surface reaction rate constant, k_r, and the equilibrium adsorption coefficient, K.

When $k_r = 0$, no reaction occurs, and the dimensionless zero moment is unity. The expression for the normalized first moment for this reversible adsorption case is

$$m_1/m_0 = V_L(1 + m_sK)/HQ + \tau_g \quad (5)$$

and the relatively small gas residence time, τ_g, is negligible. Then the equilibrium adsorption coefficient K can be obtained from Eq. (5) and the reversible adsorption experiments by plotting m_1/m_0 versus V_L/Q.

For the reaction case the expression for the zero moment may be cast in a form such that a plot of $1/(1 - m_0)$ versus Q/V_L will be a straight line if the model is consistent with the data. The intercept gives the gas-to-liquid mass transfer coefficient, and the slope is a known function of the Thiele modulus, listed in Table 3, and hence of the combined rate constant

$$1/k_0 = 1/k_a + 1/Kk_r. \quad (6)$$

This calculation relies upon known values of the intraparticle diffusivity, D_e, and the gas-to-particle mass transfer coefficient, k_s, but the sensitivity to these parameters is low due to the small particle diameter and high degree of turbulence in the liquid.

The zero moments are not affected by the dead volume as they represent the uncon-

verted fractions of reactant. However, experimentally observed first moments include the residence time in the dead volume between the sample loop and the fritted-glass sparger, and in the space above the solvent in the reactor. The first moment m_1/m_0 in terms of the dead volume, V_0, indicates that a straight line should result if m_1Q/m_0V_L is plotted versus $m_0/(1 + 1/K_L - 1/m_0K_L)^2$, which can be estimated from the zero-moment plot. The ratio of volumes, V_0/V_L, can be obtained from the intercept of the first-moment plot and compared to the known geometric volumes of the reactor system. The slope of the first-moment plot provides the value of

$$\zeta = K/(1 + Kk_r/k_a)^2 \quad (7)$$

from which the ratio k_r/k_a can be evaluated if K is known.

Although in principle K could be obtained from second-moment data, the error in computing the second moment from gas concentration response data is excessive, and we utilized another method. The results of Ref. (7) showed that the total adsorption equilibrium coefficient was unchanged for fresh, partly poisoned, or completely poisoned catalyst. We interpreted this result to mean that the physical adsorption by $K = k_a/k_d$ is unaffected by the presence of a strongly adsorbed CS$_2$ poison molecule. This implies that we can directly measure K in methyl styrene on completely poisoned catalyst ($k_r = 0$) from Eq. (5). Values of solubility constants, H, along with D_e and k_s used in the calculations are listed in Table 3.

RESULTS AND DISCUSSION

Adsorption runs in methyl styrene for completely poisoned catalyst yielded the first moments plotted in Figs. 1–3 for different Pd loadings. Each figure shows data points for three operating temperatures, 25, 38, and 50°C. Because the temperature dependence of H compensates for that of K, the plots show no significant temperature effect on slope for the same catalyst. The
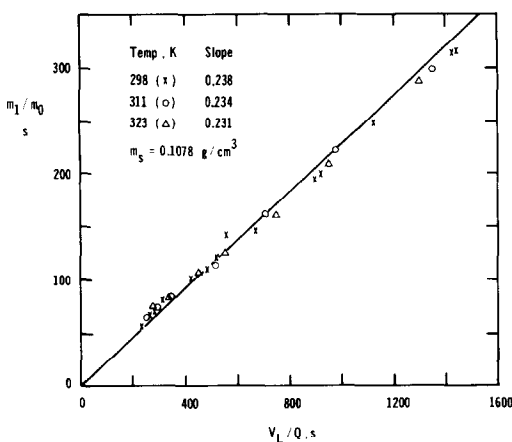
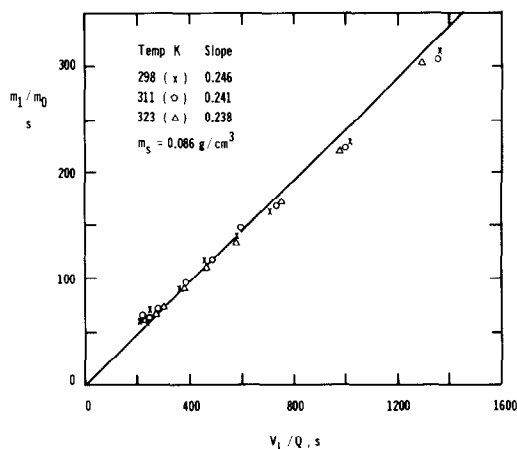FIG. 1. First moments of pulse responses for H_2 adsorption on completely poisoned 0.050 wt% Pd/Al_2O_3 catalyst in α-methyl styrene.

