A Novel Reactor System That Permits the Direct Determination of Deactivation Kinetics for a Heterogeneous Catalyst

L. W. JOSSENS AND E. E. PETERSEN

Department of Chemical Engineering, University of California, Berkeley, California 94720

This reactor system consists of a differential reactor and a single-pellet reactor both with external recycle of the inlet feed. The design and operation of these two reactors permit direct determination of the deactivation kinetics for a heterogeneous catalyst and a better value for the initial reaction rate. Direct determination of deactivation kinetics is not possible in systems operating at constant space velocity because the reaction mixture composition varies with time. For the system presented in this paper deactivation data are obtained at constant reaction mixture composition by varying the space velocity to compensate for catalyst deactivation. Feed rates, recycle rates, and reactor system volumes in our system are designed to minimize system response time which for this system is on the order of a few seconds. To demonstrate the operation of this novel reactor system, the fouling of a platinum catalyst was studied using a model reaction.

INTRODUCTION

Most studies on the deactivation of heterogeneous catalysts are difficult to analyze and interpret because they have been taken in differential reactors wherein the reaction mixture composition varies with time. In some cases the data have been taken in integral reactors wherein the reaction mixture composition varies in both time and space. In the apparatus described in this paper, data can be taken under conditions of constant temperature and constant reaction mixture composition in both time and space.

Data obtained at constant temperature and reaction mixture composition are particularly simple to interpret when the deactivation kinetics are separable; i.e., the separable form for the overall chemical reaction rate expression is composed of a reaction rate function multiplied by a deactivation function. Thus, by keeping the reaction mixture composition and the temperature constant, the variation in the rate of reaction is due solely to the deactivation process and is studied directly. The separability form has been noted previously in the literature; viz., Löwe (1) and Levenspiel (2).

Others have reported nonseparable deactivation kinetics; viz., Onal and Butt (3), Bakshi and Gavalas (4), and Fuentes and Figueras (5). Systems exhibiting nonseparable kinetics can be directly identified under conditions of constant reaction mixture composition in space and time. The interpretation and analysis of nonseparable deactivation kinetics remains complicated even when the reaction mixture remains constant.

A differential external recycle reactor serves to keep the reaction mixture constant in space. These kinds of reactors have been reviewed in the literature by Anderson (6) and Carberry and Butt (7). However, in the traditional differential recycle reactor the conversion changes as the heterogeneous catalyst deactivates, so that the catalyst experiences a time variation in the reaction mixture composition. To keep the conversion constant, the temperature can be increased or the flow rate decreased as the catalyst deactivates. The former would seriously complicate the analysis, whereas the latter serves to accomplish the desired mode of operation. That is, in the system to be described, the exit product concentration is continuously monitored in an infra-

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red cell and any deviations, including those owing to catalyst deactivation, are utilized as an error signal to change the inlet flow rate to keep the outlet composition at a constant predetermined level. The overall control function then is to decrease the flow rate as the catalyst deactivates to keep the conversion constant. Of course, any continuous monitoring device would serve the same function.

In a reacting system where the number of independent reactions is greater than one, maintaining a single product concentration at a constant value during a deactivation study does not ensure constant reaction mixture composition. This is because the selectivity of the catalyst can change with deactivation. Nevertheless, the differential recycle reactor operated at a constant product concentration offers important advantages in deactivation studies where selectivity is an important consideration.

Another serious problem in the study of deactivating catalysts is to establish an initial rate, presumably one corresponding to no deactivation, with which to compare the deactivated rates. In many studies reported in the literature the first experimental activity check is taken an hour or more after the catalyst is put on stream. Other points follow at spaced time intervals. The initial value of the rate is then obtained by extrapolating the first few points back to zero time. As will become apparent from the results presented, the activity of our system changed rapidly during the first few minutes on stream. Accordingly, to achieve a meaningful initial rate requires that the nominal residence time in the recycle reactor be of the order of a few seconds. This is, of course, accomplished by minimizing the reactor free volume and by using high reactant flow rates.

