NONUNIFORM ACTIVITY DISTRIBUTION IN CATALYST PARTICLES: BENZENE HYDROGENATION ON SUPPORTED NICKEL IN A SINGLE PELLET DIFFUSION REACTOR

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Abstract—A single pellet diffusion reactor (SPDR) of new design has been used to investigate the influence of nonuniform distributions of active ingredient on the Ni-catalyzed hydrogenation of benzene. Five different distributions, ranging from preferential shell-loading to uniform to preferential core loading, have been studied under isothermal conditions. Analysis of results has been carried out using a simple one-dimensional diffusion/reaction analysis, which the configuration of the SPDR is set to mimic. The rate of the reaction follows an Eley-Rideal model, effectively positive fractional-order under the experimental conditions, for which kinetics the nonuniform distribution problem has not been studied experimentally before. Preferential shell-loading yields the highest catalytic effectiveness but because of the complex interactions between the reaction kinetics and the activity profiles within the pellets, there is no simple relationship between diffusion lengths and effectiveness even for large values of the Thiele modulus.

INTRODUCTION AND BACKGROUND
It has been known for some time that nonuniform intraparticle distribution of activity (i.e., active ingredient) has a significant effect on the performance of granular catalysts, and can provide a means for optimizing catalyst performance (Dougherty and Verykios, 1987; Gavrilidis et al., 1993). Due to the interactions between chemical kinetics and physical transport processes, a spatially nonuniform deposition of the catalytically active material in a support matrix can often lead to improved performance — in terms of effectiveness or selectivity, or in resistance to deactivation, or in prevention of thermal runaway — compared to the uniform case. As might be expected, effective strategies are highly dependent upon specific reaction system characteristics such as reaction kinetics, diffusional resistance, influence of deactivation and thermal properties. Most of the literature dealing with nonuniform catalysts consists of theoretical studies, although more recently some experimental studies have appeared, as detailed below. Considerable work has also been done in the related area of preparation of nonuniform catalysts by use of competitive sorbents and control of impregnation conditions.

Theory for first-order isothermal reactions
Linear kinetics have provided the favorite playground for theoretical studies. It is easy to envision that when a single first-order reaction takes place in a nonuniform pellet with activity concentrated in the outer shell there will be a higher overall effectiveness than in a uniform pellet, since this type of profile best counteracts any diffusional resistance. This has been analyzed by Corbett and Luss (1974) for monofunctional and Dadyburjor (1982) for bifunctional catalysts.

Selectivity problems are of particular interest. Pavlou and Vayenas (1990) have developed a general optimization procedure for solving such problems in reaction networks with arbitrary numbers of chemical species and arbitrary kinetics, applicable to both isothermal and nonisothermal systems. For the important case of sequential selectivity (A ---, B ~ C) with B the desired product in a diffusion-limited pellet, Corbett and Luss showed that the selectivity (ratio of the rates of consumption of A and B) is the same for all activity profiles at the low and high limits of Thiele modulus, \( \phi \). Selectivity is affected only in the intermediate diffusion regime, where the most egg-shell-like profile has the highest selectivity because of the proximity of the active ingredient to the highest concentration of A. Shadman-Yazdi and Petersen (1972) reached the same conclusion for power-law activity profiles which increase towards the surface. Some studies of intrareactor catalyst composition gradients for bifunctional catalysts, which provide a rough analog to the intraparticle problem, have been reported by Gunn and Thomas (1965) and Gunn (1967) for selectivity in several complex reaction sequences involving reversible and parallel steps.

Nonisothermal reactions
In cases with high heats of reaction and high Thiele modulus, significant intraparticle temperature gradients may occur. This has been investigated in a thorough study by Juang and Weng (1983), who considered polynomial distributions for surface-active...
and core-active, as well as uniform, catalysts. Maximum effectiveness increases with heat build-up inside the particle; at low Thiele modulus a concave profile (core-active) of active ingredient gives highest effectiveness because of higher intraparticle temperatures, while at high values of the modulus the convex distribution is best (as in the isothermal case). Juang and Weng also examined selectivity in both series and parallel reaction systems. As has been shown, selectivity in either case is strongly influenced by the relative magnitude of the activation energies for the two steps (Butt, 1966). For either series or parallel reactions the selectivity is independent of the activity gradient and relative activation energies at low values of the Thiele modulus; for the important case of series reaction selectivity at high Thiele modulus, highest selectivity is obtained with a convex distribution profile and when \( E_1 \) (activation energy for the first step) is greater than \( E_2 \). A large number of other cases are also treated in the work of Juang and Weng.

