Rate Enhancement and Multiplicity in a Partially Wetted and Filled Pellet: Experimental Study

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Phase transition during an exothermic multiphase reaction was studied experimentally using a single catalytic pellet reactor. Cyclohexene hydrogenation (to cyclohexane) and disproportionation (to benzene and cyclohexane) on Pd/Al_2O_3 comprised the test reaction system. The steady-state behavior of the pellet exposed on part of its surface by a flowing liquid rivulet containing the liquid reactant (cyclohexene) and the other part by a flowing gas containing the gaseous reactant (hydrogen) was examined. Measurements included the pellet weight (liquid holdup), degree of external wetting, center and surface temperature and overall reaction rates. Two regimes observed are: a low-rate regime for all hydrogen gas-phase concentrations in which the partially wetted pellet is filled mostly with liquid and nearly isothermal; a high-rate regime for hydrogen concentrations exceeding a critical value in which the pellet is filled only partially with liquid and the pellet temperature rise is considerable. Benzene formation was observed in this state. The difference in overall cyclohexane formation rates between the two states was as high as a factor of 20 for the same bulk conditions. Over the range where multiple states were observed, the steady state of the pellet depended on whether the pellet was prefilled with the reactive gas mixture or with liquid cyclohexene. The range over which the high-rate state was sustained was the largest for the most active catalyst and declined as the catalyst slowly deactivated. Data features are interpreted using the theoretical foundations of the half-wetted catalytic slab model (Harold and Watson, 1993).

Introduction

When an exothermic multiphase reaction is carried out in a fixed bed of catalyst the heat generated by the reaction can drive the vaporization of the liquid phase. On one hand, this situation is problematic because of the increased potential for hot spot formation and the subsequent sintering of the catalyst, initiation of side reactions or even a reactor runaway. Previous experimental observations of hot spot formation in the fixed-bed multiphase reactor were cited in a previous study (Watson and Harold, 1993). On the other hand, overall rates on the nonwetted catalyst are typically higher. As a result, the conversion of a targeted component potentially can be achieved in a smaller reactor. Whether vaporization of the liquid phase within a multiphase fixed-bed reactor is to be avoided or exploited, there is a need to better understand at the local level the coupling between the exothermic catalytic reaction, multiphase transport, wetting and phase transition processes.

The existence of several different local steady states of the catalyst within the multiphase fixed-bed reactor has been established (Harold, 1993). These states span the completely wetted and liquid-filled pellet to the completely nonwetted and dry pellet. Catalyst performance in these bounding states is well understood. As a result of active research for the past 20 years, also well understood is the performance of the isothermal pellet that is partially wetted by one or more liquid rivulets but which is completely filled with liquid. The impact of capillary condensation on the performance of a pellet exposed to a gaseous mixture containing a highly volatile reactant and a less volatile reactant was examined experimentally by Kim and Kim (1981) and theoretically by Jaguste and Bhatia (1991). Least understood is the steady-state behavior of the catalytic

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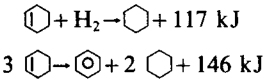
pellet which is partially contacted on its surface by a flowing liquid and which is partially filled with liquid as a result of exothermic reaction-induced vaporization.

Several noteworthy theoretical studies have examined the problem of reaction with phase transition within a partially wetted catalytic pellet. These studies are critically examined elsewhere (Harold, 1993). The key finding in these studies is that vaporization of liquid within the pores can lead to a partially filled steady state. The main implication of such a state is the potentially large increase in pellet temperature and overall rate because of the more rapid transport in gas-filled compared to liquid-filled pores. Simulations by Harold (1988) and Harold and Watson (1993) of a half-wetted catalytic slab reveal an interesting competition between the gas and liquid phases to fill the intraslab void space. Liquid imbibition and condensation promote the filling of pores with liquid. The fraction of the heat released by the exothermic reaction that is not removed by convection to the surrounding supplies the latent energy demands of liquid vaporization within the pores. A steady state of partial pore filling is a possible consequence.

The objective of this study is to experimentally examine the steady-state behavior of a heterogeneous porous catalyst that is partially wetted on the exterior surface by a flowing volatile liquid and which catalyzes an exothermic reaction. The complexity of this nonisothermal multiphase reaction system demands an experiment in which the local environment of the catalyst can be controlled and measured as unambiguously as possible. For this reason, a single-pellet multiphase reactor is employed, following the lead of Kim and Kim (1981), Funk et al. (1991) and Watson and Harold (1993). The model reaction system is chosen so that under the moderate conditions investigated the liquid components are volatile. Moreover, several techniques developed in two previous studies (Funk et al., 1991; Watson and Harold, 1993) are employed to assess the state of the single pellet as completely as possible under reaction conditions. Measurements include the degree of external wetting, liquid holdup, overall rate(s) and center and surface pellet temperatures. By following this strategy, the couplings between extent of pore emptying, partial external wetting, transport, and reaction can be assessed directly. To this end, conclusions put forth in the aforementioned single-pellet modeling studies are confronted. Finally, the implications of these data on the behavior of the overall reactor are also discussed.

Given the stated objective of this study, the reaction system studied is the Pd-catalyzed cyclohexene/hydrogen reaction system. This model reaction system consists of two overall exothermic reactions, proceeds rapidly under moderate operating conditions and involves liquid components that are highly volatile. The overall reactions are the hydrogenation and disproportionation of cyclohexene:



As a point of comparison, the heats of vaporization for the main liquid components are: 30.5 kJ/mol (cyclohexene) and 30.0 kJ/mol (cyclohexane). Other kinetic features of these reactions and other physical property aspects of the participating components were provided by Watson and Harold (1993). Previous studies of cyclohexene hydrogenation and disproportionation provide guidance for interpreting the experimental findings of this work. Rebhan and Haensel (1988) have demonstrated for a Pd/Al_2O_3 catalyst that disproportionation occurs in the absence of hydrogen, while hydrogenation occurs in a hydrogen-rich environment. It is interesting to note that the disproportionation reaction does not explicitly indicate any role of molecular hydrogen. However, the overall disproportionation stoichiometry is a linear combination of the cyclohexene hydrogenation to cyclohexane and the cyclohexene dehydrogenation to benzene. Nevertheless, in a hydrogen-deficient environment the disproportionation need not occur in a sequential manner. Rather, Rebhan and Haensel (1988) have shown that intramolecular hydrogen transfer occurs over a carbonaceous layer on the catalyst. Hanika and Ehlova (1988) have also studied the liquid-phase hydrogenation and disproportionation of cyclohexene on activated-carbon catalysts. In another study using the same catalyst, cyclohexene was trickled over a bed of catalyst pellets (Hanika and Stanek, 1986). The disproportionation reaction was shown to occur in the hot regions in the bed. Multiple steady-state behavior was noted to exist corresponding to a gas-phase regime with a high reaction rate and a liquid-phase regime with a much lower rate. Hanika and Ehlova (1988) proposed that the rate of disproportionation is controlled by cyclohexene diffusion through a solvent, while the rate of hydrogenation is controlled by hydrogen diffusion through the solvent.

The occurrence of disproportionation, while complicating an already complex system, adds to the important issue of selectivity. That is, hydrogenation selectivity losses may be encountered at the higher temperatures which accompany the drying-out of the catalyst. In general, selectivity losses are of crucial importance in industrially important multiphase reaction systems. The experiments in the current study were carried out over a sufficiently wide range of cyclohexene/hydrogen feed ratio and catalyst temperature that both overall reactions were encountered.

Experimental Setup and Procedures

Overall setup

The experimental setup employed is similar to that used in our previous study of the single-pellet dynamic behavior (Watson and Harold, 1993), as shown in Figure 1.

The gas fed continuously to the reactor comprised a mixture of hydrogen (high-purity) and helium (high-purity). Prior to mixing, each gas passed through a deoxygenation unit, and beds of molecular sieves and Drierite. A prescribed hydrogen feed fraction was obtained by adjusting its flow rate and that of helium to maintain a constant total gas flow rate of 200 std. cm^3/min throughout the course of the experiments. The gas inlet location for all of the steady-state experiments was at the top of the reactor. Effluent gas from the reactor passed through a 0.5-m-long water-cooled condenser which returned vaporized organics to the recycled liquid stream.

Flowing liquid was fed to the top of the pellet within the reactor and was completely recycled throughout the course of a run. The liquid passed through a gas-liquid contactor unit within which helium was bubbled to strip any dissolved hydrogen from the liquid. The initial liquid composition for all the runs was at least 99% or higher-purity cyclohexene (Aldrich). A prepurification step was undertaken to remove any peroxide species that form in a cyclohexene that is exposed

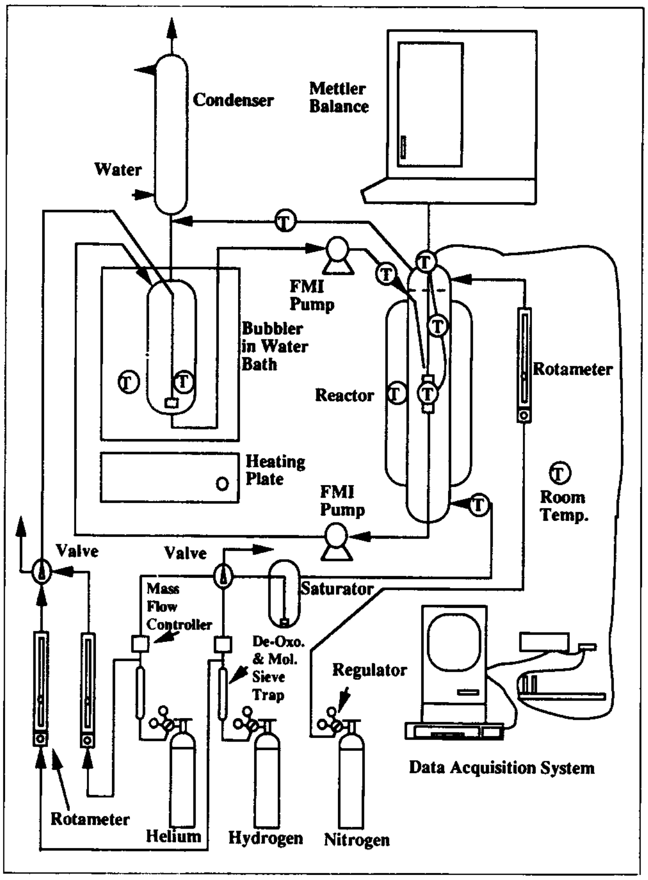


Figure 1. Overall experimental setup.