In addition to the differential recycle reactor, the single-pellet reactor (8) has proved useful in the study of solid heterogeneous catalyst deactivation. This experimental reactor was principally used to obtain insight into the mechanism of catalyst deactivation. The differential recycle reactor served to establish the deactivation kinetics. Inherent in the operation of a single-pellet reactor are product and reactant concentration gradients through the single pellet. Operating this reactor at constant bulk reaction mixture composition will therefore not decouple reaction and deactivation kinetics, but it will provide constant physical boundary conditions during the run to simplify the modeling of the results.

An experimental reactor ensemble containing both a single-pellet reactor and a differential reactor each with external recycle flow was developed to study the deactivation of bifunctional reforming catalysts. These reactors have a flow control loop to keep constant conversion and are designed to minimize free volume and to accommodate high feed rates. The intent of this report is to describe the experimental ensemble and to present sufficient deactivation data for a platinum reforming catalyst (0.3% Pt, 0.6% Cl on γ-alumina) to substantiate its performance. The dehydrogenation of methyl cyclohexane (MCH) to toluene was chosen as a model reforming reaction to test these reactors.

The data presented in this paper are a portion of a larger body of data obtained to isolate plausible deactivation mechanisms and determine deactivation kinetics for both Pt and Pt–Re reforming catalysts in the sulfided and unsulfided state. Results from this more comprehensive deactivation study will be presented in subsequent papers.

APPARATUS

Much of the discussion of the apparatus will be devoted to methods and design consideration needed to accomplish automatic flow rate control and small reactor volumes. Other features such as the physical configuration of the differential and single-pellet reactor will be discussed only in sufficient detail to permit an understanding of the operation. Lastly, details common to
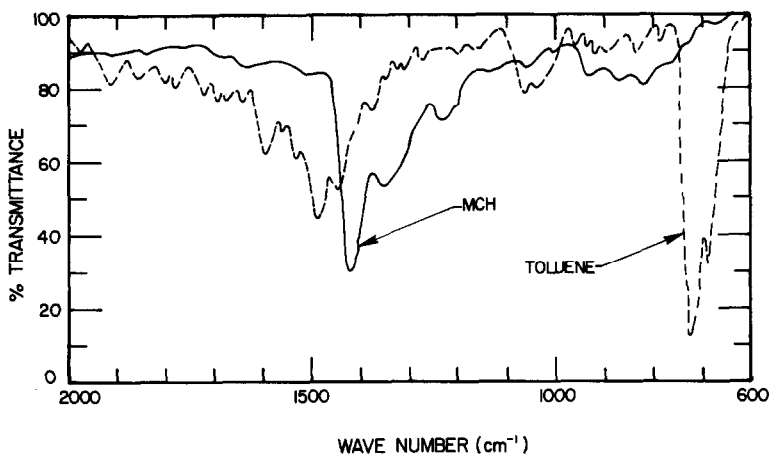
FIG. 1. Comparison of MCH and toluene infrared spectra.

both reactors such as chromatographic sampling will only be briefly addressed.

Flow Controller

There is a large difference between reactant and product infrared spectra shown in Fig. 1 for the model reforming reaction: dehydrogenation of MCH to toluene, over a 0.3% Pt, 0.6% Cl on γ-alumina catalyst. Selectivity for the production of toluene is in excess of 95% at 400 Torr hydrogen and 350°C, the nominal test conditions. This high selectivity to toluene permits continuous monitoring of the conversion by measuring the exit toluene concentration. A Beckman IR-8 spectrometer equipped with a 12-cm path length gas infrared cell is used as the monitor. The windows of the infrared cell are made from potassium bromide to assure transparency at low wavenumbers. During operation, the spectrometer is fixed at 726 wavenumbers. At this setting, transmittance versus toluene concentrations follows Beer's law and 50% transmittance is achieved with a toluene partial pressure of 4.4 Torr and a temperature of 70°C. An output signal proportional to the percent transmittance is directed from the ir spectrometer to a proportional–integral–differential flow controller (Honeywell R7355C). Control is by direct logic and the set point of this controller fixes the outlet

toluene concentration by passing its 4. to 20. milliA output signal to a 3 to 15 psig current–pressure transducer. The output pressure from this transducer operates a stainless-steel pneumatic control valve (Research Control Valve 735 ATC with an "M" trim).

