

Transient Study of Cyclohexane Dehydrogenation on Pt-Al₂O₃ Catalyst in a Constant Flow Stirred Tank Reactor (CSTR)

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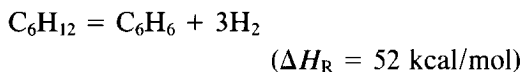
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Transient response data for the cyclohexane dehydrogenation reaction on a commercial Pt-Al₂O₃ catalyst at 1.2 atm and in the temperature range of 555–672°K was best correlated by a surface coverage type model with simultaneous catalyst deactivation followed by regeneration to the initial level of activity. The nature of the response can be exploited to yield kinetic information on the mechanistic steps of the overall reaction. Preliminary findings on the reaction kinetics indicate that surface reactions of the adsorbed hydrocarbon species and benzene desorption are very rapid (cyclohexane adsorption and hydrogen desorption are slow) and that hydrogen coverage impedes cyclohexane chemisorption. © 1986 Academic Press, Inc.

INTRODUCTION

In a previous study we investigated the use of the reversible cyclohexane dehydrogenation–benzene hydrogenation reaction on Pt–Al₂O₃ catalyst



as a promising candidate for energy collection and retrieval in a thermochemical cycle and presented steady-state rate data (*I*). Since the mode of operation of the endothermic reactor used for energy collection is inherently transient (focused solar collectors are to be used as an energy source), simulation and design of the endothermic reactor will require a dynamic model. In addition, the dynamic model may also be useful in the study of the start-up characteristics and/or control of perturbations of a reactor.

With the objective of testing various dynamic models, we have obtained transient data for the cyclohexane dehydrogenation reaction on Pt–Al₂O₃ catalyst at 1.2 atm in

the temperature range of 555–672°K employing an internal recirculation reactor. The data consistently exhibited an overshoot type of response followed by a steep minimum in the benzene fraction of the effluent hydrocarbons (Eq. (1)). We have found out that, for the indicated reaction conditions, the data cannot be explained by invoking the pseudo-steady-state approximation for the active site concentrations. In this study we will illustrate that the response can be predicted if allowance is made for the variation of the active site concentrations with time provided that the following conditions for the surface kinetics are applicable: (a) surface reactions of the adsorbed hydrocarbon species and benzene desorption are very rapid whereas cyclohexane adsorption and hydrogen desorption are slow, (b) surface coverages of the adsorbed hydrocarbons are negligibly low, (c) the adsorbed hydrogen impedes cyclohexane adsorption and covers the majority of sites as steady state is approached, (d) catalyst deactivates early in the reaction but is regenerated to the initial level of activity as more hydrogen is produced in the gas phase. It is believed that the study here sets the stage for further experimentation

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which could eventually yield all the rate constants for the individual mechanistic steps over the complete temperature and concentration ranges of interest.

METHODS

The experimental system consisting of a Berty type recirculation reactor has been described in a previous communication (1). A commercial $\frac{1}{8}$ -in. cylindrical reforming platinum catalyst was employed. Data collection was initiated with the introduction of cyclohexane to the reactor which contained only nitrogen and had been preheated to the desired temperature. Gas chromatograms were obtained at 3-min intervals. The gas analysis technique consisted of a Carbowax column equipped with a flame ionization detector which allowed for the detection of the hydrocarbon fractions of both benzene and cyclohexane but not the detection of either hydrogen or nitrogen. The chromatograms displayed two major peaks, one for cyclohexane and the other for benzene. The area percentages of other hydrocarbons which appeared on the chromatogram were negligibly small.

Data were collected at 1.2 atm in a temperature range of 555–672°K for a range of space velocities. Typical sets of data are

shown in Figs. 1, 2, 3, and 5 where the fraction of benzene in the effluent defined by

$$\phi = y_B / (y_A + y_B) \quad (1)$$

is plotted vs time. ϕ represents the benzene fraction of hydrocarbons in the effluent since the amount of hydrocarbons in the product other than cyclohexane (A) and benzene (B) is negligibly small. From Eq. (1) it is apparent that ϕ would represent cyclohexane conversion at steady state. The value of $\phi(0)$ was not measured due to the difficulty in obtaining accurate measurements near time zero. However, one can infer that $\phi(0) = 0$; although $y_A(0)$ and $y_B(0)$ are both zero, it is apparent from Eqs. (2), (3), and (4) that

$$\left. \frac{dy_B}{dt} \right|_{t=0} = \left. \frac{dy_H}{dt} \right|_{t=0} = 0$$

whereas

$$\left. \frac{dy_A}{dt} \right|_{t=0} > 0.$$

As illustrated in the figures, an overshoot type of response immediately followed by a minimum is discernible in all the data sets.