FIG. 3. First moments of pulse responses for H_2 adsorption on completely poisoned 0.450 wt% Pd/Al_2O_3 catalyst in α-methyl styrene.

equilibrium adsorption coefficients, evaluated from Eq. (5) by substituting the values of V_0, V_L, m_s, and H, are presented in Table 4. For 0.050% Pd catalyst, the results agree with the values of K from previous studies (5–7), which were measured in cumene for reactive catalyst of same Pd loading.

Figure 4 shows the results plotted as ln K versus $1/T$. The slopes of the straight lines provide the heats of adsorption listed in Table 5, which are nearly independent of Pd content. In our earlier study (7) it was demonstrated that the adsorption equilibrium coefficient of H_2 on fresh Pd equaled that on completely poisoned catalysts for the same solvent. Therefore K values obtained from adsorption runs on completely poisoned catalysts were used in the calculation of adsorption and surface reaction rate constants.

For reaction runs, zero-moment plots of $1/(1 - m_0)$ versus Q/V_L are presented in Figs. 5–7 for three catalyst loadings. The intercepts of the straight lines provide the values of gas-to-liquid mass transfer coefficients. The overall (combined) rate con-
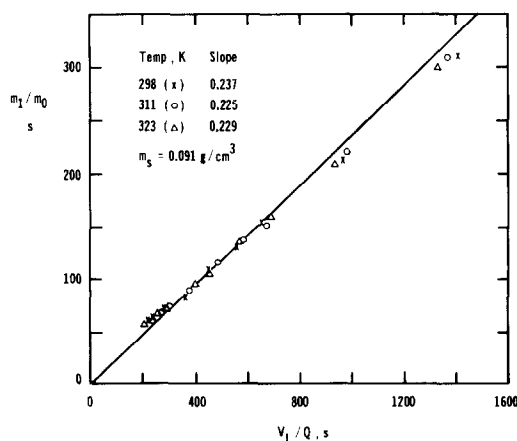

FIG. 2. First moments of pulse responses for H_2 adsorption on completely poisoned 0.150 wt% Pd/Al_2O_3 catalyst in α-methyl styrene.

TABLE 4

Adsorption Equilibrium and Rate Constants

Temp (°C)	Pd content (wt%)	K (cm³/g)	k_0 (cm³/g · s)	k_r (s⁻¹)	k_a (cm³/g · s)	Kk_r/k_a
25	0.05	15.0	0.296	0.0256	1.29	0.298
	0.15	17.2	0.531	0.0427	1.89	0.389
	0.45	19.8	0.685	0.0519	2.05	0.501
38	0.05	11.7	0.582	0.0605	4.91	0.144
	0.15	13.0	0.792	0.0856	2.52	0.442
	0.45	16.3	1.20	0.0889	7.16	0.202
50	0.05	9.3	0.783	0.112	3.61	0.289
	0.15	11.2	1.30	0.136	6.54	0.233
	0.45	13.1	1.67	0.140	18.7	0.098
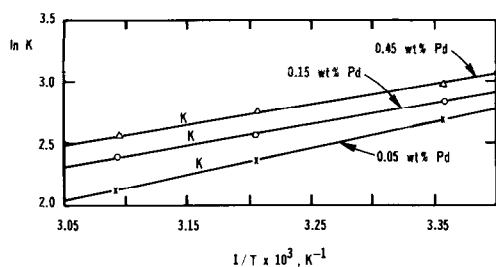
FIG. 4. The temperature dependence of adsorption equilibrium coefficients.