The action of this valve compensates for decreased catalytic activity by decreasing the reaction mixture inlet flow rate. In the fully open position, this valve will nominally deliver a flow of 3. liters/min (20°C and 1. atm) at 2.7 psi pressure drop across the valve. Nominally, the reactant gas mixture is comprised of 40 Torr partial pressure MCH, 380 Torr hydrogen and 340 Torr helium.

Reaction Stream

Hydrogen-to-helium ratio in the inlet reactant feed is set by mixing valves using ultra-high-purity hydrogen (+99.999%) and distilled helium (+99.995%). Constant inlet reactant feed concentration is achieved by saturating either the hydrogen or helium inlet stream with reactants in a packed column 60 cm long and 5 cm in diameter. The column is operated countercurrently with a liquid reactant recycle stream. A large recirculating temperature-controlled water bath surrounds the packed column, and both inlet gas and the recycle stream

are thermally equilibrated with the water before entering the packed column.

Reactors

Overall, there are a number of common construction features in the gradientless and single-pellet reactors. Both reactors have external recycling of the inlet feed, and are constructed with similar countercurrent heat exchangers. In addition, both reactors have separate isolation valves which allow them to share the common conversion control system and the same inlet reactant feed make-up system.

Countercurrent heat exchangers are needed to permit high-temperature reactions to be studied and to maintain low temperatures in the recycle pump. The exchangers form the bodies of reactors. Each exchanger is composed of three concentric stainless-steel tubes. A series of equally spaced slots are milled in the axial direction around the outside perimeter of the center two tubes. These slots allow countercurrent heat transfer between the reactor inlet and outlet gases. After slotting, the tube bundle and appropriate flow distribution plenums are welded into a single unit. External recycling of the inlet feed is provided by a large integral metal bellow pump. Recycle rates are in excess of 10 to 1. Recirculating flow is directed upward from the pump through the outer ring of slots and then returned to the pump through the inner ring of slots.

The total pressure in the catalyst bed remains essentially constant even though the flow stream to the reactor decreases as the catalyst deactivates. This nearly constant pressure results because the internal recirculation rate is very large compared to the inlet flow rate.

The reaction zone of the differential recycle reactor, Fig. 2, is a fixed catalytic bed with a 3.8-cm² cross section. Here, catalyst is retained between two sintered stainless-steel woven wire mesh screens. The upper and lower screens have a 98% capture probability for dry particle of 11. and 3.5
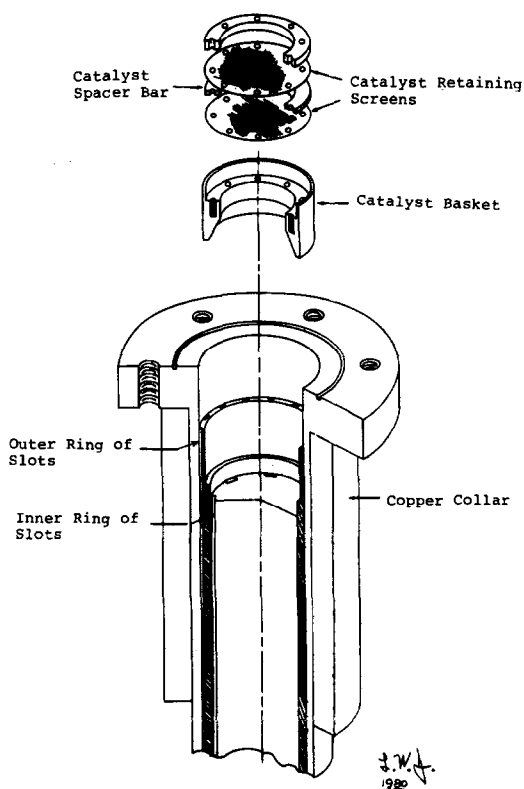

FIG. 2. Assembly of the differential recycle reactor.

μm in diameter, respectively. Catalyst loadings between 0.015 to 1.25 g are obtainable. Flow through the bed is directed downward. At a catalyst loading of 50 mg, there is an 8 Torr pressure drop across the bed.