**Theory for Langmuir-Hinshelwood kinetics**

No great deviations from the observed patterns above are seen except when the reactant is strongly adsorbed on the catalyst, in which case the overall rate can exhibit negative-order behavior. Effectiveness factors for negative-order reactions demonstrate maxima greater than unity at intermediate values of the Thiele modulus, thus one might expect such reactions to be expedited in catalyst particles with subsurface active zones. This case is of practical importance because the kinetics of CO oxidation follow such a form, and was first studied by Becker and Wei (1977) and then extensively by Morbidelli and coworkers (1982, 1986). For single particles the most important result of Morbidelli et al. was that the optimal activity distribution is a Dirac \( \delta \) function in cases both with and without external mass transfer resistance. In practical application, the \( \delta \) performance is well-approximated by a finite square wave centered at a specified position, \( s \). A width of up to 5% of pellet dimension can be tolerated with no deviation from optimal performance, with \( s \) moving from the core to the surface with increasing values of \( \phi \). Extension of the analysis to the isothermal plug flow reactor (PFR), uniformly packed with \( \delta \) distribution particles, showed the existence of multiple steady states with the reactor multiplicity and stability intimately related to that of the first axial layer of particles. The case where pellet activity distribution varied with bed position, though impractical to carry out, yielded better performance (maximization of outlet conversion) than when all pellets had the same distribution.

**Some experimental studies**

At present there is no comprehensive review available describing procedures in detail for the preparation of nonuniform catalyst particles, and a treatment of this is beyond the scope of our interests here. However, Hartman and Prater (1957) and Vincent and Merrill (1974) describe some general procedures and a (incomplete) list of specific cases would include work of Shyr and Ernst (1980) on Pt in Pt/Al\(_2\)O\(_3\), Rice and Hahn (1984) on Ni in Ni/Al\(_2\)O\(_3\) and Pavlou and Vayenas (1990) on Pt and Ag in Pt/Al\(_2\)O\(_3\) and Ag/Al\(_2\)O\(_3\).

To test how well experimentally prepared nonuniform pellets approximate the performance predicted from idealized distributions, Brunovskova and coworkers (1987, 1989) have developed a procedure for estimating activity distribution from experimental kinetic data. This was tested using a single pellet reactor with ethylene hydrogenation over Pt/Al\(_2\)O\(_3\) as a model reaction; reasonable agreement was found between theory and experimental evidence. However, pitfalls may exist. Ostrovskii et al. (1989) prepared four distributions of Pt/Al\(_2\)O\(_3\) (uniform, outer, middle, inner) using impregnation with competitive sorbates. When these catalysts were used for cyclohexene dehydrogenation it was observed that the shell-active catalyst with no diffusion resistance exhibited different kinetics from the others even though there was no discernible difference in Pt dispersion. On the face of it there does not seem to be any particular reason why reaction kinetics might vary with catalyst distribution, but the point has not been investigated.

Wu et al. (1988) have studied in some detail the effect of near-\( \delta \) distributions in nonisothermal pellets for ethylene hydrogenation on Pd/Al\(_2\)O\(_3\) (region of first-order kinetics in hydrogen) and CO methanation on Ni/Al\(_2\)O\(_3\) (region of bimolecular Langmuir–Hinshelwood kinetics). They used a modified single pellet reactor, with catalyst \( \delta \)-widths of 0.1 (Pd/Al\(_2\)O\(_3\)) and 0.22 (Ni/Al\(_2\)O\(_3\)) relative to total pellet length. It was concluded from experiments that an optimal step location existed for any given set of reaction conditions for ethylene hydrogenation; effectiveness factors > 1 were observed, and the optimal \( \delta \) location moved toward the catalyst surface with increasing \( \phi \), approaching a shell-like profile. For small values of \( \phi \) all activity profiles yield the same effectiveness; overall, in the absence of deactivation the optimal step location and catalyst effectiveness were reasonably predicted from theory. The bimolecular methanation reaction is much more complex; a detailed discussion is given by Wu et al. (1990).