TABLE 5

Activity Energy and Adsorption Heat for Unpoisoned Catalysts of Different Pd Content

	0.05 wt%	0.15 wt%	0.45 wt%
ΔH, kJ/mole	−13.8	−13.8	−13.4
E_0, kJ/mole	30.0	29.0	29.4
E_r, kJ/mole	48.0	40.0	32.0
E_a, kJ/mole	34.0	39.0	71.0

stants, k_0, were calculated from the slopes of the lines determined by linear regression and are listed in Table 4. Arrhenius plots, given in Fig. 8, yield activation energies of 30.1, 28.9, and 28.9 kJ/mole for catalyst loadings of 0.05, 0.15, and 0.45% Pd, respectively, as reported in Table 5. These values are in reasonable agreement with the values 28.8 kJ/mole given by Germain et al. (9), 33.4 kJ/mole given by Ahn et al. (5), and 28.0 and 30 kJ/mole given by Chen et al. (6, 7).

The first-moment plots for three catalyst loadings and three operating temperatures are displayed in Figs. 9–11. The intercepts of these straight lines are V_0/V_L, the ratio of the dead volume to solvent volume. Although first-moment data are inherently less accurate than the zero-moment results, the values of V_0/V_L obtained by regression

analysis from the graphs agree well with values directly measured from the apparatus. Since the slopes of the lines are less accurate and the values of k_a are sensitive to these slopes, the results for k_a are subject to at least 50% uncertainty.

The adsorption and surface reaction rate coefficients can be calculated from the slopes of the lines, given values of D_e and k_s. Owing to the insensitivity of the rate constants to these parameters, the values estimated by Ahn et al. (5) (Table 3) were sufficiently accurate. Results for k_a and k_r for different metal loadings are reported in Table 4, together with adsorption equilibrium and overall rate constants. The values of k_r are estimated to be accurate to within ±15%. The Arrhenius plots of k_r (Fig. 8), yield activation energies listed in Table 5, showing E_r increasing with increasing Pd
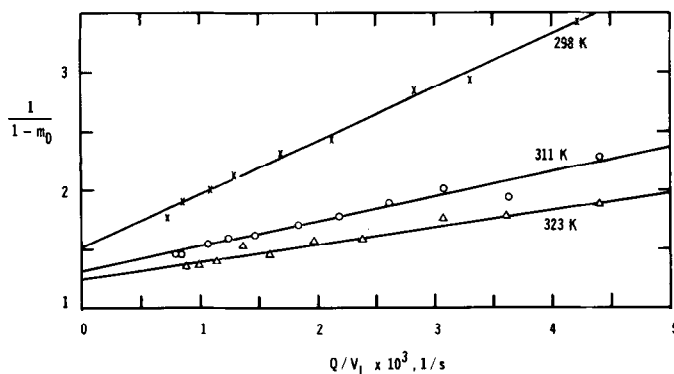

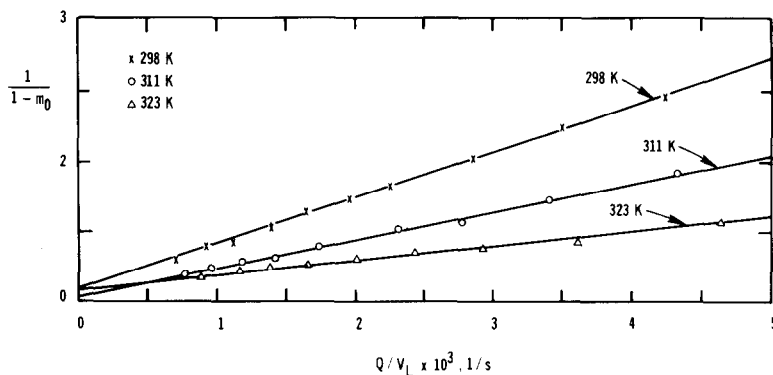FIG. 5. Zero moments of pulse responses for the hydrogenation of α-methyl styrene on 0.050 wt% Pd/Al$_2$O$_3$ catalyst.