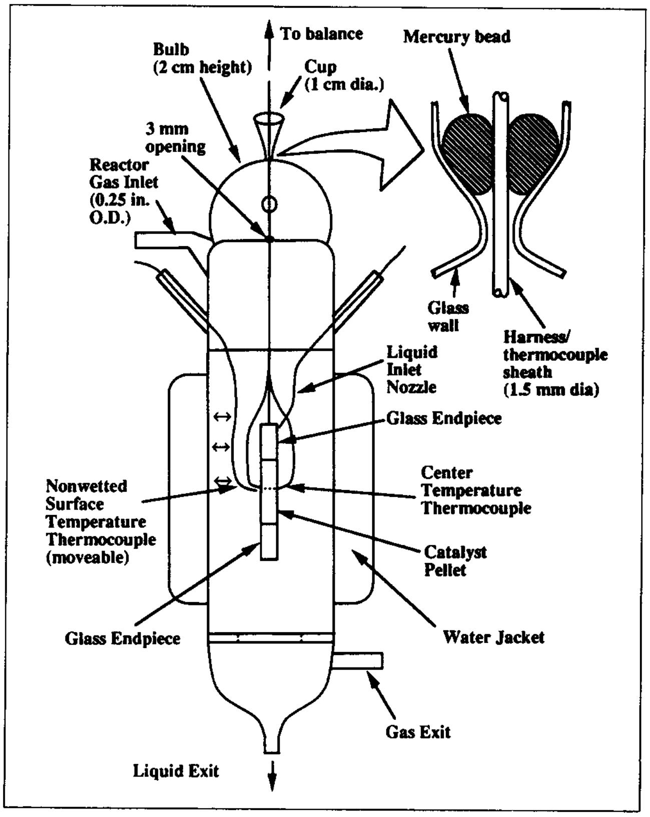


Figure 2. Single-pellet reactor.

even briefly to air (Jackson et al., 1970). These peroxides can deactivate the catalyst. The purification involved contacting the fresh charge (200 cm^3) of cyclohexene over a bed of activated alumina beads (details by Watson, 1993).

Throughout the course of a run, a buildup in the recycled liquid of reaction products cyclohexane and benzene occurred. Overall reaction rates (of cyclohexane and benzene formation) were determined from a chromatographic analysis of liquid samples for the gas-continuous, liquid-batch system (following the procedures of Funk, 1990; Watson, 1993). Liquid samples were withdrawn from the liquid recycle stream at timed intervals. The compositions of the liquid samples were determined using a gas chromatograph (GC) equipped with a capillary column and a flame ionization detector (FID). The time dependence of the product concentration in the recycled liquid stream provided a measure of its rate of production. The chromatography procedure and rate calculations are detailed by Watson (1993).

Single-pellet reactor

Some of the key modifications made to the single-pellet reactor, Figure 2, used in the previous dynamics study (Watson and Harold, 1993) are now discussed.

The first modification involved the attachment of glass pieces to each end of the cylindrical pellet of the same diameter as the pellet (following Funk et al., 1991, who used ceramic end pieces). The glass end pieces were roughened with a grinding wheel to mimic more closely the surface of the porous pellet. Each glass end piece was 2 cm long and the catalyst pellet was 3 cm long. Use of the roughened glass end pieces eliminated several complications. The pieces minimized end effects associated with the liquid flowing onto the top of the catalyst pellet and flowing off the bottom of the pellet. Without the end pieces, it was observed that the liquid fed to the top of the pellet typically resulted in complete external wetting of the pellet by a thin film even at the lowest controllable liquid flow rates (1 cm^3/min). While it was possible to obtain partial pore-filling steady-state data by feeding the liquid to the side of the pellet without end pieces, the external wetting and intraparticle pore filling were difficult to evaluate. For example, a bead of liquid formed at the base of the pellet. This led to a nonuniformly wetted pellet. Moreover, the bead of liquid would drip from the base of the pellet at regular intervals complicating the evaluation of liquid holdup. The liquid was fed to the curved side of the upper glass end piece, about 1/16 in. (1.6 mm) below the top flat surface. Steady, fully developed liquid rivulet flow was usually established along the upper glass section (some exceptions are described below).

The second modification involved an improved liquid temperature control and measurement system. The liquid feed temperature was measured by a sheathed 0.002-in. (0.05-mm)-dia. type-K thermocouple mounted at the tip of the liquid inlet tube, at the point where the liquid was fed to the pellet. The thermocouple was fed through a 1/8-in. (3.2-mm)-OD glass port on the top of the reactor and through a Swagelok fitting that was used to secure the liquid inlet tube. The thermocouple was covered up to, but not including, the junction by 1/32 in. (0.8-mm) OD fiberglass sleeves to prevent contact with the metal tubing. The sleeves were wrapped with Teflon tape and fed through a 1/4-in. (6.4-mm) rubber septum disk that was mounted on the side of a three-way 1/4-in. (6.4-mm) Swagelok connection. The thermocouple was held tightly in the septum disk, sealing the opening through which the thermocouple wire passed. To secure the thermocouple junction at the end of the liquid inlet tube, Teflon tape was wrapped around the stainless steel inlet tube and the sleeved thermocouple wire. Some elevation of the liquid feed temperature was observed for liquid fed at room temperature, if the gas feed was heated. For experiments in which the liquid feed temperature was above the ambient (room) temperature, heating was provided by insulated heating tape that covered the approximate 5-ft (1.5-m) length of liquid feed tubing.

The third modification involved an improved gas temperature control and measurement system. The gas feed temperature was measured by the same 1/32-in. (0.8-mm)-dia. thermocouple used to measure the nonwetted catalyst surface temperature. The design of the temperature probe assembly permitted the thermocouple junction to be pressed against the nonwetted face of the catalyst pellet for a nonwetted face surface temperature measurement and enabled the tip of the thermocouple probe to be moved away from the catalyst pellet to obtain the bulk gas (feed) temperature. The 1/32-in. (0.8-mm) thermocouple probe was passed through a 1/16-in. (1/6-mm) stainless-steel tube that was bent to provide the desired range of motion to swing from the pellet surface to the bulk gas phase. Epoxy (Devcon 2-ton) was used to seal the space between the thermocouple probe and the inside walls of the stainless-steel tube. The stainless-steel tube was secured at the top of the reactor vessel with Swagelok fittings. The reported gas feed temperature value was taken with the tip of the thermocouple probe located approximately 2.5 cm from the nonwetted face of the catalyst pellet and approximately 0.8 cm from the glass wall of the reactor vessel. Under conditions of a high rate of reaction (discussed below) a thermal boundary layer was noted at distances less than about 1.9 cm from the nonwetted face of the catalyst pellet. Beyond the 1.9-cm distance, the temperature was approximately constant and was taken to be the gas feed temperature.

The reactor contents were heated by the water jacket located around the reactor walls. A heating tape was wrapped around the outside of the water jacket. Occasionally, minor power supply adjustments to the variac controlling the heating tape around the water jacket were necessary to obtain the desired feed gas temperature because of variations in the room temperature.

The pellet was partially wetted intentionally by a single liquid rivulet for all of the steady-state experiments with proper feed positioning. The purpose was to demonstrate the steady-state partial pore filling phenomena resulting from the coupling of the multiphase exothermic reaction and volatile liquid vaporization and condensation. A single liquid stream was fed to the side of the top prewetting section. Typically, the total external surface covered by liquid was between about 15 to 50% of the external surface of catalyst. It should be emphasized that the degree of wetting depended on the extent of reaction. These points are described below.

The degree of external liquid coverage was estimated by visual inspection through the glass reactor vessel during the course of an experiment. A hand-held glass mirror was used to view the entire pellet circumference. Following Funk (1990), equally spaced tick marks were placed around the circumference to the end pieces to estimate the degree of wetting. It should be noted that this measurement required some subjective judgment in locating the contact line of the rivulet. In most cases, proper illumination of the pellet enabled the location to be established. The most uncertainty was encountered when there was little pore emptying of the pellet, that is, when the rate was low. We return to this point in the Results Section. For most of the experiments, the width of the liquid rivulet flowing over the upper portion of the pellet exterior surface was approximately the same as the width of the rivulet flowing from the lower portion of the pellet curved surface. The vertical locations of entry (to the upper portion of the pellet) and exit (from the lower portion of the pellet) were typically not the same, but were offset up to approximately 23°. That is, some circumferential meandering of the rivulet occurred. In experiments in which the liquid feed was heated, there was some decrease in the rivulet width along the length of the pellet. In these cases, a length-average value of the degree of wetting was used.

The weight of the entire pellet, glass end pieces, and holder was measured during the course of an experiment using a bottom loading electronic balance (Mettler AE50). The total liquid holdup (weight) was determined in an experiment by subtracting from the total weight with liquid present the total weight without liquid present. The liquid holdup, therefore, represents the liquid inside and outside the catalyst pellet.

Catalyst characterization and activity

The catalytic pellet used for the steady-state experiments was pellet No. 3 of the dynamics study (for a detailed characterization of the catalyst, see Watson and Harold, 1993).

Over the course of the steady-state experiments, the activity of the catalyst pellet varied from what we call "fresh" to "deactivated." Several experiments were used to check the activity of the catalyst pellet over time to determine the extent of deactivation and to validate any data comparisons. To this end, one complete set of experiments was performed with the fresh catalyst and two complete sets with the deactivated catalyst.