The residence time in the reactor ranged from 40 to 435 min. The duration of each experiment was typically 1–2 residence

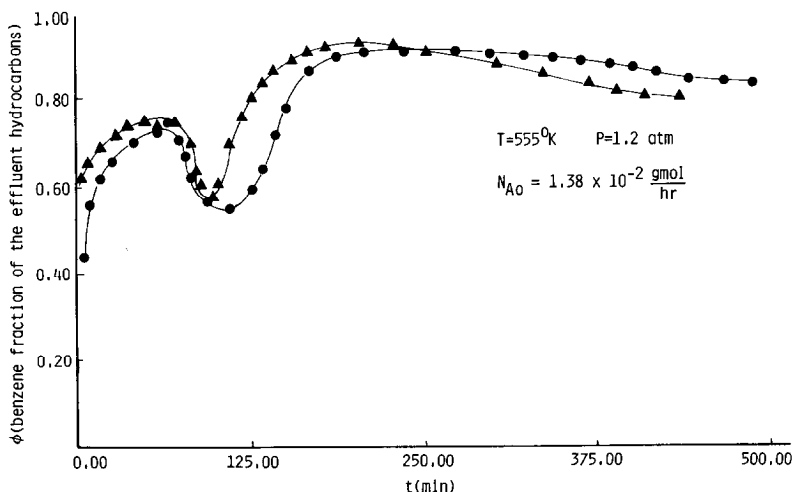


FIG. 1. Reproducibility of data. Data points indicated by triangles and circles represent subsequent experiments.

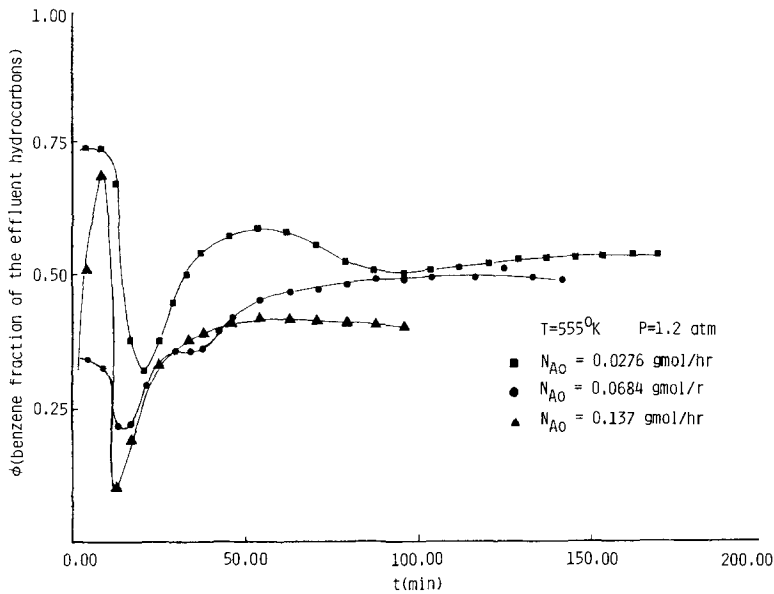


FIG. 2. Experimental data.

times. Therefore, although ϕ values at the end of the experiments approach steady state, they cannot be assumed to represent the steady state.

Reproducibility of the data is presented in Fig. 1. There is some discrepancy in the ϕ values early in the experiment. The observed variance can probably be ascribed to both deviations from perfect mixing at very low hydrocarbon concentrations and the

imprecision of the measurements at low hydrocarbon concentrations early in the experiment. Nevertheless, the initial overshoot type of response and subsequent minimum were consistently observed in all the experiments.

The effect of feed flow rate is indicated in Figs. 2 and 3. As the feed flow rate increases the overshoot type of response occurs earlier in the transient period and the

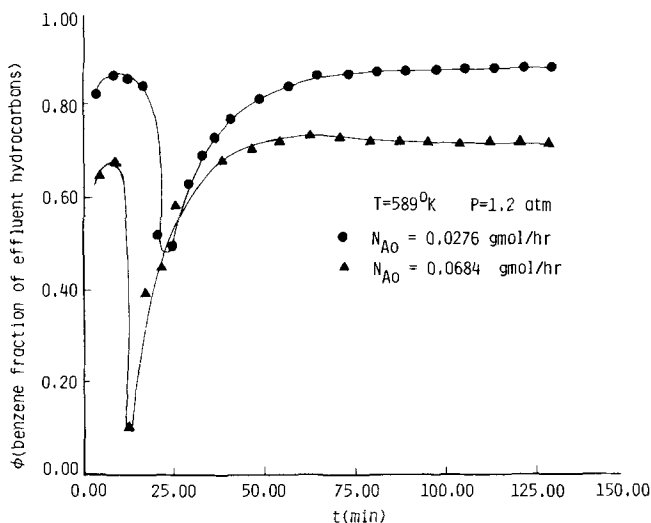


FIG. 3. Experimental data.

minimum corresponds to lower ϕ values. In addition, ϕ values at the end of the experiments decrease, as expected.

A model invoking the pseudo-steady-state approximation (PSSA) failed to predict the overshoot type of response; but rather always predicted a monotonic rise in the benzene fraction of the effluent hydrocarbons with time. The two most likely causes for the model's inability to predict the data are: (a) the catalyst may have deactivated in the beginning of the reaction followed by regeneration to the initial level of activity as more hydrogen is produced in the gas phase. (If catalyst deactivation indeed occurred, it will have to be assumed that the catalyst must have somehow regenerated to the initial level of activity. This is because the values for the benzene fraction in the effluent (i.e., the ϕ values) as steady state is approached have always been found to be reproducible even though no attempt was made to reactivate the catalyst), and (b) PSSA for the concentration of the active sites may not be applicable.