FIG. 6. Zero moments of pulse responses for the hydrogenation of α-methyl styrene on 0.150 wt% Pd/Al$_2$O$_3$ catalyst.

loading. Values of E_a (Table 5) are less certain, but apparently the values of E_a and E_r for different metal contents compensate each other so that E_0 is relatively constant (Table 5).

The ratio Kk_r/k_a, indicated in Table 4, is in the range 0.1–0.5, demonstrating that the catalyzed hydrogenation reaction is controlled by neither adsorption nor surface reaction. This conclusion is the same as in previous papers (5–7).

Combined rate constants, k_0, for poisoning experiments were determined from zero moments for three catalysts at 25°C, by using K_L values obtained from reaction runs at the same temperature. The results are reported in Fig. 12 and in Table 6 in units of

cm^3/(g Pd)(s) and cm^3/(g cat)(s), as they depend on the fraction of poisoned sites. These poisoning curves (Fig. 12) each consist of two essentially straight lines, apparently indicating two different kinds of active sites. There is no doubt that a nonnegligible reaction occurred for the higher number of poisoned sites, since the reduced zero moment (Eq. (2)) was less than unity. Only when the quantity $1 - N_A/N_t$ equals one in Fig. 12 was the measured value of m_0 found to be 1.00, indicating no loss of H$_2$ by catalyzed hydrogenation. The reason for the change in activity per site is not entirely clear. The dual nature of the sites is consistent with the observation of Babcock et al. (10) that two phases of Pd
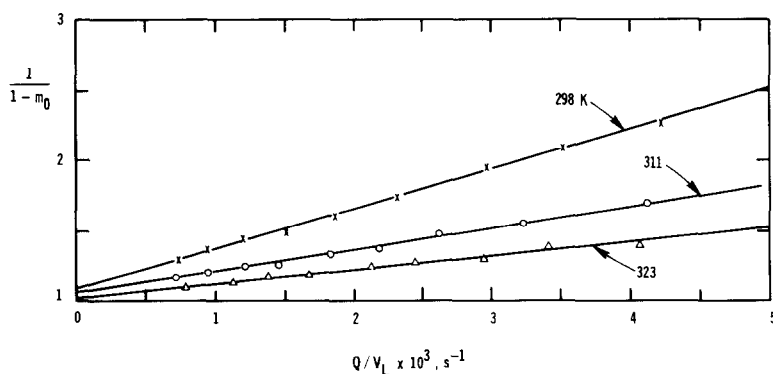

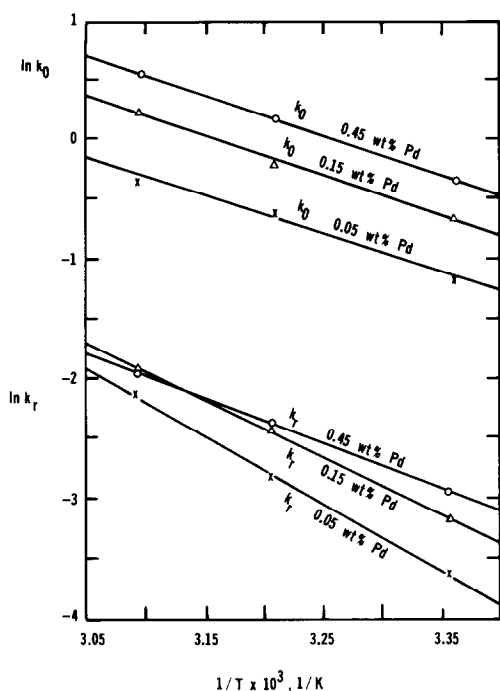FIG. 7. Zero moments of pulse responses for the hydrogenation of α-methyl styrene on 0.450 wt% Pd/Al$_2$O$_3$ catalyst.