The fresh catalyst experiments were performed with the catalyst pellet shortly after its reduction in 350°C flowing hydrogen. Further experiments with a freshly reduced catalyst were not performed because of the experimental difficulties in rereducing the catalyst pellet: the epoxy used to secure the end pieces onto the catalyst could not be exposed to temperatures above 120°C. The fresh catalyst runs were carried out in a sufficiently short time period (about 2 weeks) that a complete data set was obtained while the catalyst remained at a high activity level. The deactivated catalyst experiments were performed with the same pellet but after a period of time in which some loss in activity had occurred. Each of the two sets of deactivated catalyst pellet experiments were carried out over a short time period. Several experiments were performed to check the activity and hence to check reproducibility.

Catalyst state vs. hydrogen feed fraction

The experimental study was carried out by measuring the dependence of the *catalyst state* on the fraction of hydrogen in the feed gas (y_{H2} in diluent helium). The *catalyst state* was characterized by six variables:

- Degree of external wetting, E_w
- Liquid holdup, m_L
- Center pellet temperature, T_c
- Nonwetted surface pellet temperature, T_{ns}
- Overall rate of cyclohexane formation, r_C
- Overall rate of benzene formation, r_B

This dependence was established for three different combinations of the feed liquid and feed gas temperatures (T_{fL}, T_{fG}). Table 1 summarizes various operating conditions used in the steady-state experiments. The activity level of the catalyst differed for the three sets of runs. All other experimental conditions were fixed, including the feed liquid flow rate and composition, and the total gas flow rate. Room temperature (20-25°C) feeds were used with the fresh catalyst pellet to achieve partial pore-filling phenomena over a wide range of conditions, while elevated temperature feeds were necessary to achieve similar partial pore-filling phenomena after the catalytic activity had declined. The steady-state experiments were carried out in random order from the standpoint of startup procedure and feed gas composition.

Startup procedures

Two types of startup procedures were followed in obtaining the dependence of the catalyst state on the hydrogen feed fraction. The rationale for starting the experiments two different ways was to check for suspected multiple steady states. As pointed out earlier, multiplicity was observed in reactor studies and predicted by single-pellet models. The starting condition was either a gas-prefilled pellet or a liquid-prefilled pellet.

Experiments started from a gas-prefilled state most often yielded a partly liquid-filled, high-rate steady-state (with a sufficient hydrogen concentration). An experiment started from a liquid-prefilled state typically resulted in a mostly liquid-filled, low-rate steady state. The nature of the startup, as well as the feed condition and catalytic activity, influenced the final steady state of the pellet in the region of operation in which multiple steady states were encountered. The Results Section provides example time traces of the center pellet temperature and liquid holdup for the liquid- and gas-prefilled pellet. It should be emphasized that no systematic order was followed in spanning the entire range of hydrogen feed fractions. Thus, a gas-prefilled experiment was carried out directly following a liquid-prefilled experiment, and *vice versa*. This reduced the likelihood that deactivation was responsible for the observed hysteresis phenomena described below.

The *liquid-prefilled procedure* was carried out as follows. In flowing helium (200 std. cm^3/min), the pellet was contacted by cyclohexene flowing at 4 cm^3/min for a period of time sufficient to completely fill the pellet pore structure, as determined by the tared pellet weight reading (about 10 min). The positioning of the feed liquid tube relative to the pellet gave a degree of wetting of approximately 0.5 for this flow rate. Thus, the pellet was initially completely filled with liquid, but partially wetted on its external surface. The desired hydrogen/helium mixture was then applied by adjusting the mass-flow controllers. The total volumetric gas flow rate was maintained at 200 std. cm^3/min. The pellet state was then allowed to reach a pseudo-steady state. A time period of at least 60 min was allotted for equilibration. As described earlier, several liquid samples were then withdrawn during the remainder of the run for subsequent chromatographic analysis of composition vs. time.

The *gas-prefilled procedure* was carried out as follows. The initially dry pellet was exposed to the desired hydrogen/helium mixture flowing at 200 std. cm^3/min for 15-40 min. Then, the liquid was turned on at its prescribed flow rate of 2 or 4 cm^3/min. The pellet was then allowed to equilibrate for a sufficient time period as in the other type of run.

Data collection was typically started prior to reaching the steady state so that the approach to steady state could be compared. The data selected for steady state was chosen based on the point in which the catalyst temperatures, weight and qualitative appearance (including the coverage of liquid on the outside of the pellet) were steady. Each steady-state run was carried out for a total time of approximately 3 h.

Results

This section reports on the steady-state experimental results: change in catalytic activity during the investigation; impact of startup procedure on the approach to steady state; dependence of the pellet state on the hydrogen feed fraction for three different situations; fresh catalyst pellet with room temperature feeds; deactivated catalyst pellet with elevated, equal-temperature feeds; and deactivated catalyst pellet with elevated feed gas and room temperature feed liquid.

In the following data, each open circle or triangle data point in the figures represent a separate steady-state experiment started up as described above, open circle symbols indicate that the particular run followed the gas-prefilled procedure, and open triangles indicate that the run followed the liquid-prefilled procedure. When appropriate, the bulk-phase temperature feed value given is represented by a square symbol.

Table 1. Summary of Operating Conditions Used in the Steady-State Experiments

Gas Composition	Catalyst Activity (Relative)	Liquid Flow Rate (cm^3/min)	Total Gas Flow Rate (cm^3/min)	Gas Feed Temp.	Liquid Feed Temp.	Method of Startup
varied	high	4	200	room temp. (23-25°C)	room temp. (23-25°C)	gas- and liquid-prefilled
varied	low	2	200	29°C	62°C	gas- and liquid-prefilled
varied	low	2	200	43°C	43°C	gas- and liquid-prefilled

Catalyst deactivation

As mentioned earlier, differences in the activity of the pellet were observed over the course of the experimental investigation. To clearly establish the activity level of the pellet before a collection of runs, a standard experiment was performed. A complete data set was obtained with the fresh catalyst. A rather sharp decline in activity was observed after approximately 11 individual runs were carried out (two-week period). This decline was pinpointed by the inability of the pellet to sustain the high rate, partially filled state when using a room temperature, pure hydrogen feed gas. Table 2 shows the results of a standard experiment over which all of the deactivated catalyst experiments were carried out. The standard experiment for the deactivated catalyst pellet used feed gas of pure hydrogen at 62°C and initially pure cyclohexene feed liquid at room temperature. The gas-prefilled procedure was followed in this standard run; the gas flow rate was 200 cm^3/min, while the liquid flow rate was 2 cm^3/min. Changes in the dependent variables with time are attributed to differences in catalytic activity. It is apparent that some deactivation occurred during the period in which the deactivated catalyst data were obtained. However, the random order in which the data sets were obtained ruled out the possibility that deactivation caused the hysteresis.

Impact of startup procedure

Figures 3a and 3b convey the typical response of the pellet when it was initially contacted by the gaseous reactant mixture containing a sufficiently low, but nonzero, fraction of hydrogen (*gas-prefilled pellet procedure*). The data in Figures 3a and 3b correspond to a pure-hydrogen, room temperature feed using the deactivated pellet. The time dependence of the center pellet temperature (T_c, Figure 3a) and the liquid holdup (m_L, Figure 3b) are shown. The small temperature rise early on corresponds to the introduction of the hydrogen gas feed to the previously helium-purged reactor. That is, some unreacted cyclohexene was adsorbed on the catalyst initially. The feed liquid was admitted at approximately the 49-min mark. Upon introduction of the pure cyclohexene feed liquid, a large increase in the pellet temperature is noted. During this temperature increase, there was an increase in the liquid holdup. After a short period of approximately 3 min, T_c began to decrease while m_L continued to increase. The pellet gradually approached a state in which there was a minor temperature difference between the pellet and bulk and in which there was a negligible change (start to finish) in the liquid holdup.

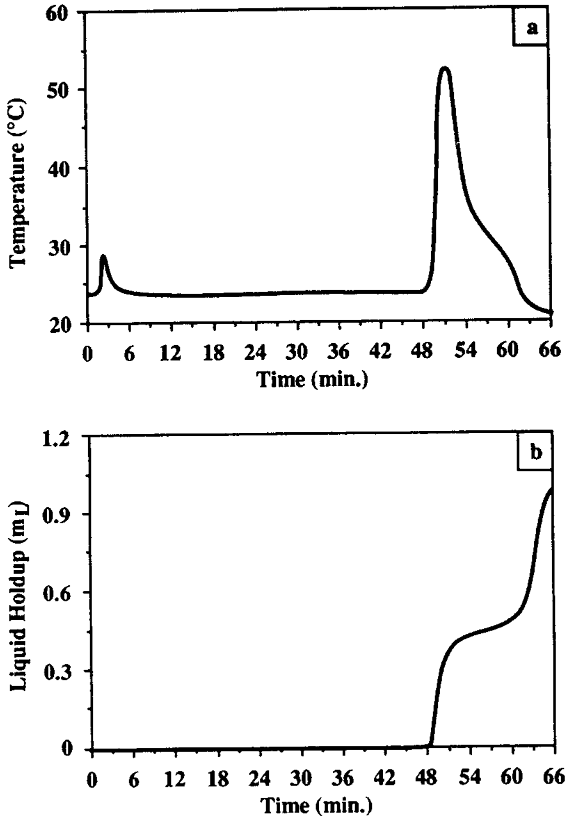


Figure 3. Typical pellet response following the gas-prefilled procedure in which the pellet ignites momentarily but eventually returns to the low-rate state.

(a) and (b) show the time dependence of the center pellet temperature and liquid holdup, respectively. The conditions are: deactivated catalyst, room temperature feeds, 4-cm^3/min liquid cyclohexene, 100% hydrogen gas.