The reaction zone of the single-pellet reactor is depicted in Fig. 3. A review of single-pellet reactor design and analysis is given in Refs. (8, 9). Fabrication of a single pellet in this study is accomplished by pressing catalyst particles, nominally 54 μm in diameter into a removable titanium pellet holder at 450 atm and 25°C. Titanium closely matches the thermal expansion characteristics of γ-alumina and therefore greatly facilitates pellet integrity at reaction conditions.

Encircling the reaction zone of each reactor is a thick annular copper collar which provides a solid thermal buffer for thermal control of these reactors. Control is

achieved by a millivolt signal from a thermocouple placed in close proximity to the active catalyst in each reactor.

Analysis of Reaction Mixture Compositions

Figure 4 shows schematically the gas chromatographic sampling system employed to obtain inlet, outlet, and center plane gas samples. This system is composed of two 10-port sampling valves and one 6-port switching valve. A 10-ft-long, $\frac{1}{8}$-in. diameter column of 10% TCEPE on chromasorb "W" is used to separate the various components in each sample.

One ten-port sampling valve is used to sample both inlet reactant and outlet product gas streams. The other ten-port valve is used to extract a gas sample from the single pellet center plane. Two sample loops are built into this sample valve. The smaller loop is a sacrificial loop used to purge the connections from the single-pellet reactor to the sampling valve automatically. Sampling of the center plane is accomplished by isolating the center plane sampling valve with the six-port switching valve followed by this series of steps: evacuate both sample loops, trap a gas sample in each sample loop, reestablish carrier flow to the center plane sampling valve, trap an outlet product gas sample in the inlet/outlet sampling valve, inject the major center plane sample into the carrier gas, and finally reestablish flow in the inlet/outlet sampling valve. This procedure yields the simultaneous collection of an outlet and a purged center plane sample.

OPERATIONS

Either reactor in the dual reactor ensemble can be used to determine initial reaction rate kinetics or deactivation rate kinetics and it is important to discuss operational characteristic and physical limitations of each reactor.

Reactants are introduced to the appropriate reactor by switching from a pure hydrogen feed to a stabilized reactant feed stream. The inlet reactant feed is a mixture of hydrogen, helium, and a single reactant. Inlet partial pressures vary between 10 and 50 Torr MCH and between 100 and 770 Torr hydrogen. Helium is added to the inlet reactant feed as a diluent so that the total pressure in the reactor is always slightly above atmospheric. Typical inlet reactant flow rates for the differential recycle and single-pellet reactors are, respectively, 2.5 and 0.6 liter/min (25°C and 1 atm pressure).

Normally these reactors are operated at moderate conversions, about 30% total or approximately 3% per pass. Catalyst loadings consistent with the above inlet reactant flow conditions are 30 and 48 mg, respectively, for the differential recycle and sin-
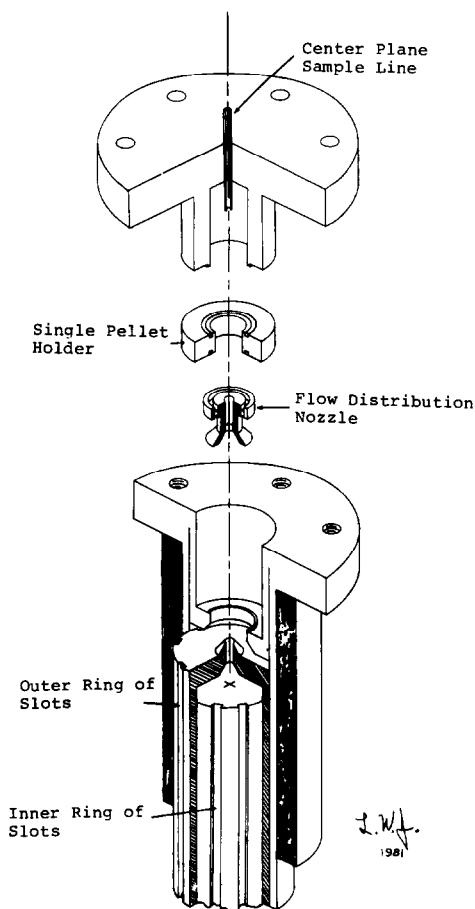