FIG. 8. The temperature dependence of the overall (combined) rate constant, k_0, and of the surface reaction rate constant, k_r.

a minimum small number of palladium atoms in aggregation (*13*). The number of aggregates would be expected to decrease with the extent of poisoning. Palladium on charcoal catalysts, for example, shows a sharp break in activity when the metal content falls below 0.1% for benzene hydrogenation.

The number of active sites (Table 7) was estimated on the assumption that one molecule of CS_2 poisons one active site. However, if one CS_2 poisons more than one active site, then our estimate of N_t will be proportionally less, by an integer, to the actual number of active sites. That a CS_2 molecule poisons the same number of active sites over the entire poisoning range is indicated by our earlier data (*7*), showing k_r constant with poisoning level. The ratio of metal surface area to that of the Al_2O_3 support is probably very low even allowing for the spillover effect. Also, many Pd atoms are likely to be occupied by adsorbed styrene. Therefore, it may be reasonable to infer that one CS_2 molecule poisons but a few sites. The total moles of CS_2 needed to poison the catalyst completely is uncertain by ±15%, due to difficulty in determining the exact point when the catalyst becomes inactive.

The Pd content of the catalyst affects the distribution of active sites as shown in Table 7. The number of active sites per gram
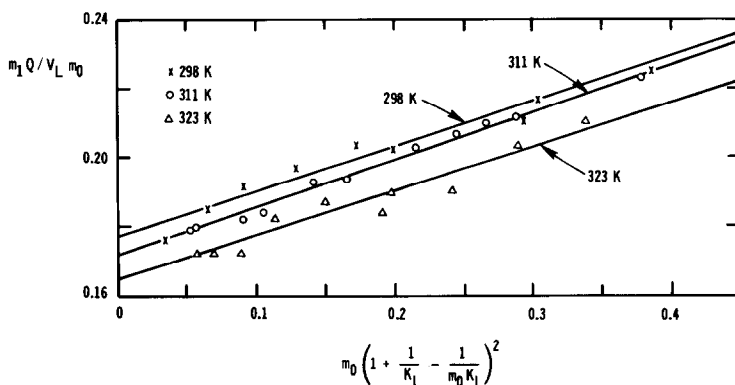
are possible, with one being much more active for the hydrogenation of α-methyl styrene. Also, the sharp reduction in activity with poisoning could be explained by Balandin's "multiplet hypothesis." That is, for activity to occur, there must be present

FIG. 9. First moments of pulse responses for the hydrogenation of α-methyl styrene on 0.050 wt% Pd/Al$_2$O$_3$ catalyst.
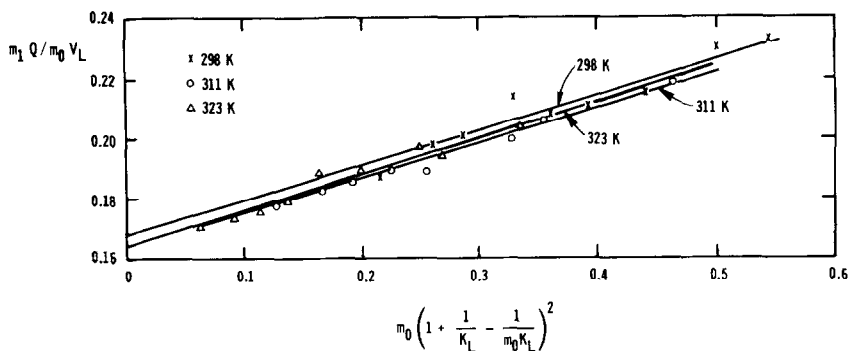
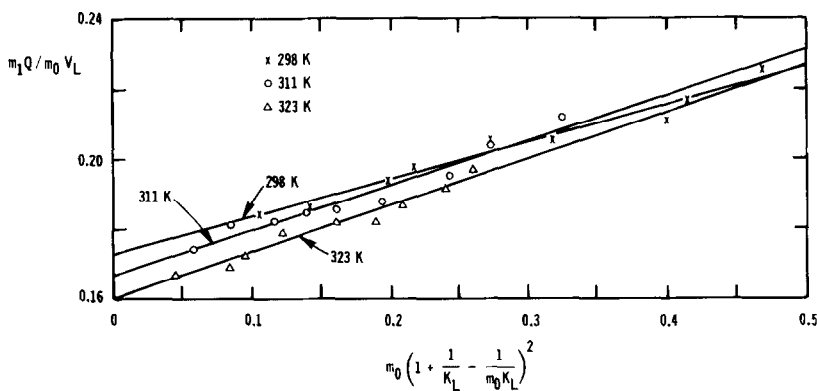FIG. 10. First moments of pulse responses for the hydrogenation of α-methyl styrene on 0.150 wt% Pd/Al$_2$O$_3$ catalyst.