Table 2. Catalytic Activity Values as a Function of Time Over the Course of Investigation: Standard Experiment

	Date of Run			
	8/1/92	8/6/92	8/12/92	8/15/92
Wt. of liquid (g)	0.48	0.47	0.50	0.52
Temp. at center of catalyst (°C)	57.5	57.6	51.7	51.0
Temp. at nonwetted surface of catalyst (°C)	69.5	67.1	65.8	63.4
% of external surface of catalyst covered with liquid	19	19	19	19
Rate of cyclohexene production (mol/g/s)	4.46×10^{-6}	3.97×10^{-6}	3.64×10^{-6}	lost data
Rate of benzene production (mol/g/s)	3.32×10^{-7}	2.62×10^{-7}	2.37×10^{-7}	lost data

Some interesting qualitative observations were made during the commencement of liquid flow in such an experiment. The liquid rivulent would initially wander along the length of the pellet surface, meandering back and forth. The catalyst pellet surface near the liquid rivulet had a light gray shade, indicating that the Pd/Al_2O_3 pellet was dry. The surface would appear dry immediately after the film shifted from a location previously covered with liquid. The maximum translational amplitude of the shifting rivulet was approximately 0.5 cm. This hydrodynamic fluctuation had no measurable effect on the catalyst temperature or liquid holdup. Eventually, the rivulet would relax into a generally straight path down the side of the pellet.

When the same gas-prefilled procedure was applied, but with higher feed temperatures (43°C), the response of the pellet was quite different. Figures 4a and 4b show the response in T_c and m_L when the feed gas contained 100% hydrogen. Upon the introduction of the cyclohexene (at the 60-min mark), there was a similar sharp increase (decrease) in the pellet temperature (liquid holdup). However, the pellet remained at a temperature

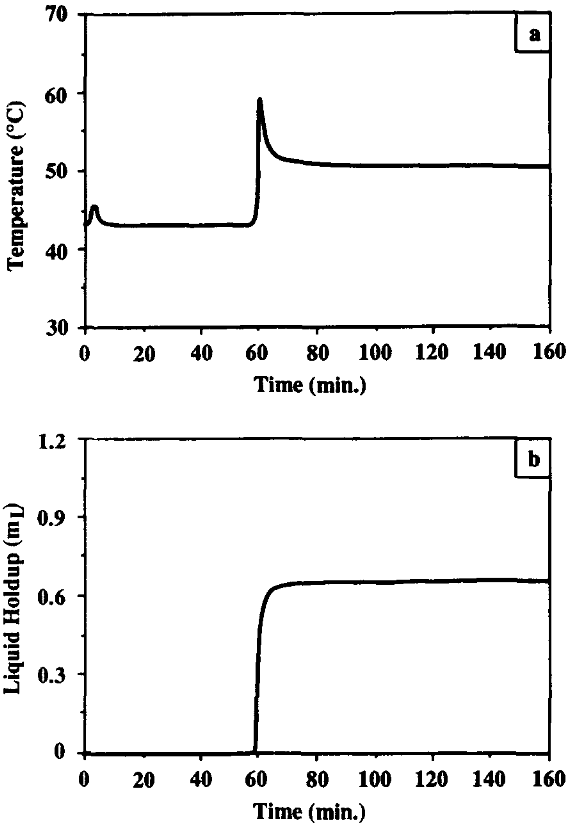


Figure 4. Typical pellet response following the gas-prefilled procedure in which the pellet ignites and remains in the high-rate state.

(a) and (b) show the time dependence of the center pellet temperature and liquid holdup, respectively. The conditions are: deactivated catalyst, 43°C feeds, 2-cm^3/min liquid cyclohexene, 100% hydrogen gas.

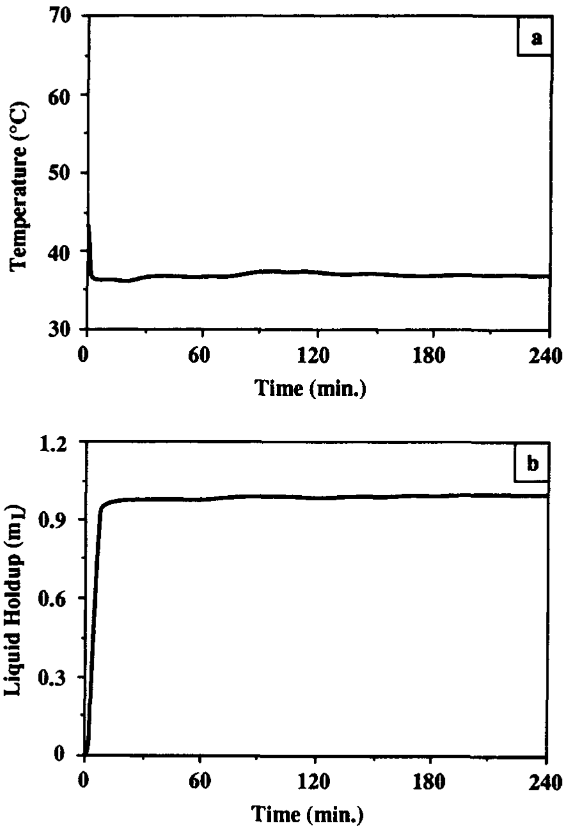


Figure 5. Typical pellet response following the liquid-prefilled procedure in which the pellet remains in the low-rate state.

(a) and (b) show the time dependence of the center pellet temperature and liquid holdup, respectively. The conditions are: deactivated catalyst, 43°C feeds, 2-cm^3/min liquid cyclohexene, 100% hydrogen gas.

higher than the feed temperatures of the liquid and gas. Moreover, the liquid holdup indicated that a partially filled state was sustained at long times. It is interesting to compare Figure 4 (43°C feed) with Figure 3 (room temperature feed, 24°C). The existence of an intermediate plateau of sorts in the liquid holdup vs. time data in the lower feed temperature experiment indicated some inclination toward the high rate, partially filled state. However, the bulk temperature was apparently insufficient to maintain this state.

Finally, Figures 5a and 5b show a typical response of the pellet when it was initially filled by a flowing cyclohexene liquid stream and then contacted by the flowing gaseous reactant mixture. In all cases tested involving this *liquid-prefilled procedure*, the pellet did not exhibit any significant change in its temperature or weight. For the data shown, the liquid cyclohexene was fed to the pellet at the 1.5-min mark, while the reactive gas mixture of 100% hydrogen was started at approximately the 12-min mark.

Fresh catalyst pellet, room temperature gas and liquid feeds

The dependence of the catalyst state on the hydrogen feed fraction (y_{H2}) is presented in Figures 6–8. Shown are the center pellet temperature (Figure 6a), nonwetted surface temperature (Figure 6b), liquid holdup (Figure 7a), degree of external wetting (Figure 7b), rate of cyclohexane formation (Figure 8a) and rate of benzene formation (Figure 8b). A quick glance at all the plots reveals the existence of two branches of states. The continuous low temperature and rate state will be discussed, and then the discontinuous high temperature and rate state.

For all of the experiments in which the liquid-prefilled procedure was followed, the pellet remained mostly liquid-filled and in a relatively low rate state throughout the course of the run. A continuous steady-state branch was observed for y_{H2} over its feasible range of 0 (pure helium gas) and 1 (pure hydrogen). This branch was characterized by a low center pellet temperature (T_c) and nonwetted surface temperature (T_{ns}). Figures 6a and 6b reveal no clear trend in T_c or T_{ns} along the low branch, as y_{H2} was varied over its entire range. However, both T_c and T_{ns} were lower than the feed gas and liquid temperatures. The feed temperature is indicated by solid squares in each figure (bounded between 22–25°C). The feed temperature exceeded T_c by up to a 4–5°C margin; T_c, in turn, exceeded T_{ns} by up to a 6–7°C margin.

Along the low-rate branch, the pellet remained mostly filled with liquid, as revealed in the dependence of the liquid holdup (m_L) on y_{H2} (Figure 7a). The liquid holdup exhibited a slight monotonically decreasing dependence on y_{H2}. For example, in pure hydrogen ($y_{H2}=1$), the liquid holdup was 0.99 g, while

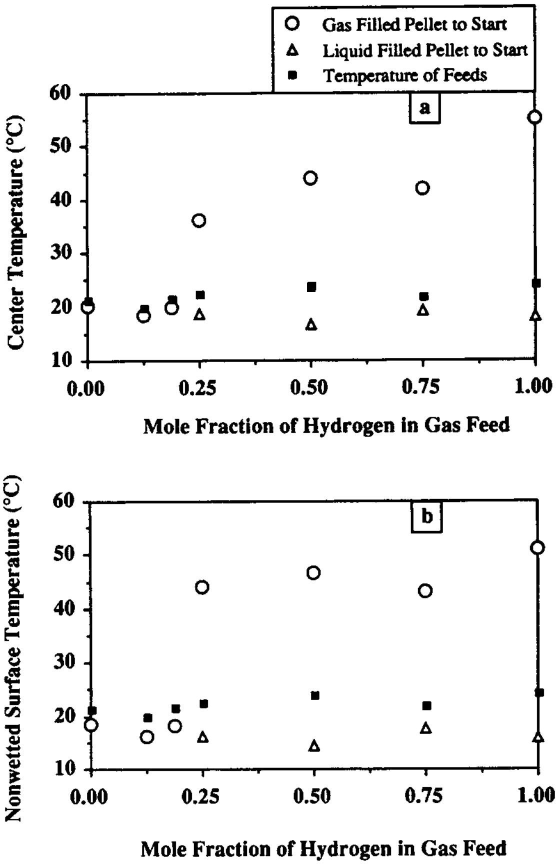


Figure 6. Steady-state fresh catalyst data contacted by room-temperature liquid and gas feeds.