Previous steady-state experiments of the cyclohexane dehydrogenation reaction in this laboratory at 4.74 atm and in the temperature range of 678–706°K indicated significant activity loss of the Pt–Al₂O₃ catalyst at conversions of 10% or less (2). Deactivation which occurred after a time period of at least 2 h was attributed to coking. The catalyst was regenerated by air oxidation. In the transient studies reported here, the catalyst always displayed reproducible activity without regeneration; and since the extrema in the benzene fraction were observed to occur in a relatively short period of time, deactivation by coking was considered unlikely.

Maatman *et al.* (3) observed deactivation of Pt–Al₂O₃ catalyst at low conversions and attributed this to the poisons formed from side reactions catalyzed by acid sites associated with the alumina. Rohrer and Sinfelt (4) pointed out, that in the dehydrogenation of methylcyclohexane to toluene, the addition of hydrogen improves catalyst activity

and therefore they suggest that hydrogen may be responsible for the removal of the poisons which are believed to be hydrogen deficient surface residues. These observations suggests that a similar sequence of poisoning may be occurring in our experiments. (Initial catalyst poisoning by hydrogen-deficient residues is followed by regeneration to the initial level of activity as sufficient hydrogen accumulates in the gas phase.)

Linear and exponential deactivation functions have been frequently used for reactions involving deactivation by poisoning and coking (5). We have tested the ability of a linear deactivation–regeneration function to accommodate the data by allowing the preexponential factor in the rate constant to first decrease and then increase with time to a steady-state level. The activity profile was empirically selected on the basis of the agreement between the simulated and experimental transient responses. The extrema, displayed in the experimentally determined transient response data, were successfully modeled by this procedure; the catalyst first deactivating followed by regeneration as the reaction proceeds. However, the steady-state activity was determined to be about an order of magnitude smaller than the initial activity. Simulation at 555°K predicted qualitatively similar results.

This observation that the steady-state activity will have to be significantly lower than the initial activity, if the data is to be interpreted on the basis of deactivation–regeneration functions, is in conflict with the arguments put forth previously indicating that if deactivation had indeed occurred then the catalyst should have regenerated to its initial level of activity. Therefore, it was concluded that the transient response data cannot be explained on the basis of catalyst deactivation–regeneration alone.

The pseudo-steady-state approximation requires that the concentration of active sites, and the elapsed time for the steady-state concentration of the active sites to be

approached (i.e., relaxation time), be very small. Under certain transient reaction conditions, the change in the concentration of the active sites must be included in the mathematical model; and it is under these conditions that the transient response data can be used to study the reaction mechanism. Bennett (6) and Kobayashi (7) have illustrated how transient response data can be exploited to delineate the appropriate reaction mechanisms and how the kinetic parameters of the elementary steps of the reaction can be evaluated.

We have attempted to predict the transient data by employing surface coverage type models without accounting for catalyst deactivation and reactivation. These models are capable of predicting the overshoot response early in the reaction but are incapable of predicting the subsequent minimum in the response. Reviewing these results, it was surmized that combining the surface coverage model with catalyst deactivation and reactivation might enable us to predict both the observed maximum and minimum of the transient response curve with complete catalyst reactivation being observed at steady state.

The simplest surface coverage models incorporating catalyst deactivation and regeneration may be formulated if it is assumed that the overall reaction is irreversible and that the surface reactions are rapid with little or no accumulation of the reaction intermediates. (At 672°K cyclohexane dehydrogenation can be considered to be essentially irreversible.) Here, three models will be postulated. In one model hydrogen is presumed to desorb rapidly. In another, rapid benzene desorption is assumed. A third model hypothesizes slow desorption of hydrogen and benzene in which case there is high surface coverage by both products.

The data was best correlated with the rapid benzene desorption model. This model consists of material balances for both the reactor and the cylindrical catalyst. An additional equation describing the rate at

which the sites are occupied by hydrogen is also needed. The model is isothermal as previous work employing a nonisothermal model (8) indicated predictive capabilities roughly equivalent to the isothermal model. For simulating the data at 672°K, irreversibility of the overall reaction can be assumed. The material balances for the reactor and the cylindrical catalyst are given by

$$N_{AO} - qy_A - A_s D_{e,A} \left(\frac{\partial C_A}{\partial r} \right) \Big|_{r=R} = V_R \frac{dy_A}{dt} \quad (2)$$

$$-qy_B - A_s D_{e,B} \left(\frac{\partial C_B}{\partial r} \right) \Big|_{r=R} = V_R \frac{dy_B}{dt} \quad (3)$$

$$-qy_H - A_s D_{e,H} \left(\frac{\partial C_H}{\partial r} \right) \Big|_{r=R} = V_R \frac{dy_H}{dt} \quad (4)$$

$$D_{e,A} \left(\frac{\partial^2 C_A}{\partial r^2} + 1/r \left(\frac{\partial C_A}{\partial r} \right) \right) - \rho_p S_g k_A C_A (1 - \theta_H(r,t) - \theta_P(t)) = \frac{\partial C_A}{\partial t} \quad (5)$$