FIG. 11. First moments of pulse responses for the hydrogenation of α-methyl styrene on 0.450 wt% Pd/Al$_2$O$_3$ catalyst.
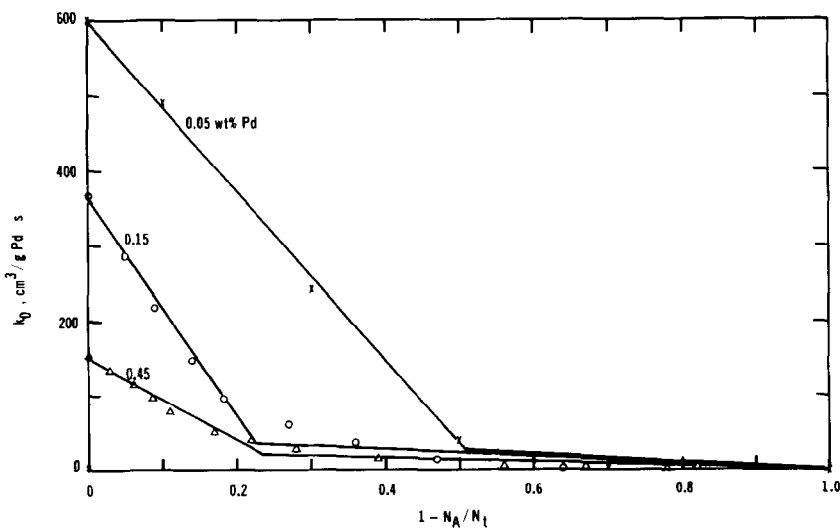

FIG. 12. Poisoning curves for three catalysts of different Pd loadings. Values of the overall rate constant, k_0, per mass of palladium are plotted versus the number of poisoned sites.

TABLE 6

The Results of Poisoning Experiments

0.05 wt% Pd/Al$_2$O$_3$			0.15 wt% Pd/Al$_2$O$_3$			0.45 wt% Pd/Al$_2$O$_3$		
N_A/N_t	k_a (cm^3/g cat · s)	k_0' (cm^3/g Pd · s)	N_A/N_t	k_a (cm^3/g cat · s)	k_0' (cm^3/g Pd · s)	N_A/N_t	k_a (cm^3/g cat · s)	k_0' (cm^3/g Pd · s)
1.0	0.300	600	1.0	0.553	368.7	1.0	0.682	151.6
0.9	0.245	490	0.95	0.430	286.7	0.97	0.588	130.7
0.7	0.122	244	0.91	0.328	218.7	0.94	0.500	111.1
0.5	0.0194	38.8	0.86	0.222	148.0	0.92	0.440	97.8
0.3	0.00474	9.5	0.82	0.137	91.3	0.89	0.344	76.4
0.0	0.0	0.0	0.73	0.0941	62.7	0.83	0.225	50.0
			0.64	0.0588	39.2	0.78	0.185	41.1
			0.55	0.187	12.5	0.72	0.140	31.1
			0.36	0.00411	2.74	0.61	0.0661	14.7
			0.18	0.00200	1.3	0.56	0.0416	9.2
			0.0	0.0	0.0	0.44	0.0198	4.4
						0.33	0.0106	2.3
						0.22	0.00357	0.8
						0.0	0.0	0.0