(a) and (b) show the center pellet temperature and nonwetted-surface temperature as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

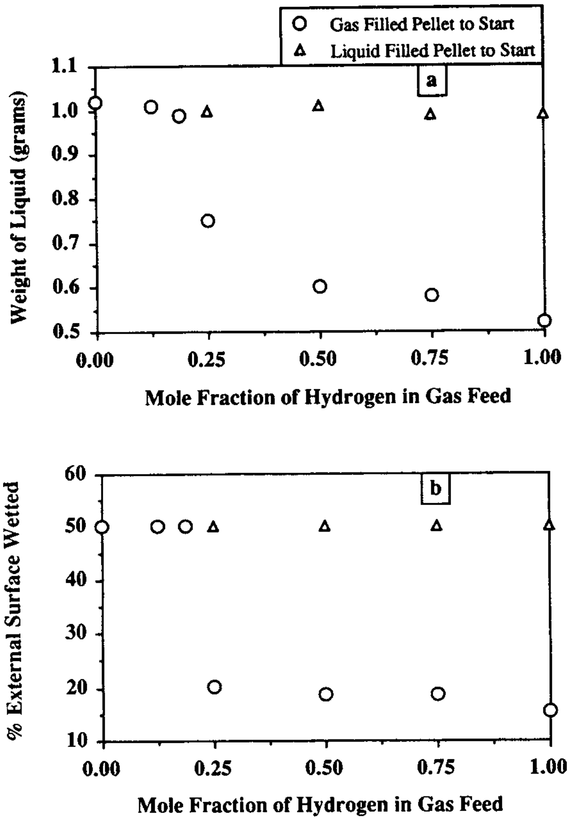


Figure 7. Steady-state fresh catalyst data contacted by room-temperature liquid and gas feeds.

(a) and (b) show the liquid holdup and degree of external wetting as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

for an equimolar hydrogen/helium feed ($y_{H2}=0.5$) m_L had a slightly larger value of 1.01 g. Figure 7b reveals that the degree of liquid contacting remained essentially constant ($E_w=0.5$) over the entire y_{H2} range.

A small, but measurable, increase in the rate of cyclohexane production (r_C) was observed as y_{H2} was increased over its feasible range (Figure 8a). (Note that rates are not reported for the run with pure helium because of difficulties encountered with the GC). For example, r_C ($y_{H2}=0.5)=7.5\times10^{-8}$ mol/g/s and r_C ($y_{H2}=1)=2.1\times10^{-7}$ mol/g/s. Benzene was not detected in the liquid over the entire range of y_{H2} (Figure 8b). This indicates that only the hydrogenation occurred along the low branch.

More significant variations in the catalyst state dependence on y_{H2} were observed when the gas-prefilled procedure was followed. Figures 6-8 reveal that for y_{H2} below a critical value the catalyst relaxed to a state virtually identical to that of the low branch observed for the liquid-prefilled pellet. However, when the pellet was prefilled by a flowing gas containing hydrogen exceeding this critical value, a much higher temperature and rate state was obtained.

Figures 6a and 6b reveal that both the center temperature (T_c) and nonwetted-surface temperature (T_{ns}) decreased as y_{H2} was decreased from 1 to 0. A marked drop in T_c and T_{ns} was noted between $y_{H2}=0.25$ and 0.19. For example, T_c dropped from 36°C to 20°C, and the nonwetted-surface temperature dropped from 44°C to 18°C. For $y_{H2}\leq0.19$, the temperature of the center and nonwetted surface of the pellet was not only significantly lower than at higher mole fractions of hydrogen in the gas feed, but also lower than the feed temperature, as pointed out above. Along the high-temperature branch ($y_{H2}\geq0.25$), T_{ns} exceeded T_c by 1-10°C except at $y_{H2}=1$ where T_c exceeded T_{ns} by 2-3°C.

Both the liquid holdup (m_L) and degree of external wetting (E_w) exhibited similar discontinuous behavior for y_{H2} between 0.25 and 0.19, as revealed in Figures 7a and 7b. For example, as y_{H2} was decreased from 1.0 to 0.25, m_L increased monotonically from 0.52 g to 0.75 g. However, a subsequent decrease in y_{H2} from 0.25 to 0.19 resulted in a step increase in m_L to 0.99 g. A further decrease in y_{H2} to 0 resulted in a slight increase in m_L to 1.02 g. E_w increased nearly linearly from 0.16 at $y_{H2}=1$ to 0.20 at $y_{H2}=0.25$. E_w increased sharply to 0.5 as y_{H2} was decreased to 0.19. For y_{H2} values at or below 0.19, E_w exhibited an essentially constant value of 0.5.

Two regimes of cyclohexane and benzene formation rates were encountered in the gas-prefilled pellet experiments, as shown in Figures 8a and 8b. Unfortunately, due to the approximately one order of magnitude lower rate of benzene formation compared to that of cyclohexane, more scatter in the benzene rate data was encountered. Despite the scatter, some trends can still be established. Very low cyclohexane

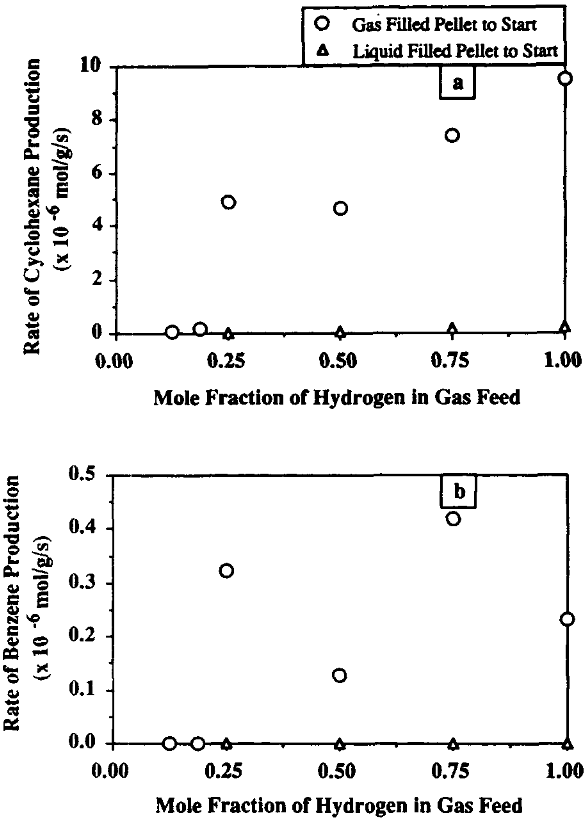


Figure 8. Steady-state fresh catalyst data contacted by room-temperature liquid and gas feeds.

(a) and (b) show the cyclohexane and benzene production rates as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

formation rates and undetectable benzene formation rates were observed for $0<y_{H2}<0.25$. On the other hand, significantly higher rates of cyclohexane and benzene formation were encountered for $y_{H2}\geq 0.25$. A definite discontinuity in the cyclohexane formation rate was encountered for y_{H2} between 0.25 and 0.19. For example, the rate decreased from 4.9×10^{-6} mol/g/s at $y_{H2}=0.25$ to 1.6×10^{-7} mol/g/s at $y_{H2}=0.19$, a factor of 30.

Finally, some comments should be made about the appearance of the contact line corresponding to the interface between the actively wetted and nonwetted pellet surface. The distinction of liquid-covered surface to dry surface was the sharpest for the highest rate state (including highest catalyst temperature and highest production rate of product). In general, the higher the fraction of hydrogen present in the gas feed, the higher the rate, and hence the sharper boundary between the liquid-covered pellet surface and the nonwetted pellet surface. In some cases, it was noted that while a fairly distinct contact line between the rivulet and the nonwetted pellet surface was noted during startup, the contact line was not as sharp when steady state was reached. Rather, there seemed to be a gradual change in appearance from the flowing liquid to the completely dry surface. In a relatively narrow zone intermediate between the flowing liquid and the completely dry surface, there appeared to be nearly motionless liquid. Proceeding beyond this zone, the pellet surface changed from a dark, damp appearance to that of a lighter, dryer one. The degree of wetting reported in this study corresponds to the width of the actively wetted zone.

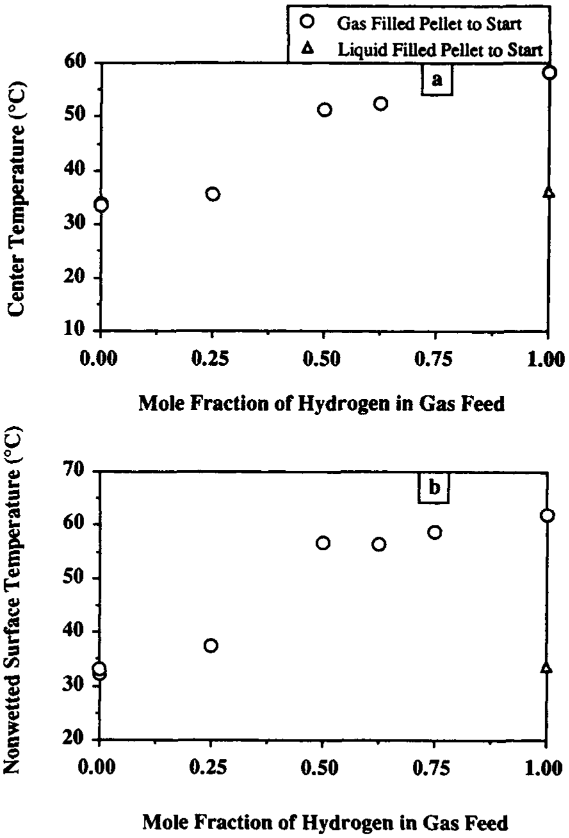


Figure 9. Steady-state deactivated catalyst data contacted by elevated temperature (43°C) liquid and gas feeds.