Finally, for CO oxidation Lee and Varma (1988) carried out isothermal fixed-bed experiments for Pt/Al\(_2\)O\(_3\) catalysts with four \( \delta \)-like distributions within the particles (but the same distribution throughout the bed). Two steady states were observed for all of the catalysts, however the activity distribution clearly could be optimized since a catalyst with Pt \( \delta \) centered at \( s = 0.65 \) gave the widest range of high conversion regime. A dual-zone configuration \( (s = 1 \text{ and } s = 0.27) \) was found to provide a third steady state with superior conversion to any of the single-zone versions.

**The single pellet diffusion reactor**

The single pellet diffusion reactor (SPDPR) is a system for studying reactions under the influence of transport effects and may be thought of as a "specified
Nonuniform activity distribution in catalyst particles

gradient" reactor at the opposite end of the spectrum from the class of "gradientless" reactors. It is central to the methodology involved in the present work and has been used in some previous studies as mentioned above.

In isothermal operation the ideal SPDR is designed to mimic the Thiele-Zeldovich model for diffusion and reaction in a porous catalyst particle, and the first significant application appears to have been that of Roiter et al. (1950). The original concept has been refined considerably in design and operation for isothermal systems by Petersen and coworkers (1968, 1972, 1984) and for nonisothermal systems by Butt and coworkers (1967, 1972, 1977), Hughes and Koh (1970) and Trimm et al. (1974).

To fit the isothermal Thiele-Zeldovich model the catalyst pellet in the SPDR plays the role of a "half-slab", with exposure to a bulk reactive mixture on one face and with the other face exposed to a closed chamber (center-plane chamber) where the reaction mixture composition can be measured. Thence, experimentally measured surface and center-plane concentrations are interpreted in terms of the solutions to the appropriate conservation equations, allowing kinetic models to be tested and kinetic and transport parameters determined. In nonisothermal SPDR's temperature gradients are measured instead of concentration gradients by use of thermocouples embedded in the catalyst particle and/or suspended in the interphase region. As in the isothermal case, these profiles can then be interpreted via solutions to the conservation equations and used to obtain kinetic, transport and thermal properties. In most designs intraparticle temperatures can be measured at several locations, so that a little more detail concerning the nature of the gradient is provided than by the surface-center-plane ∆C of the isothermal design.

OBJECTIVES

In the present study, a SPDR of new design has been used to investigate the effects of nonuniform distributions on catalysis of benzene hydrogenation on Ni/Kieselguhr. The kinetics of this reaction are well-correlated by an Eley-Rideal-type rate equation (Kehoe and Butt, 1972; Marangozis et al., 1979), a form that has not been investigated before in such application. We are concerned primarily with the relationship between the nature of the distribution and catalytic effectiveness, both observed and predicted. Experiments have been conducted to compare the steady-state performances of five power-law activity profiles at different Thiele moduli: uniform, first-order shell-active, first-order core-active, second-order shell-active and second-order core-active. These are shown schematically in Fig. 1.

EXPERIMENTAL

General

A simplified schematic diagram of the flow system employed is given in Fig. 2. Hydrogen and nitrogen feeds were each treated with a set of oxygen (Alltech Oxytrap™) and moisture traps (4A molecular sieves). Hydrogen flow was controlled by a Brooks 5850 thermal mass flow controller (0–500 SCCM), and nitrogen flow monitored by a Brooks 5810 mass flow meter and manually controlled by a Nupro fine metering valve (0–500 SCCM). Benzene (liquid) was fed at rates up to 400 ml/h via an Isco LC-5000 syringe pump, and this feed mixed and vaporized with hydrogen in packed-bed vaporizer maintained at 150°C. The feed mixture was then passed through a final MnO-4A oxygen–water trap (not shown in the figure) before entering the reactor. An extensive series of step-function nitrogen–helium tests was carried out to ensure that there was complete mixing and no bypassing of the catalyst pellet surface under experimental conditions. Details of this are give by Au (1992).