of Pd decreases, while the number of active sites per gram of catalyst increases with increasing Pd loading. One infers from these results that metal dispersion decreases with the increase in metal loading. This decrease in dispersion was confirmed by independent gas–solid, hydrogen chemisorption measurements as described earlier. The values of measured dispersion, displayed in Table 7, indeed decrease with metal loading. If metal dispersion and N_t' measure the same characteristic, namely, the amount of metal that is catalytically active, it is required that their ratio for a given metal

loading is constant. Table 7 provides this ratio, which, within the experimental errors of the measurements, is constant. The agreement of separate determinations of active metal catalyst supports the validity of the poisoning method proposed in this work.

Values of K, k_0, and k_r increase with N_t, the number of active sites. Values of $k_0^* = k_0/N_t$, $K^* = K/N_t$, $k_r^* = k_r/N_t$, and $k_a^* = k_a/N_t$ are listed in Table 7. The values show that a ninefold increase in palladium gives only about a threefold increase in activity, i.e., about a threefold decrease in rate con-

TABLE 7

Number of Active Sites (per Gram of Catalyst and per Gram of Pd) on Catalysts of Different Metal Content; and Adsorption and Reaction Rate Parameters per Active Site at 25°C

	0.050 wt% Pd	0.150 wt% Pd	0.450 wt% Pd
$N_t \times 10^{-17}$, site/g · cat	1.16	3.20	5.52
$N_t' \times 10^{-20}$, sites/g Pd	2.32	2.13	1.23
Metal dispersion (d), %	11.4	10.2	7.2
$d/(N_t' \times 10^{-20})$, g · Pd/site	4.9	4.8	5.8
$k_0^* \times 10^{17}$, cm^3/(site)(s)	0.26	0.17	0.14
$K^* \times 10^{17}$, cm^3/site	12.9	5.4	3.6
$k_a^* \times 10^{17}$, cm^3/(site)(s)	1.11	0.59	0.37
$k_r^* \times 10^{17}$, g cat/(site)(s)	0.022	0.013	0.0094

stants per site. Note that k_0^* multiplied by dissolved hydrogen concentration corresponds to the usual definition of turnover frequency (11).

CONCLUSION

The dynamic response technique for a three-phase slurry reactor allows determination of adsorption equilibrium, and adsorption and surface reaction rate coefficients for hydrogenation of α-methyl styrene on Pd/Al$_2$O$_3$ catalyst. Our experiments at 25, 38, and 50°C reveal that these coefficients increase with increasing Pd content. The adsorption heat and the energy of activation for k_0 are independent of Pd content, while the energies of activation for k_r and k_a compensate each other by, respectively, decreasing and increasing with Pd content. Neither the adsorption nor surface reaction rate controls the overall hydrogenation reaction.

The results of poisoning experiments at 25°C show that the number of active sites per gram of metal, and thus metal dispersion, decreases with Pd content. For the conditions of these experiments the individual adsorption and reaction coefficients increase with number of active sites. The error in measuring N$_t$ ($\pm 15\%$) is due to difficulty in determining the point of complete deactivation of the catalyst.

The quantitative description of the transient system requires that K, k_r, and k_a be known separately (12). Only when the following relationship is satisfied will $(k_0)(c_i)$ be a valid approximation to the rate of reaction in the unsteady state (12):

$$\zeta = K/(1 + Kk_r/k_a)^2 \ll 1. \tag{8}$$

The experimental results reveal that ζ, the same quantity defined in Eq. (7), is of the order of 10. Thus, a pseudo-steady-state approximation applied to Eq. (4) for the adsorbed H$_2$ concentration, n, would be inadequate to represent accurately the dynamic responses of these experiments.