(a) and (b) show the center pellet temperature and nonwetted surface temperature as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

Deactivated catalyst pellet, elevated temperature gas and liquid feeds

The steady-state behavior obtained for the catalytic pellet after it had deactivated to the level indicated in Table 2 was examined to check the generality of the trends obtained at a higher activity. Our attempts to reproduce the data at the same conditions resulted in only the low rate, mostly liquid-filled state. Elevation of the feed temperature was necessary to sustain a higher rate, partially filled state for some hydrogen feed fractions. Figures 9-11 show the dependence of the catalyst state on the hydrogen feed fraction for the deactivated pellet. The feed gas and liquid streams were heated to an elevated temperature of 43°C. In addition, the feed liquid flow rate was reduced by a factor of 2 from the fresh catalyst runs to 2 cm^3/min. All other experimental conditions are provided in Table 1.

A single liquid-prefilled pellet experiment was carried out in a pure-hydrogen gas feed ($y_{H2}=1.0$). This procedure resulted in a low-temperature, low-rate state as was encountered in the fresh catalyst runs. An appreciable depression in the center

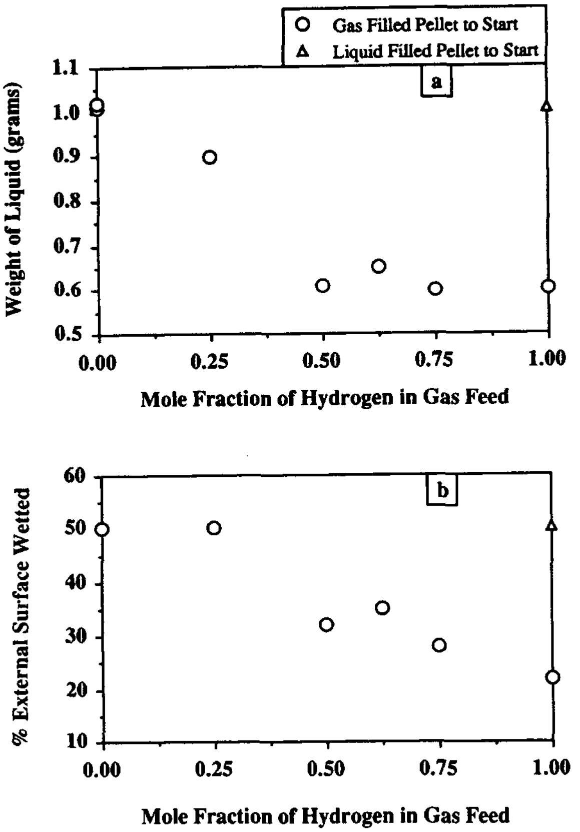


Figure 10. Steady-state deactivated catalyst data contacted by elevated temperature (43°C) liquid and gas feeds.

(a) and (b) show the liquid holdup and degree of external wetting as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

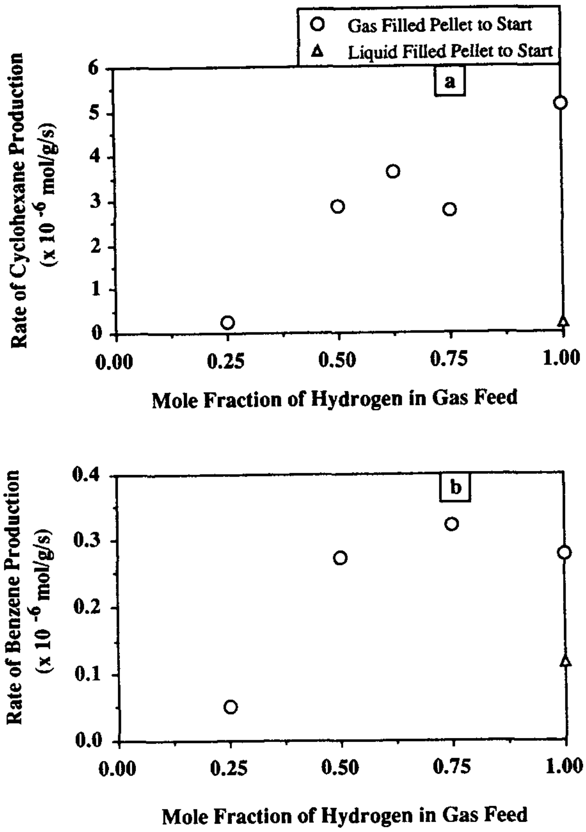


Figure 11. Steady-state deactivated catalyst data contacted by elevated temperature (43°C) liquid and gas feeds.

(a) and (b) show the rates of cyclohexane and benzene formation as functions of the feed fraction of hydrogen, respectively. All other conditions are specified in Table 1.

pellet temperature and nonwetted surface temperature below the bulk value of 43°C was observed, as noted in Figures 9a and 9b. A drop in T_c of 6.8°C to 36.2°C and in T_{ns} of 9.2°C to 33.8°C was observed. The degrees of liquid filling and of external wetting were similar to those for the fresh catalyst pellet, as noted in Figures 10a and 10b, respectively. The pellet maintained a mostly liquid-filled steady state with a liquid holdup of approximately 1.0 g. The degree of wetting was approximately 0.5 in this state. Finally, low production rates of cyclohexane and benzene were measured (Figures 11a and 11b).

Additional low-rate state data were obtained when the gas-prefilled procedure was applied and the hydrogen feed fraction was below a critical level, as in Figures 9-11. This critical level was bounded between 0.25 and 0.5. Insignificant differences in the final pellet state were obtained for the pure-hydrogen run in which the liquid-prefilled procedure was followed and for the low-hydrogen feed fraction runs in which the gas-prefilled procedure was followed. Since the pellet remained in a low-rate state in the pure-hydrogen run, this ruled out the existence of an ignition point at a sufficiently large hydrogen feed fraction. Based on these findings and the behavior observed for the fresh catalyst pellet (Figures 6-8), it is reasonable to conclude that a continuous branch of low-rate states also existed for the deactivated catalyst pellet.

The behavior of the deactivated pellet when prefilled with gas exhibited the same qualitative behavior as when it was at a higher activity level. For hydrogen feed fractions at or above 0.5, the pellet existed in a partially filled, higher temperature, and rate state. The dependencies of the catalyst state variables (T_c, T_{ns}, m_L, E_w, r_C and r_B) on y_{H2} along the high-rate branch are similar to those observed in the fresh catalyst runs. Moreover, a noted discontinuity in the key catalyst state indicators occurred as y_{H2} was decreased from 0.5 to 0.25. For example, T_c decreased from 52°C to 37°C, T_{ns} decreased from 57°C to 37°C, m_L increased from 0.61 g to 0.91 g, E_w increased from 0.32 to 0.5, r_C decreased from 3.0×10^{-6} mol/g/s to 0.29×10^{-6} mol/g/s and r_B decreased from 0.28×10^{-6} mol/g/s to 0.05×10^{-6} mol/g/s.

Deactivated pellet, unequal gas and liquid feed temperatures

An additional set of experiments with the lower activity pellet was carried out for conditions in which the gas and liquid were fed in at different temperatures: 29°C and 62°C, respectively. The details of these data are reported by Watson (1992). The pellet exhibited many of the same trends as in the previous two sets: a low-rate state was observed over the entire feasible range of y_{H2}. A much higher temperature and rate branch was

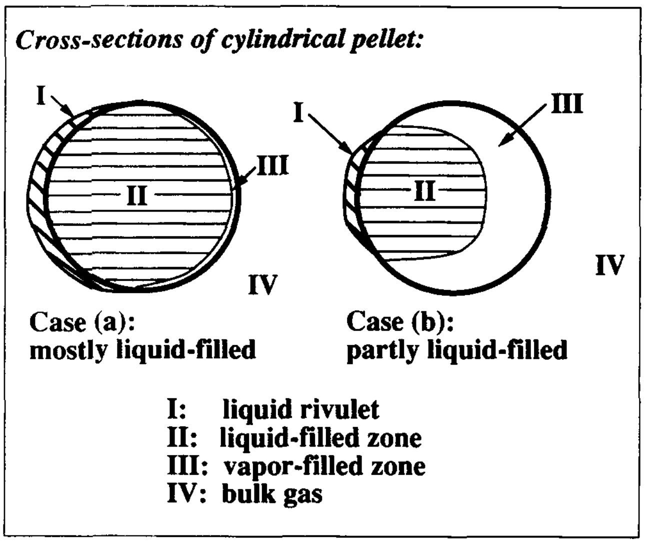


Figure 12. Cross sections of the cylindrical pellet in (a) the low-rate state and (b) high-rate state.

encountered above a critical value of y_{H2}. This critical y_{H2} value was bounded between 0 and 0.25.

Discussion

This experimental study provides direct evidence of partial pore filling in a partially wetted pellet under steady-state operation. The data reveal the existence of two distinctly different regimes: a low overall rate state in which the temperature rise is negligible (or even negative) and the pellet is mostly liquid-filled; a high-rate state in which the temperature rise is appreciable and the pellet is only partly liquid-filled. The former regime exists for all hydrogen fractions in the feed gas. The latter regime exists for all hydrogen feed fractions exceeding a critical value. Thus, a multiplicity of two observable states exists. The magnitude of the critical hydrogen fraction is sensitive to the liquid and gas feed temperatures and activity level of the catalyst.

In interpreting the data it is helpful to consider schematic cross-sectional views of the partially wetted cylindrical pellet, as in Figure 12 for two cases. For each case, the cylindrical pellet is exposed to a flowing bulk gas (region IV) and is contacted on a fraction of its surface by a flowing liquid rivulet (I). The internal pore volume of the pellet is envisioned to comprise a completely liquid-filled zone (II) and a completely gas-filled zone (III). Not coincidentally, the two cases in Figure 12 are constructed to provide interpretive snapshots of the interior of the pellet in the two-rate regimes encountered experimentally. Case a represents an approximately half-wetted, mostly liquid-filled pellet. Case b represents a pellet that is wetted on approximately 20% of its exterior and for which about half of its pore volume is filled with liquid. Although not shown in case b, it is possible that capillary condensation of the less volatile components (cyclohexene and cyclohexane) occurred in the smallest pores within the "dry" zone III. Jaguste and Bhatia (1991) have shown that if the bulk gas-containing reactive components, one of which is condensable, are exposed to a pellet at a sufficiently low temperature, then condensation is likely under reaction conditions. In describing the reaction-transport interactions for each case, it is also helpful to refer to the key findings of the half-wetted catalytic slab model of Harold and Watson (1993). A more detailed quantitative comparison between model and experiment is the subject of ongoing research (Kharbanda et al., 1993).