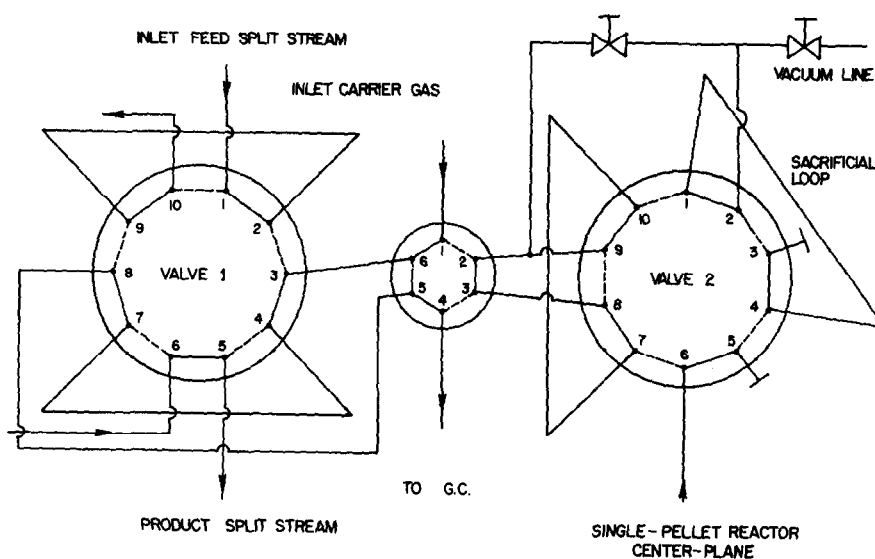FIG. 3. Assembly of the single-pellet recycle reactor.

FIG. 4. Schematic of the gas chromatographic sampling system.

gle-pellet reactors operating at 350°C and 400 Torr hydrogen partial pressure.

Deactivation kinetics are determined by allowing the catalyst to deactivate at constant temperature and product concentration. Continuous operation at 500°C is possible. In practice, the inlet flow can be varied automatically up to a factor of 20., and the maximum duration of an experiment is about 2 days. Reaction rates are determined from the product of the exit flow rate and exit product concentration. The latter is determined using a gas chromatograph.

When the differential recycle reactor is used, the initial sample of the exit product stream is taken 15 sec after introducing reactant feed. This time is in excess of the minimum time required to obtain 95% of the steady-state product concentration. The product time constant for this system is larger than the reactant time constant and therefore the controlling time constant (See Appendix).

Similarly, for the single-pellet reactor, the initial gas samples drawn from the center plane chamber and exit product stream are taken 45 sec after switching to reactant feed. This time span is sufficient to obtain a

reasonable steady state in the bulk (Appendix) and greater than the center plane time constant. A center plane time constant is defined somewhat arbitrarily as the time required to obtain 95% of the inlet reactant concentration in the single-pellet center plane. The latter is determined at operating conditions with an inactive single pellet, and it depends upon both the single-pellet nominal residence time and the diffusion time constant through the single pellet. A value of 25 sec was measured for the center plane time constant.

Reactor Performance Verification

This section is devoted to the discussion of the various steps taken to assure that the measured reaction rates are not masked by mass transfer limitations. The test conditions chosen are 350°C and 400 Torr hydrogen: conditions that highly favor the production of toluene from MCH and suppress the reverse reaction.

Prior to each experimental run a "standard" catalyst pretreatment procedure is followed *in situ*. Fresh catalyst is initially heated from room temperature to 500°C in a flowing stream of helium, calcined for 4 hr in a flowing stream of gas containing 100

Torr oxygen and the balance nitrogen, cooled for 2 hr to 360°C in a flowing stream of helium, and finally reduced in a flowing stream of hydrogen at 360°C for 15 hr.

The catalyst particles used in the differential recycle reactor were nominally 88 μm in diameter, had an average micropore diameter of 91 Å, a pore volume of 0.588 cm³/g, an apparent density of 1.2 g/cm³, and a surface area of 211 m²/g. The extent of intraparticle mass transfer limitations is measured by the deviation of the catalyst effectiveness factor from unity. A value for reaction rate without intraparticle mass transfer limitations is obtained from the traditional set of experiments where the nominal particle size is varied. The effectiveness factor for particles used in deactivation experiments is approximately 0.95. Although a value closer to unity could be obtained with smaller particles, the pressure drop would increase greatly through the catalyst bed. It should be noted that the dehydrogenation reaction is very fast and extremely small particles are required to eliminate internal mass transfer influence. The sensitivity of catalyst effectiveness factor to particle size is shown in Fig. 5. The fitted curve is obtained by assuming spherical pellet geometry, first-order kinetics in MCH, and a negative 0.33 power for toluene inhibition.