The optimization of catalytic processes requires understanding quantitatively the effects of a variety of variables and parameters on rate of reaction, yield, and selectivity. For example, one would wish to know how catalyst preparation, amount of metal, presence of impurities, nature of solvent, etc., affect the reaction process. The intrinsic surface phenomena will determine which of these factors are important in a given system. We have developed an experimental technique, based on an accurate mathematical description of the pertinent mass transfer and kinetics, that shows promise for answering these questions, at least for a certain kind of liquid–solid catalytic reaction. The method allows us to uncover the relative influence of adsorption and surface reaction for processes that are overall first-order in the soluble gas reactant.

APPENDIX: NOMENCLATURE

a_B surface area of gas bubbles per unit volume of bubble- and particle-free liquid, cm^2/cm^3

c_g H$_2$ concentration in gas phase, mole/cm^3

c_i H$_2$ concentration in liquid-filled pores of catalyst, mole/cm^3

D_e effective diffusivity in the liquid-filled pores of catalyst particle, cm^2/s

H Henry's law constant for solubility of H$_2$ in solvent, cm^3 gas/cm^3 liq

K_L $= k_L a_B V_B/HQ$, dimensionless group

K adsorption equilibrium constant for H$_2$ in liquid phase, cm^3/g

k_a adsorption rate constant, cm^3/(g catalyst)s

k_d $= k_a/K$, desorption rate constant, liters/s

k_0 overall reaction rate constant, cm^3/(g catalyst)s

k_L gas bubble-to-liquid mass transfer coefficient, cm/s

k_r surface reaction rate constant, liters/s

m_0 zero moment, Eq. (2)

m_1 first moment, Eq. (3), s

n concentration of H$_2$ adsorbed in catalyst particles, mole/g

N_A concentration of active sites for poisoning experiments, sites/g catalyst

N_t total concentration of active sites, sites/g catalyst

Q volumetric gas flow rate, cm^3/s

t time, s

V_B bubble volume per unit volume of bubble- and particle-free liquid

V_L volume of liquid in the vessel, cm^3

τ_g $= V_B V_L/Q$, residence time of gas in slurry, s

Superscripts

$()'$ prime indicates a quantity per gram Pd

$()^*$ asterisk indicates a quantity per site

ACKNOWLEDGMENTS

REFERENCES

1. Gonzalez-Tejuca, L., Alba, K., Namba, S., and Turkevich, J., *J. Phys. Chem.* **81**, 1399 (1977).
2. Yang, X.-Y., and Pang, L., *Int. Chem. Eng.* **22**, 125 (1982).
3. Ahn, B.-J., McCoy, B. J., and Smith, J. M., *AIChE J.* **31**, 541 (1985).
4. Recasens, F., Smith, J. M., and McCoy, B. J., *Chem. Eng. Sci.* **39**, 1469 (1984).
5. Ahn, B.-J., Smith, J. M., and McCoy, B. J., *AIChE J.* **32**, 566 (1986).
6. Chen, S.-Y., Smith, J. M., and McCoy, B. J. *Chem. Eng. Sci.*, in press.
7. Chen, S.-Y., McCoy, B. J., and Smith, J. M., *AIChE J.*, in press.
8. Madon, J. J., O'Connell, J. P., and Boudart,,M., *AIChE J.* **24**, 104 (1978).
9. Germain, A. H., Lefebvre, A. G., and L'Homme, G. A., *Chem. React. Eng. II.* ACS Monograph Ser. No. 133, 164 (1974).
10. Babcock, B. D., Mejdell, G. T., and Hougen, O. A., *AIChE J.* **3**, 366 (1957).
11. Boudart, M., and Djega-Mariadassous, G., "Kinetics of Heterogeneous Catalytic Reactions," Chaps. 1 and 5. Princeton Univ. Press, Princeton, N.J., 1984.
12. McCoy, B. J., *Chem. Eng. Sci.* **39**, 1524 (1984).
13. Bond, G. C., "Catalysis by Metals," pp. 230, 319. Academic Press, New York, 1962.
14. Herskowitz, M., Carbonell, R. G., and Smith, J. M., *AIChE J.* **25**, 272 (1979).