Mostly liquid-filled state

The experimental results showed that the half-wetted pellet was mostly filled with liquid for all the conditions and catalytic activity levels examined. Case a in Figure 12 represents the pellet cross section and liquid distribution. The pellet center temperature (T_c) and nonwetted surface temperature (T_{ns}) were up to 10°C below the bulk temperature for the fresh and deactivated catalyst (Figures 6b and 9b). Thus, despite the fact that the catalyst was mostly liquid-filled, the rate of vaporization was sufficient to reduce the pellet temperature. The slight decrease in liquid holdup with increasing y_{H2} (Figure 7a) is added evidence of a steady-state vaporization process. In most of the runs, the center pellet temperature exceeded the nonwetted surface temperature. This explains why the endothermic vaporization occurred primarily at the nonwetted surface of the pellet.

These findings concur with the model predictions of Harold and Watson (1993). The half-wetted slab simulations revealed that the catalyst exists in a completely or mostly liquid-filled state for sufficient low catalytic activity. Moreover, the overall rate is limited by the transport of the dissolved sparingly soluble reactant (hydrogen). Direct exposure of a fraction of the pellet surface to a flowing gas which has a composition that is *not* equilibrated with that of the rivulet promotes the vaporization process. The resulting capillary-driven convection of liquid from the wetted to nonwetted face helps supply dissolved hydrogen to the active sites within the liquid-filled pores. However, the convection-assisted transport is not sufficient to avoid a severely transport-limited situation. Further evidence for such transport control in the experiments is obtained by computing the observable Weisz-Prater modulus Φ (Weisz and Prater, 1954):

$$\Phi = \left(\frac{R_p}{2}\right)^2 \frac{r_{\text{obs}}\rho_p}{D_{eH} C_{HL}} \qquad (1)$$

where R_p and ρ_p are the pellet radius and apparent density, and D_{eH} and C_{HL} are the dissolved hydrogen effective diffusivity and bulk liquid solubility, respectively. Using $R_p = 0.4$ cm, $\rho_p = 1.13$ g/cm^3, $D_{eH} = 10^{-5}$ cm^2/s, $C_{HL} \sim 3 \times 10^{-6}$ mol/cm^3, and $r_{\text{obs}} \sim 2 \times 10^{-6}$ mol/g/s gives $\Phi = 301$. Clearly, since $\Phi \gg 1$ this is a severely diffusion-limited state.

Partially-filled state

Significant increases in the overall rate and pellet temperature were encountered when the pellet was only partly filled with liquid. This state is represented by case b in Figure 12. The fresh catalyst data (Figures 6-8) reveal overall cyclohexane production rates in the range 4.5-9.5 × 10^{-6} mol/g/s. This compares to the range obtained in the low-rate state of 0.5-2 × 10^{-7} mol/g/s, a rate increase of up to a factor of 50. The rate enhancement is due in part to the higher pellet temperatures achieved in the high-rate state ($T_c \sim 35$-55°C) compared to the low-rate state ($T_c \sim 15$-$20°C$). However, a 35°C temperature increase without an accompanying phase change does not account for the large magnitude of the rate increase. For example, using a liberal estimate of an overall activation energy of 40 kJ/mol gives a rate increase of a factor of 5.75 corresponding to a pellet temperature increase from 20 to 55°C. The most likely factor for the rate increase is the more rapid reaction in the pores that are directly exposed to vapor as a consequence of the intraparticle vaporization process. Moreover, the degree of wetting was lower when the pellet was partially filled ($E_w \sim 0.2$) compared to when it was mostly filled ($E_w \sim 0.5$). The reduced external contacting itself reduces the overall external resistance to supply of hydrogen. It has been shown that even under primarily isothermal conditions, decreased external wetting can result in overall rate increases for volatile reactant-limited reactions (Herskowitz et al., 1979; Ramachandran and Smith, 1979; Harold and Ng, 1987; Funk et al., 1991). This is likely to be a secondary factor in the nonisothermal system.

Along the high-rate state, the cyclohexane production rate and pellet temperatures are increasing functions of the hydrogen feed fraction. This trend is consistent with the established kinetics of Pd-catalyzed cyclohexene hydrogenation. Reaction orders with respect to hydrogen are bound between 0.5 and 1 for Pd- and Pt-catalyzed cyclohexene hydrogenation (Segal et al., 1978; Madon et al., 1978; Gonzo and Boudart, 1978; Hanika and Ehlova, 1989).

The experimentally observed state of partial pore filling has been demonstrated in theoretical studies of the half-wetted catalytic slab, which can be considered as a one-dimensional analog of the experimental system (Harold, 1988; Harold and Watson, 1993). The following set of events explains the incomplete internal wetting. A fraction of the liquid fed to the pellet imbibes into the pores by a capillary-driven process. If the catalyst is sufficiently active, a high-temperature, dry zone can be established in the vicinity of the nonwetted surface. Within the gas-filled pores, exothermic reaction occurs along with diffusion, convective mass and heat transport, and conduction. A fraction of the heat generated by reaction conducts to the vapor-liquid interfaces where it is used to vaporize the imbibing liquid. A steady state of incomplete pore filling results from a balancing of these processes. The extent of pore filling (position of interface in a 1-D system) depends on several parameters, including the catalytic activity, the support permeability, the heat of reaction, the overall activation energy, the volatilities of the liquid components, the extent of departure from vapor-liquid equilibrium between the flowing rivulet and gas, and the gas flow rate. For example, appreciable pore emptying and rate enhancement are likely if the reaction is exothermic, the liquid components are sufficiently volatile, there is a significant departure from bulk-phase vapor-liquid equilibrium, and the convective heat removal by the flowing gas is poor (that is, low gas flow rate). Most of these factors have clearly been satisfied in the cyclohexene hydrogenation system considered in this experimental study.

Steady-state multiplicity features

For a range of hydrogen feed fraction (y_{H2}) exceeding a critical value, both low- and high-rate regimes were encountered. The upper-rate branch could be realized only if the pellet was perturbed to a high temperature during startup from an initially dry state. The continuous lower-rate branch could be attained by slowly decreasing y_{H2}, while the pellet was in the high state until the extinction point was encountered. The pellet state vs. y_{H2} bifurcation diagram form is that of a continuous branch and an open-ended isola. A bifurcation diagram of this type has been encountered in purely gas-phase exothermic catalysis on a single pellet (Harold and Luss, 1985).

Single-pellet multiplicity is a well-known phenomenon in single-phase catalytic reactions (Aris, 1975; Luss, 1987). The most common mechanism is a thermokinetic one, that is, coupling between the nonlinear rate of heat generation by reaction and the linear rate of external heat removal by convection. A necessary condition for multiple states is the existence of two or more rate-controlling regimes. This condition is clearly satisfied in the multiphase single-pellet system. The partially wetted pellet may exist in a low temperature and rate, mostly liquid-filled, essentially isothermal state and a high temperature and rate, partially liquid-filled, nonisothermal state. Indeed, multiplicity may be more likely in multiphase exothermic reaction systems. For example, Hu and Ho (1990) have shown that partial external wetting of a completely liquid-filled pellet expands the parameter region in which multiplicity is encountered. Moreover, Harold (1988) and Harold and Watson (1993) have shown that multiplicity can exist even for an unactivated exothermic multiphase reaction. The additional nonlinear processes such as the capillary-driven liquid inhibition and capillary condensation are likely responsible for an expansion in parameter region giving multiplicity.

The multiplicity results obtained for the catalytic pellet at two different activity levels suggest a bifurcation map of a form in Figure 13a. This hypothetical map divides the plane of intrinsic catalytic activity and hydrogen feed fraction into regions in which one or two observed states are encountered (all other conditions fixed). The corresponding overall rate vs. y_{H2} diagrams at different activity levels are shown in Figures 13b–13e. The multiplicity region has a downward-oriented cusp shape. Consider the following reasoning behind this proposed shape. Recall that for the more active (fresh) catalyst with room temperature feeds, the critical y_{H2} value above which the high-rate state was encountered was bounded between 0 and 0.25. The less active (deactivated) pellet exposed to the same conditions exhibited only the low-rate state. On the other hand, when the deactivated catalyst was exposed to higher temperature feeds (43°C) this resulted in an observed critical y_{H2} value of 0.25–0.50. These observations suggest that the critical or extinction y_{H2} value is a decreasing function of the activity: the high-rate state is sustained over a wider y_{H2} range as the catalytic activity is increased. If one extrapolates this trend both to lower and higher activities, a branch of extinction points is established (labeled E in Figure 13). In addition, in the experiments performed at either activity level, the low-rate state was sustained even as y_{H2} was increased to 1: no ignition points were ever encountered. Thus, bifurcation diagram type (d) was observed. For a catalyst of a sufficiently high activity, it is anticipated that the low-rate state would not be sustained in a hydrogen-rich gas. This infers that an ignition from the low- to high-rate state would occur. A hypothesized branch of ignition points is provided in Figure 13 (labeled as I). At sufficiently high activity, a unique, mostly gas-filled, partially wetted pellet should result: the E and I branches coalesce at

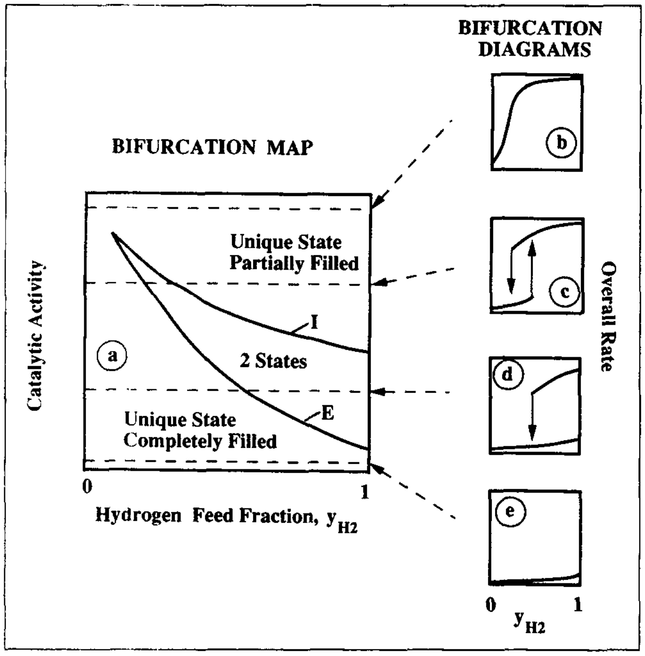


Figure 13. Proposed bifurcation features of the partially wetted catalytic pellet.