Interparticle thermal and mass transfer effects were determined by varying the recycle rates. Very little difference in observed initial rates are noted when the recycle rate is varied over a factor of 2.

Intrinsic initial rates determined with the single-pellet reactor are in good agreement (within 5%) with those obtained using the differential recycle reactor. This demonstrates that the thermal and mass transfer resistance between the bulk reactant flow and the single-pellet surface is minimal.

Intraparticle heat transfer limitations are not significant in either reactor system. The effect of coupled intraparticle heat and mass transfer on observed reaction rates has been studied by Tinkler and Metzner (10), Weisz and Hicks (11), and Petersen
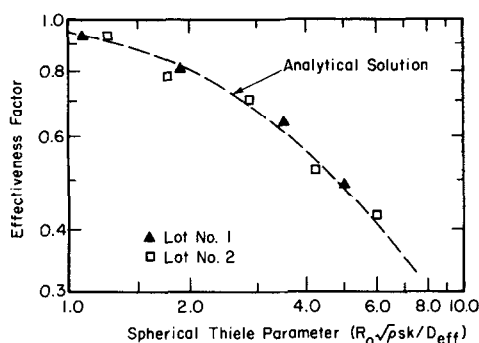

FIG. 5. Effect of particle size on observed initial MCH reaction rates, evaluated at constant bulk toluene concentration, R_0 = particle radius, ρSk = pseudohomogeneous first-order rate constant.

(12). These studies were conducted for both spherical and slab pellets over a wide range of Thiele parameters and are therefore applicable to both the differential recycle and the single-pellet reactor. The effect of heat transfer limitations in both systems depend upon the magnitude of the dimensionless variable, δ, defined as

$$\delta \equiv \frac{\Delta E(-\Delta H)D_{\text{eff}}C_0}{R_g T_0^2 \lambda},$$

ΔE = energy of activation, 17 Kcal gmole⁻¹

ΔH = heat of reaction, 51.4 Kcal gmole⁻¹

D_{eff} = effective diffusion coefficient, 0.126 cm² sec⁻¹

C_0 = bulk MCH concentration, 6 × 10⁻⁷ gmole cm⁻³

R_g = gas constant

T_0 = absolute temperature, 625 K

γ = thermal conductivity, 6 × 10⁻⁴ cal cm⁻¹ sec⁻¹ K⁻¹.

For the dehydrogenation of MCH, the numerical value of δ is 0.14 which corresponds to less than a 3% reduction in observed reaction rate. This effect is even smaller for the single-pellet reactor because both the center plane surface and the exterior pellet surface are heated.

RESULTS

Both initial rate kinetics and deactivation kinetics are determined from a deactivation
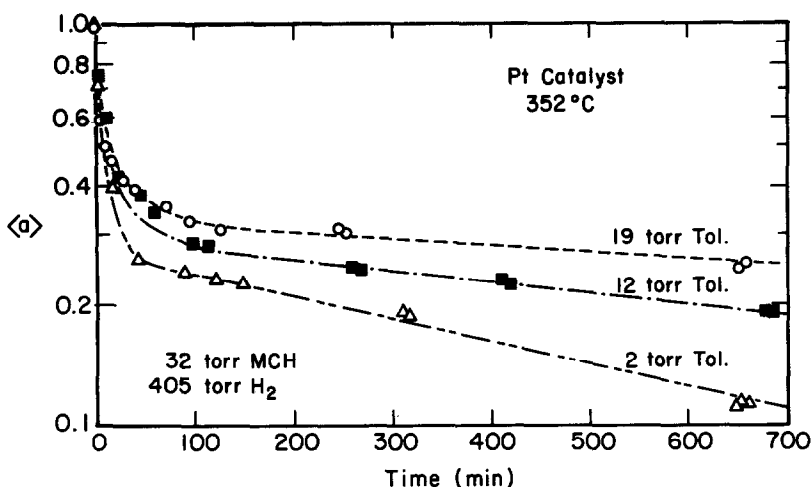
FIG. 6. Toluene deactivation kinetics at constant reactant conditions.

study. The experimental utility of this reactor system can be demonstrated by presenting typical results from such a study. As mentioned earlier, the dehydrogenation of MCH to toluene was chosen as the study reaction.