$$D_{e,B} \left(\frac{\partial^2 C_B}{\partial r^2} + 1/r \left(\frac{\partial C_B}{\partial r} \right) \right) - \rho_p S_g k_A C_A (1 - \theta_H(r,t) - \theta_P(t)) = \frac{\partial C_B}{\partial t} \quad (6)$$

$$D_{e,H} \left(\frac{\partial^2 C_H}{\partial r^2} + 1/r \left(\frac{\partial C_H}{\partial r} \right) \right) + \rho_p S_g k_H \theta_H^n(r,t) = \frac{\partial C_H}{\partial t}, \quad (7)$$

where the effluent volumetric flow rate (q) was evaluated from a total molar balance for the gas phase in the reactor system:

$$N_{AO} + A_s \left(D_{e,A} \frac{\partial C_A}{\partial r} \Big|_{r=R} + D_{e,B} \frac{\partial C_B}{\partial r} \Big|_{r=R} + D_{e,H} \frac{\partial C_H}{\partial r} \Big|_{r=R} \right) - qy_T = 0. \quad (8)$$

N_{AO} represents the total inlet molar flow rate since the feed is pure cyclohexane. If the gas phase is ideal, there can be no accumulation of moles since the pressure, temperature, and gas volume are constant. Since the amount of nitrogen originally oc-

cupying the catalyst void volume is small, nitrogen diffusion out of the catalyst was neglected.

Initial and boundary conditions are

$$y_A(0) = y_B(0) = y_H(0) = C_A(r,0) \\ = C_B(r,0) = C_H(r,0) = 0 \quad (9)$$

$$-D_{e,i} \left. \frac{\partial C_i}{\partial r} \right|_{r=R} = k_{m,i} (C_i(R,t) - y_i(t)) \quad (10)$$

$$\left. \frac{\partial C_i}{\partial r} \right|_{r=0} = 0 \quad t > 0 \quad (11)$$

The measured (9) and estimated values for the physical parameters which appear in the mathematical model are listed in Table I. Since pore diffusion takes place predominantly by the Knudsen mechanism (average pore size is 16.5 Å), the effective diffusivity can be estimated from

$$D_{e,i} = \frac{\varepsilon}{\tau} D_{K,i} \quad (12)$$

The Knudsen diffusivity is given by

$$D_{K,i} = 9.70 \times 10^3 \bar{r} \left(\frac{T}{M_i} \right)^{1/2}, \quad (13)$$

where \bar{r} is in centimeters, T is in °K, and $D_{K,i}$ is in square centimeters per second.

Mass transfer coefficients are time dependent since the physical properties of the bulk gas and the mass density change as the gas composition changes. However, the transient response was found to be insensi-

tive to variations in the transfer coefficients due to physical property changes. Therefore, the transfer coefficients were taken to be constant for each data set. They were evaluated by employing the Petrovic and Thodos correlation (10) and by assuming j -factors for heat and mass transfer to be equal.

$\rho_p S_g k_A C_A (1 - \theta_H - \theta_p)$ is the rate of cyclohexane adsorption per unit volume and it is also equal to the rate of benzene desorption as hydrocarbon coverages are negligible. Langmuir type of adsorption is assumed. For negligible hydrocarbon coverages, $(1 - \theta_H - \theta_p)$ represents the fraction of sites available for adsorption. When cyclohexane adsorption is slow, cyclohexane desorption can be neglected if the overall reaction is irreversible, which is the case at 672°K.

The model will be complete with additional equations describing the change in the surface coverage by hydrogen (θ_H) with time, at any radial location, and an empirical relationship for the poison coverage (θ_p), as a function of time. The equation describing the change in θ_H with time, at any radial location, was developed based on the following considerations.

The rate at which the sites are occupied by hydrogen, due to cyclohexane chemisorption, for a differential volume dV , is given by $\rho_p S_g k_A C_A (1 - \theta_H - \theta_p) \Delta v dV$. One cyclohexane molecule is associated with

TABLE I

Parameter Values

Reactor and reaction parameters	
$V_R = 3.785 \times 10^3 \text{ cm}^3$; $N_{A_0} = 1.38 \times 10^{-2}$ to $1.37 \times 10^{-1} \text{ gmol/h}$; $\Delta H = 52,000 \text{ cal/gmol}$;	
$P = 1.2 \text{ atm}$; Recirculation rate = 43.99 gmol/h	
Catalyst parameters	
$A_s = 1.387 \times 10^3 \text{ cm}^2$; $R = 7.95 \times 10^{-2} \text{ cm}$; $\bar{r} = 16.5 \times 10^{-8} \text{ cm}$;	
$\rho_p = 1.09 \text{ g/cm}^3$; $\rho_s = 7.5 \times 10^{19} \text{ sites/g}$;	
$S_g = 4.064 \times 10^6 \text{ cm}^2/\text{g}$; $\tau = 1.25$; $\varepsilon = 0.63$	
Catalyst weight = 40 g	
Mass transfer parameters ($T = 672^\circ\text{K}$)	
$k_{m,A} = 3.125 \times 10^{-4} \text{ gmol/cm}^2\text{s}$; $k_{m,B} = 2.434 \times 10^{-4} \text{ gmol/cm}^2\text{s}$;	
$k_{m,H} = 6.225 \times 10^{-4} \text{ gmol/cm}^2\text{s}$	