The bifurcation map (a) shows the region in the plane of catalytic activity and hydrogen feed fraction in which two observed states exist. (b)-(e) are the four qualitatively different rate vs. hydrogen feed fraction bifurcation diagrams at the four different activity levels in (a).

a cusp. Experimental construction of such a map, while challenging, could provide a rational means of locating operating condition regions in which pellet-scale hot spots are encountered. This was beyond the scope of this study.

Degree of external wetting

The feed liquid flow rate was fixed, as the dependence of the catalyst state on hydrogen feed fraction (y_{H2}) was established for the fresh and deactivated pellet. However, the degree of wetting or wetting efficiency (E_w) was not a constant. Rather, it was observed to be a sensitive function of the extent of reaction. In the low-rate state, E_w was nearly constant and equal to 0.5 (Figures 7b and 10b). A significant decrease in E_w was observed in shifting from the low- to high-rate state in the y_{H2} range in which both regimes existed. For example, for the fresh catalyst and $y_{H2} = 0.5$, the degree of wetting decreased from 0.5 in the low-rate state to 0.19 in the high-rate state. In the high-rate state, E_w was a decreasing function of y_{H2}. For the fresh catalyst, E_w varied from 0.2 to 0.16 as y_{H2} was varied from 0.25 to 1. For the deactivated catalyst, E_w varied from 0.3 to 0.2 as y_{H2} was varied from 0.5 to 1. These results show that accompanying the decrease in the extent of liquid filling was a corresponding decrease in E_w.

A dependence of the degree of external wetting on the extent of reaction was observed during α-methylstyrene (AMS) hydrogenation (to cumene) in a similar single-pellet experiment (Funk et al., 1991). In that study, a switch from a pure-hydrogen to pure-nitrogen gas resulted in an increase of up to 30% in E_w with all other conditions fixed, including the feed liquid flow rates. The liquid holdup was not measured in the AMS study. While appreciable pore emptying was unlikely because of the low volatilities of AMS and cumene, a link between external wetting and reaction was clearly established. In the current study, a 150% decrease in E_w (0.5 to 0.2) was observed between the low- and high-rate states.

Several factors can explain the link between wetting and reaction. The key factors in the cyclohexene system are most likely the high vaporization rate, or equivalently, liquid consumption rate encountered along the high-rate branch. Quite simply, a fraction of the generated heat of reaction is used to vaporize liquid within the pores of the pellet. This creates a large capillary driving force for liquid flow into the pellet, thus reducing its external flow down the pellet. Correspondingly, a decrease in the flow rate decreases the degree of coverage on the pellet surface (following Towell and Rothfield, 1966; Bentwich et al., 1976). Other factors contributing to the decrease in E_w are thermocapillary, vapor thrust and a reduced wettability of the rivulet on the dry surface. These factors were previously put forth by Funk et al. (1991) to explain the wetting-reaction link in the AMS system. The behavior of the pellet in the cyclohexene hydrogenation system during the extinction process following a gas-prefilled startup provides some evidence supporting the reduced wettability argument. After the H_2-He-filled pellet was contacted by the liquid rivulet for some time, a simultaneous increase (decrease) in the liquid holdup (center pellet temperature) occurred. These observations indicated that an extinction process was proceeding. However, only after appreciable filling of the pellet occurred (based on liquid holdup measurement), was there a corresponding increase in the width of the rivulet. This increase in wetting appeared to occur when the pellet void space in the vicinity of the nonwetted surface adjacent to the contact line became saturated with liquid.

Hydrogenation and disproportionation selectivity

The rates of hydrogenation (r_H) and disproportionation (r_D; per mole of cyclohexene) may be obtained from the experimentally measured formation rates of cyclohexane (r_C) and benzene (r_B) using the relations:

$$r_H = r_C - 2r_B \tag{2}$$

$$r_C = 3r_B \tag{3}$$

The hydrogenation selectivity, S_H, is given by:

$$S_H = \frac{r_H}{r_H + r_D} \tag{4}$$

Analytical limitations prevented the detection of benzene production for all conditions except along the high-rate state (Figures 8b and 11b). Using Eqs. 2-4, it is estimated that the hydrogenation selectivity (S_H) is bounded between 0.7 and 0.9 along the high-temperature state. This range is in line with the findings of Hanika and Stanek (1986) who found that disproportionation more likely occurred at higher temperatures. The reduction in hydrogenation selectivity under conditions, in which a hot, dry section of the pellet was sustained, points to a pressing issue in multiphase fixed-bed reactor operation. That is, the formation of hot spots within the reactor can lead to a reduction in desired product selectivity. The single-pellet data indicate that wetting plays an important role in the selectivity issue. The single-pellet approach should provide a means of identifying operating conditions in which vaporization can be exploited for rate enhancement, but for which detrimental selectivity losses are minimized.

Deactivation mechanisms

The mechanism leading to the observed decline in catalytic activity throughout the course of the study was not determined. The likely candidates are (i) irreversible peroxide-poisoning of the Pd and (ii) carbonaceous deposits on the Pd. There is some evidence for the former. Preliminary steady-state experiments were carried out without following the peroxide-removal step described earlier. This led to a rapid, complete deactivation of the pellet. Atomic absorption analysis of the deactivated pellet revealed an appreciable loss of Pd from the surface. Thus, one possibility is that the activated alumina pretreatment step did not remove all peroxides from the cyclohexene. Consequently, a slow deactivation occurred. Evidence for the formation of carbonaceous residue was observed during gas-phase cyclohexane hydrogenation on Pt/Al_2O_3 by Rebhan and Haensel (1988). The overall rate and activation energy declined with time, indicating that a coke layer had formed: the rate-limiting step became the diffusion of hydrogen through the layer. Such a phenomenon has also been put forth by Wieckowski et al. (1985) for ethylene hydrogenation on Pt catalyst. Unfortunately, in the current study, the possibility of coking could not be checked by, for example, attempting a high-temperature reduction because of temperature limitations (120°C) of the epoxy used in securing the glass pieces to the pellet.

Concluding Remarks

Thermokinetic interactions are well known to have a significant effect on catalyst performance in single-phase catalytic reaction systems. This study demonstrates that such interactions, when coupled with wetting and vaporization processes, can lead to significant increases in the overall rate. Previous studies of isothermal multiphase reactions have clearly shown that incomplete wetting of a catalytic pellet enables the limiting volatile reactant to be more rapidly supplied. If the catalyst is sufficiently active, this translates into an enhancement in the overall rate. If dewetting is induced within the catalyst pores by the generated heat of reaction, then the rate enhancement is more pronounced, as has been demonstrated for the case of cyclohexene hydrogenation. A factor of up to 20 increase in rate was observed for the same bulk conditions.

The magnitude of the rate enhancement phenomenon and the existence of steady-state multiplicity point out the need to account for phase transition and wetting effects during exothermic multiphase catalysis in the fixed-bed reactor. Not doing so could certainly lead to improper design and operation of the reactor. The confirmation that a hot spot can be sustained within a single partially wetted catalytic pellet underscores the importance of liquid distribution within the bed. The existence of partial wetting at sufficiently low liquid flow rates has been established in many studies of lab-scale trickle-beds. Lutran et al. (1992) have shown using an X-ray tomographic technique that single-pellet partial wetting is more likely to be encountered if the bed of particles is not prewetted; this is the so-called "filament flow regime." Partial wetting set the stage for single-pellet overheating and internal dewetting when carrying out an exothermic reaction. The consequence is the establishment of local hot spots within the bed. There is a definite need to link the pellet-scale phenomena demonstrated in this study to overall reactor performance.

Finally, an unraveling of the complex interactions between wetting, multiphase transport and reaction clearly demands the development and analysis of two-dimensional and possibly three-dimensional single-pellet models. Such models would permit a detailed check of some of the explanations of trends established in this study, for example, prediction of the intrapellet liquid distribution of considerable importance because of the wide differences in rates in the liquid- and gas-filled sections of the catalytic pellet. An additional challenge would be to include an analysis of the rivulet flow and wetting.

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Notation

C_{HL} = hydrogen solubility
D_{eH} = effective hydrogen liquid phase diffusivity
E_w = degree of wetting
m_L = liquid holdup
r_B = rate of benzene formation
r_c = rate of cyclohexane formation
r_d = rate of disproportionation
r_H = rate of hydrogenation
r_{obs} = observed rate of cyclohexane formation
R_p = pellet radius
S_H = hydrogenation selectivity
T_c = center pellet temperature
T_{fG} = gas feed temperature
T_{fL} = liquid feed temperature
T_{ns} = nonwetted surface temperature
y_{H2} = hydrogen feed gas mole fraction

Greek letters

ρ_p = apparent pellet density
Φ = Weisz-Prater modulus

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