This reaction is described by first-order kinetics in MCH and by product inhibition. The effect of product concentration on initial rate can be expressed empirically as toluene concentration to the −0.33 power. Reaction conditions are as follows: 350°C, 400 Torr hydrogen partial pressure and low MCH concentration (6×10^{-7} moles/cm³, 23 Torr).

Deactivation studies are conducted at constant temperature and constant reaction mixture composition by use of the apparatus described above. Typical deactivation results are shown in Fig. 6 in which catalytic activity is plotted versus time. The catalytic activity, $\langle a \rangle$, is defined as the ratio of reaction rate R at a specified time to the initial reaction rate, R_0, where the initial reaction rate is the rate as determined 15 sec after switching between pure hydrogen feed to reactant feed. Therefore,

$$\langle a \rangle = R/R_0. \qquad (1)$$

In Fig. 6, $\langle a \rangle$ versus time curves are presented for three different toluene con-

centrations; MCH concentration is held constant throughout each run and approximately constant for all three runs. As shown in this figure, each deactivation curve exhibits a rapid deactivation for about the first 40 min, then followed by a much slower deactivation. During approximately the first 20 min there appear to be only small differences in behavior with varying toluene concentration. In the long-term deactivation period, the logarithm of activity, log $\langle a \rangle$, appears to be approximately a linear function of time and the experiments conducted at lower toluene concentrations show larger deactivation rates. Product inhibition makes the absolute deactivation rates even larger at small toluene concentrations than for larger toluene concentrations because the respective initial rates are greater.

Use of a single-pellet reactor gives additional insight into the mechanism of deactivation during the MCH to toluene model reaction. Plotted in Fig. 7 is the observed relative reaction rate versus reduced center plane concentration for this Pt–alumina single pellet. Reduced center plane concentration is defined as

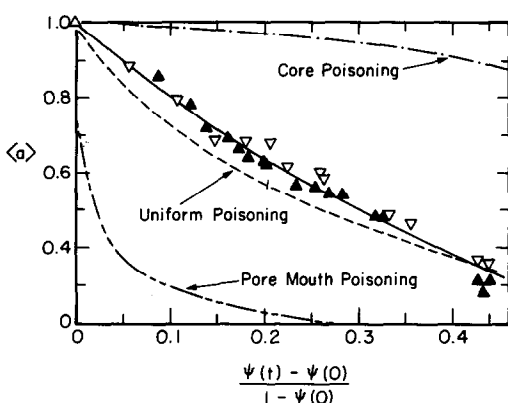$$\Phi \equiv \frac{\Psi(t) - \Psi(0)}{1 - \Psi(0)},$$

FIG. 7. Diagnostic deactivation curves evaluated at 405 Torr hydrogen and 352°C.

where $\Psi(t)$ is the ratio of center plane reactant concentration to bulk reactant concentration at time $= t$. In addition to the experimentally determined poisoning curve, the ideal poisoning curves for pore mouth, uniform poisoning, and core poisoning are also presented (8). These curves are determined using first-order MCH kinetics and product inhibition expressed as toluene concentration to the negative 0.33 power. Data for the experimental self-fouling curve are generated from two different pellets, each having a nominal thickness of 0.1 cm and a catalytic effectiveness factor of 0.21.

The time scale of events presented in Fig. 7 is very nonlinear. A relative reaction rate of 0.77 is achieved in 20 min of real time, while some 30 hr are required to obtain the remainder of the curve.

Figure 7 indicates that there is a preference for the deactivation of the center of the pellet during the short-term deactivation period. This is usually attributed to product poisoning. As shown in Fig. 7, the experimental curve lies closer to the uniform poisoning case, suggesting that during this period both MCH and toluene contribute to the fouling. This short-term poisoning is completely reversible and essentially independent of the overall rate of reaction.