one site. Benzene desorbs instantly upon cyclohexane chemisorption, however, hydrogen coverage is presumed to render the site unavailable for cyclohexane adsorption. It will be assumed that all the hydrogen must desorb from a site before the site can become available for adsorption. Since hydrogen desorption, just as cyclohexane adsorption is assumed to be slow, hydrogen adsorption can be neglected when the overall reaction is irreversible. If all the hydrogen must desorb before a site can again be available for adsorption and if the desorption is assumed to be molecular, then the rate at which the sites are being vacated by hydrogen will be equal to one-third the rate at which hydrogen molecules are desorbing, i.e., $(\frac{1}{3}) \rho_p S_g k_H \theta_H^n A_v dV$. (n can be either 1 or 2 depending on the nature of the adsorption-desorption mechanism.)

The net rate at which the sites are occupied by hydrogen is then given by

$$\rho_p S_g k_A C_A (1 - \theta_H - \theta_p) (A_v) dV - \left(\frac{1}{3}\right) \rho_p S_g k_H \theta_H^n (A_v) dV = \rho_p \rho_s \frac{d\theta_H}{dt} dV \tag{14}$$

with the initial condition

$$\theta_H(r,0) = 0. \tag{15}$$

Catalyst deactivation and reactivation are accounted for by

$$\theta_p = 1 - \exp(-a t) \quad t < t_{\min} \tag{16}$$

$$\theta_p = b - \exp(c t) \quad t > t_{\min} \tag{17}$$

where t_{\min} is the empirically determined time indicating the beginning of catalyst reactivation. The initial condition is

$$\theta_p(0) = 0. \tag{18}$$

The events described above are illustrated in Fig. 4. The length of the heavy arrows represent the rates of cyclohexane adsorption and benzene desorption. Open circles represent empty sites which are presumed to be an ensemble of Pt atoms. At time zero, all sites are empty since only nitrogen is present in the reactor. Partially shaded circles indicate at least one adsorbed hydrogen atom (θ_H) on a site. Fully shaded circles represent the sites occupied by a hydrocarbon molecule or a hydrogen-deficient residue (θ_p). Note that the length

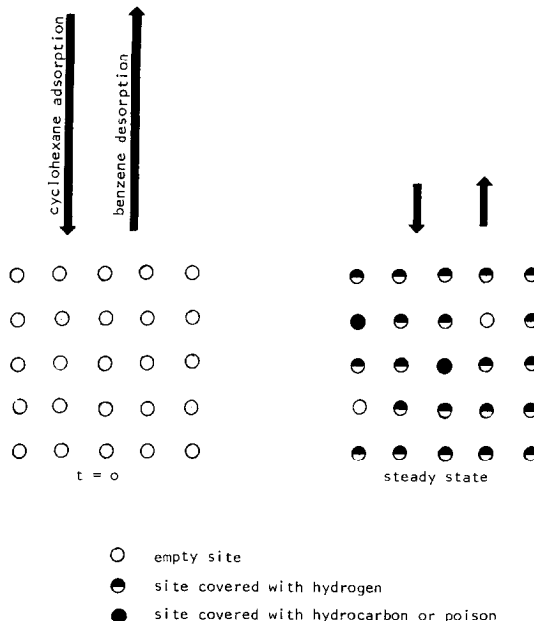


FIG. 4. Site coverage at time zero and at steady state.

of the arrows representing cyclohexane adsorption and benzene desorption are equal for any given time because it is assumed that the hydrocarbon accumulation on the surface is negligibly small.

It is apparent that the solution for the mathematical model represented by Eqs. (2) through (18) will have to be numerical. Since the ordinary and partial differential equations are coupled they must be solved simultaneously for each step taken in time. The ordinary differential equations were solved by Euler's method, whereas the partial differential equations were first linearized and transformed into algebraic equations by using the implicit Crank-Nicholson finite difference approximations for the derivatives (11). This solution technique, which is iterative with second-order convergence, is commonly referred to as "quasilinearization" (12).

The activation and deactivation constants (a , b , c , t_{\min}) in Eqs. (16) and (17) were selected empirically; whereas the adsorption and desorption constants (k_A and k_H) were evaluated using the Newton-Raphson nonlinear parametric searching method by minimizing the following objective function $\sum_{\text{data}}(\phi^{\text{calcd}} - \phi^{\text{exp}})^2$.

Two values of the exponent n were employed in the model; a value of 1 represents

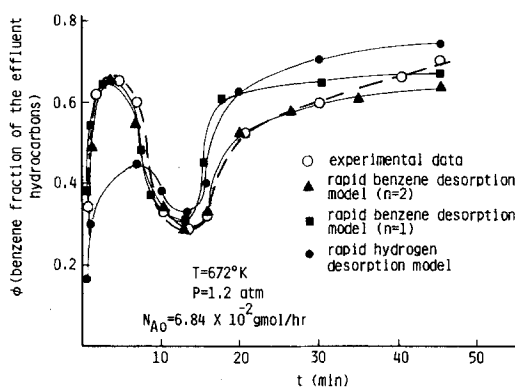


FIG. 5. Predictive capability of various surface coverage models.

unimolecular desorption of molecular hydrogen whereas a value of 2 represents diatomic desorption of molecular hydrogen. As observed in Fig. 5 and Table 2, the rapid benzene desorption model with diatomic hydrogen desorption ($n = 2$) results in nearly perfect simulation of the experimental data. The fit with $n = 1$, although adequate, is not as good as the fit with $n = 2$. This finding is in conformity with other studies which indicate that hydrogen adsorption on metals is often dissociative (5).

DISCUSSION

A better insight into the transient data can be obtained by analyzing the changes in

TABLE 2
Calculated Constants for the Transient Data

	$T = 672^\circ\text{K}; P = 1.2 \text{ atm}; N_{A0} = 6.84 \times 10^{-2} \text{ gmol/h}$		
	Rapid benzene desorption		Rapid hydrogen desorption
	$n = 1$	$n = 2$	
a	2×10^{-3}	1.6×10^{-3}	1.5×10^{-3}
b	3.06	2.78	2.78
c	1×10^{-3}	8×10^{-4}	8×10^{-4}
t_{\min} (min)	12	12	12
$k_A + 10^6 \text{ cm/s}$	0.895	0.774	40.07
$k_H \times 10^{14} \text{ gmol/cm}^2\text{s}$	15.38	16.61	—
$k_B \times 10^{14} \text{ gmol/cm}^2\text{s}$	—	—	5.98
Sum of squares (12 data points)	0.058	0.0066	0.269

the bulk gas concentrations with reaction time. The simulated bulk gas concentrations of cyclohexane (C_A), benzene (C_B), and hydrogen (C_H) are plotted versus reaction time in Fig. 6. The hydrogen concentration exhibits a steady increase with reaction time to its steady-state value. In contrast, the benzene concentration increases rapidly with time to a plateau region beginning at 6 min and extending to 13 min, followed by a steady increase to its steady-state concentration. The cyclohexane concentration increases to its maximum value at 13 min, followed by a gradual decrease to its steady-state value.

The behavior of C_A and C_B vs t plots are consistent with the trend in ϕ vs t plots. The maximum in ϕ occurs just before the C_B concentration levels off and is followed by a downward swing as C_A increases and C_B essentially holds steady. The minimum in ϕ corresponds to the maximum in C_A .

A summary of the empirically determined catalyst deactivation–reactivation constants (a , b , c , and t_{\min}) is presented in Table 2. Values for a and c ranged from a low of 0.0008 to a high of 0.002 corresponding to an observed maximum deactivation of approximately 60% (Fig. 7). The time for initiation of catalyst regeneration (t_{\min}) is 12

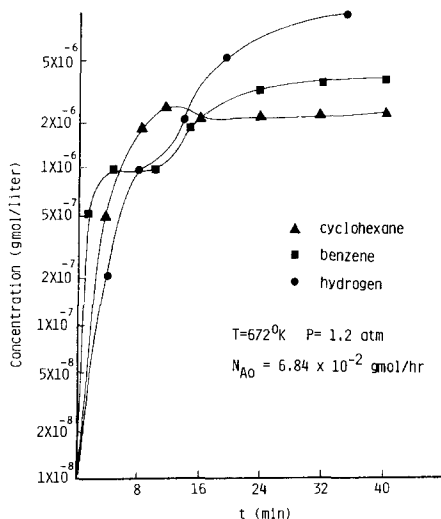


FIG. 6. Gas-phase concentrations for the rapid benzene desorption model ($n = 2$).

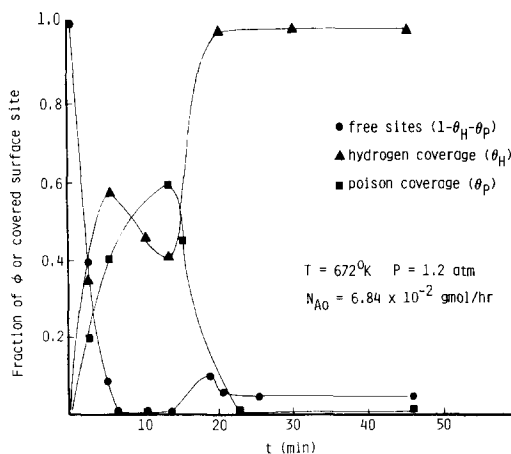


FIG. 7. Coverage on the catalyst surface rapid benzene desorption model ($n = 2$).

min. This time is 1 min less than the time of the observed minimum of ϕ in the transient response at 672°K (Fig. 5).

The fraction of the catalyst sites which are free ($1 - \theta_H - \theta_p$), or covered by hydrogen (θ_H), or poisoned (θ_p) are a function of both time and radial location in the catalyst. In Fig. 7, the values of θ_H , θ_p , and $1 - \theta_H - \theta_p$ are plotted versus time at the surface of the catalyst (i.e., at $r = R$). A comparison of Figs. 6 and 7 reveals that the plateau region of benzene concentration corresponds to the region of virtually complete coverage of free sites. During this time the catalyst can be viewed as essentially inactive. Another observation is that steady-state coverage of hydrogen is very high (about 97%), and that only a small fraction of sites (about 3%) are available for adsorption.