Values of the relative reaction rate and reduced center plane concentration taken

during the long-term deactivation domain show that the experimental curve approaches and intercepts the ideal uniform poisoning curve. This response is due to the proportionality between deactivation rate and reaction rate noted in the differential recycle reactor experiments during the long-term deactivation period (13). Initial intrinsic reaction rates and therefore deactivation rates are greater toward the exterior of the pellet. This is characteristic of pore mouth poisoning and the experimental poisoning curve crosses the uniform poisoning line.

CONCLUSIONS

A reactor ensemble has been described which operates at constant temperature and maintains constant product and reactant concentrations in space and time. Constant concentrations are maintained by coupling an in-line infrared spectrometer to an inlet flow control loop. The dual reactor system of a differential recycle and a single-pellet reactor gives an investigator complementary sets of data with which to study both kinetics and mechanisms of deactivation. Constructing these reactors in a manner to minimize reactor dead volume allows the investigation of deactivation phenomena at early times in a catalyst's life.

APPENDIX

An estimate of the minimum time span required before initial sampling of the exit gas stream is determined from the solution of the transient material balance written for a step change between a pure hydrogen feed to an inlet reactant feed in an ideal CSTR. First-order kinetics in reactants are assumed for this estimation. There are two solutions, one each for the reactant and product. The reactants differential material balance is given below:

$$\frac{V dC_m}{dt} = F(C_{MO} - C_M) - WkC_M \quad (A1)$$

C_M exit MCH concentration from the reactor, gmoles/cm³

C_{MO} MCH concentration in the feed, gmoles cm⁻³

C_{MSS} exit MCH concentration from the reactor at steady state, gmoles cm⁻³

C_T toluene concentration in the reactor, gmoles cm⁻³

W weight of catalyst times the catalyst effectiveness factor, g

k first-order rate constant, cm³ sec⁻¹ g catalyst⁻¹

F reactant volumetric flow rate, cm³ sec⁻¹

t real time, sec

V reactor volume cm³.

Substituting the definitions

$$\alpha \equiv Wk/F$$
$$\tau \equiv tF/V$$
$$\psi \equiv C_M/C_{MO}$$
$$\theta \equiv C_T/C_{MO} \tag{A2}$$

into Eq. (A1) and integrating with the boundary condition

$$C_M = 0 \qquad \text{at } t = 0 \tag{A3}$$

yields

$$\psi = \left[\frac{1}{1 + \alpha}\right][1 - exp(-(1 + \alpha)\tau)]. \tag{A4}$$

A differential material balance for the product is

$$\frac{VdC_T}{dt} = -FC_T + WkC_m. \tag{A5}$$

Substituting Eqs. (2) and (4) yields

$$\frac{d\theta}{dt} = -\theta + \frac{\alpha}{1 + \alpha}$$
$$[1 - \exp(-(1 + \alpha)\tau)]. \tag{A6}$$

Integrating Eq. (6), subject to the boundary condition that $\theta = 0$ at $t = 0$, yields

$$\theta = \left(\frac{\alpha}{1 + \alpha}\right)\left[1 - \frac{\alpha + 1}{\alpha}\exp(-\tau) + \frac{1}{\alpha}\exp(-(1 + \alpha)\tau)\right]. \tag{A7}$$

In deriving these results, first-order MCH kinetics and no deactivation are assumed. The no-deactivation assumption is justified in this case because the time required to deactive the catalyst to half-activity is in far excess of the nominal residence time. Nominal residence time is, of course, the normalizing factor for real time in the definition of τ. Typical nominal residence times are 1.0 and 3.0 sec, respectively, for the differential recycle and single-pellet reactor.

Overall conversion of MCH to toluene in our experiments is about 0.3; therefore:

$$\theta_{SS} = \left(\frac{\alpha}{1 + \alpha}\right) = 0.3$$

or

$$\alpha = 0.43.$$

At this level of conversion the value of τ needed to obtain 95% of steady-state toluene concentration is 4.1 while the required value of τ to obtain 95% of steady-state MCH concentration is 2.1. The limiting time response is for the production of toluene and in real time this corresponds to 4.1 and 12.3 sec, respectively, for the differential and single pellet reactors.

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