At the time of catalyst regeneration (t_{\min}), it is presumed that the gas-phase hydrogen concentration is sufficiently high (approximately 1.4×10^{-4} gmol/liter (Fig. 6)) so that the hydrogen-deficient surface residues which deactivate the catalyst are being removed at a faster rate than they are being formed.

At this point it has not been claimed that the rapid benzene desorption model, with catalyst deactivation and regeneration, is unique in fitting the experimental data. This

model does, however, correlate considerably better than any of the other plausible models investigated. For example, let us consider the rapid hydrogen desorption model. With catalyst deactivation, the coverage of benzene (and hence benzene production) decreases after an initial rise; and the overshoot type of response, although less dramatic than that observed in the experimental data, is still observed. However, as Fig. 5 shows, the predicted extrema are not as sharp as those observed in the transient data. (Note that if catalyst deactivation-reativation had not been allowed, then the simulated transient response would have indicated only a monotonic rise in ϕ to steady state.)

Investigation of a model which allowed for intermediate surface coverage by both hydrogen and benzene resulted in an observed transient response somewhere between that observed for the rapid hydrogen and rapid benzene desorption models. In addition, if allowance was made for the accumulation of any additional surface hydrocarbon intermediates, then the simulated transient response exhibited extrema which were dampened and in some cases even disappeared. These observations suggest that the hydrocarbon surface coverage on the catalyst is indeed very low, i.e., the surface

reactions and desorption of benzene are very rapid relative to the adsorption of cyclohexane and the desorption of hydrogen.

At lower temperatures, such as 555 and 589°K, the overall reaction cannot be assumed to be irreversible. Consequently, a complete formulation of a surface coverage model would be complicated. A first approximation, however, can be made if it is assumed, as before, that the reaction is irreversible and that the desorption of benzene is rapid (rapid benzene desorption model with diatomic desorption of hydrogen ($n = 2$)). The deactivation-reativation constants (a , b , c , and t_{\min}) are once again selected empirically; whereas the kinetic constants (k_A and k_H) were evaluated by the Newton-Raphson nonlinear parametric searching routine. The calculated constants are summarized in Table 3. The adequacy of the fit is illustrated in Figs. 8 and 9 for a flow rate of 2.76×10^{-2} gmol/h.

Figures 8 and 9 and Table 3 indicate that the rapid benzene desorption model with catalyst deactivation-reativation also provides an adequate fit to the data at 555 and 589°K. For a given flow rate, k_A and k_H increase with temperature as expected. Comparison with k_A and k_H values at 672°K (Table 2) indicates that there is no significant change in the kinetic parameters from 589

TABLE 3
Calculated Constants for the Transient Data

$T = 555\text{--}589^\circ\text{K}; P = 1.2 \text{ atm}$				
Rapid benzene desorption model ($n = 2$)				
Molar flow rate: (gmol/h)	2.76×10^{-2}		6.84×10^{-2}	
	555	589	555	589
a	1.5×10^{-3}	6×10^{-4}	2×10^{-3}	2×10^{-3}
b	2.77	2.81	2.33	2.78
c	5×10^{-4}	4.5×10^{-4}	4×10^{-4}	8×10^{-4}
t_{\min} (min)	19	22	12	12
$k_A \times 10^6 \text{ cm/s}$	1.30	2.22	0.133	0.961
$k_H \times 10^{14} \text{ gmol/cm}^2/\text{s}$	4.63	8.33	13.62	18.92
Sum of squares (12 data points)	0.027	0.030	0.011	0.092

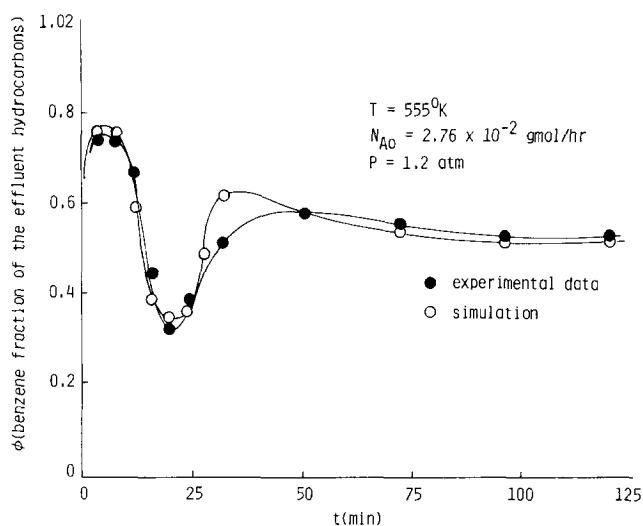


FIG. 8. Simulation with rapid benzene desorption model ($n = 2$) at 555°K.

to 672°K. However, it must be kept in mind that the irreversibility approximation was made in the range 555–589°K. One problem, however, is that k_A and k_H change with flow rate (Table 3). This is apparently a reflection of the fact that the minimum in the experimental data (and likewise t_{\min}) do not scale very well with the flow rate. Consequently, k_A and k_H should be strictly viewed as adjustable parameters. Nevertheless, despite the difficulty in extracting true kinetic parameters from the data, a surface cover-

age type of model with catalyst deactivation followed by regeneration to the initial level of activity is capable of correlating all the data. Moreover, the model suggests that the most plausible kinetic scheme is one of rapid surface reactions and benzene desorption with hydrogen coverage impeding the cyclohexane chemisorption. A rigorous surface coverage model, which would also be applicable under reversible reaction conditions, would require the kinetic parameters of all the intermediate

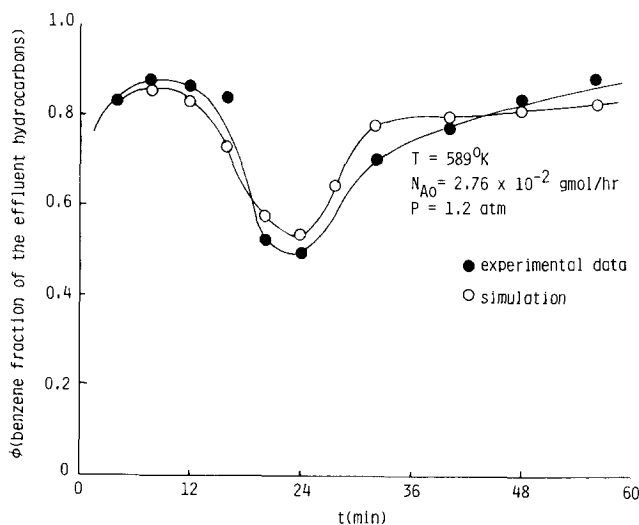


FIG. 9. Simulation with rapid benzene desorption model ($n = 2$) at 589°K.

steps of the reaction be known. The experiments described here would be suitable for estimating the true kinetic parameters with some modifications, such as the elimination of interphase and intraparticle gradients. This can be done by using high mass flow rates and surface-coated or "eggshell" catalysts. A mixed feed of hydrogen and cyclohexane should minimize or possibly eliminate catalyst deactivation.

CONCLUSIONS

Transient data for cyclohexane dehydrogenation on a commercial Pt-Al₂O₃ catalysts were collected at 1.2 atm in a temperature range of 555–672°K employing a Berty type recirculation reactor. The effluent hydrocarbons, which were analyzed at regular time intervals, consisted essentially of benzene and cyclohexane. The benzene fraction of the effluent hydrocarbons displayed an overshoot type of response followed by a steep minimum early in the reaction in all cases studied.

A mathematical model based on the pseudo-steady-state approximation for the concentration of active sites was found to be incapable of describing the transient response data obtained here. The response data, however, was explained by a surface coverage model which allows for the change in site concentration with time with catalyst first deactivating followed by complete regeneration as gas-phase hydrogen concentration increases.

Transient response data, of the type obtained here, can be exploited to yield kinetic information on the mechanistic steps of the overall reaction. Our preliminary findings indicate that cyclohexane chemisorption and hydrogen desorption are slow. Since the surface reactions where hydrocarbon molecules are stripped of their hydrogen atoms as well as benzene desorption are rapid, hydrocarbon coverages are very low. Hence, it may be assumed that the benzene desorption rate remains essentially equal to the cyclohexane chemisorption rate. Adsorbed hydrogen, which progres-

sively covers the sites, is presumed to impede cyclohexane chemisorption and therefore benzene production. The resulting decrease in the benzene desorption rate with time contributes, along with catalyst deactivation, to the overshoot type of response observed early in the reaction. The increase in the benzene fraction of the effluent hydrocarbons, after the minimum, is attributed to catalyst regeneration which takes place as the gas-phase concentration increases. It is believed that gas-phase hydrogen reacts and removes the hydrogen-deficient residues responsible for catalyst deactivation.

APPENDIX: NOMENCLATURE

a, b, c	activation–deactivation constants defined in Eqs. (16) and (17)
A	preexponential factor
A_V	Avogadro's number
A_S	total external surface area of the catalyst in the reactor
C	concentration inside the catalyst
dV	differential catalyst volume
D_e	effective diffusivity
D_K	Knudsen diffusivity
ΔH	heat of reaction
k_A	adsorption constant for cyclohexane
k_H	desorption constant for hydrogen
k_B	desorption constant for benzene
k_m	mass transfer coefficient
M	molecular weight
N_{AO}	inlet molar flow rate of cyclohexane
n	exponent in Eq. (7)
P	total pressure
q	effluent volumetric flow rate
r	radial distance
\bar{r}	average pore radius
R	radius of the cylindrical catalyst
R_g	universal gas constant
S_g	surface area per unit mass catalyst
t	time
t_{\min}	time at which catalyst regeneration begins
T	temperature
T_b	temperature in the gas phase
V_R	free reactor volume

y molar concentration in the gas phase
 y_T total molar concentration of the gas mixture

Subscripts

A cyclohexane
 B benzene
 P poison
 H hydrogen
 i chemical species

Greek Symbols

ε catalyst porosity
 θ fraction of active sites covered by adsorbed species
 ρ_p density of the catalyst
 ρ_s site density
 τ tortuosity factor for the catalyst
 ϕ parameter defined by Eq. (1)

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