Most experiments with the SPDR were conducted at an inlet benzene mol fraction of 0.05 and a total vapor feed rate (C₆H₆ + H₂) of 400 SCCM. Reaction mixture compositions downstream of the reactor were measured via direct gas sampling into an on-line GC, while reactor center-plane compositions (see below) were determined from gas syringe samples manually withdrawn from the reactor and manually injected into the GC. A temperature range from 60 to 180°C and pressures of 1.3 and 5 atm were investigated. Catalyst pellets of 0.15, 0.225 and 0.3 g were employed. A number of experiments was also conducted using a small fixed-bed reactor in the same flow system in order to verify the kinetic model. These were carried out at the same conditions as the SPDR work.

![Fig. 1. Schematic diagram of experimental catalyst distributions.](image-url)
with 0.1 g powdered catalyst but with a variable flow rate range in order to maintain low conversions with benzene feed mol fractions from 0.02 to 0.10.

In a typical procedure with the SPDR the catalyst was first purged with N\textsubscript{2} at 50 SCCM for 1 h at room temperature, then heated at 1 °C/min to 180°C. At this point N\textsubscript{2} flow was increased to 400 SCCM and the temperature/flow maintained for 4 h, after which the flow was switched to H\textsubscript{2} at 400 SCCM, 180°C, which was maintained for 12 h. The reactor was then isolated from the flow system and the assembly brought to the desired reaction temperature, normally over a period of about 4 h. During this time the H\textsubscript{2}–benzene feed was allowed to stabilize at the desired composition, temperature and pressure while flowing through an external by-pass line. After equilibration of these conditions a run was started by introducing feed into the reactor and closing the by-pass line. Steady state, as indicated by time-invariant downstream composition based on samples taken at 1 h intervals, normally required 2–4 h of operation, after which a corresponding reactor center-plane sample was removed for analysis. At the end of a run the system was purged with nitrogen at room temperature and pressure overnight.

**Reagents**

All gases used were of UHP grade. Nitrogen was used for catalyst pretreatment, pressure testing, and as a purge gas. Hydrogen was used for pretreatment, in the reaction experiments, and as the GC carrier gas. In addition to the purification traps described for the flow system, an oxygen/moisture trap (MnO and CaSO\textsubscript{4}) was used for the hydrogen carrier gas stream.

The benzene used was obtained from J. T. Baker Co. (ACS reagent grade), 99% minimum assay C\textsubscript{6}H\textsubscript{6} with maximum limits of 0.05% H\textsubscript{2}O, 0.005% sulfur compounds and 1 ppm thiophene. In operation, the main difficulty from benzene impurities came from H\textsubscript{2}O; this problem was eliminated by installing a MnO-4A trap upstream of the reactor.

**Catalyst and catalyst pellet preparation**

The active catalyst for the hydrogenation reaction was Ni-0104P supplied by Engelhard Corp., a powder of 60% nickel supported on kieselguhr (reduced and stabilized). Particle size of the powder was 75% < 45 μm, BET area of 170 m\textsuperscript{2}/g, and total pore volume (up to 10\textsuperscript{4} Å diameter) of 0.45 cm\textsuperscript{3}/g.

In runs with the SPDR this catalyst was pressed into pellets contained within a titanium collar, which was then placed within the reactor. The pure Ni-0104P powder could not be used for pellet formation because of the mismatched thermal expansion properties with the collar; however a workable formulation was developed that consisted of 13.3 wt% of Ni-0104P and the remainder pure kieselguhr support (also supplied by Engelhard). The final pellets were formed from this material, pressed into place in the collar at a pressure of 30,139 psi using a plunger-die assembly (the titanium collar is the die) with a Buehler Laboratory Press. This overall procedure is described in detail by Au (1992), and is similar to that discussed by Kehoe and Butt (1972). Under these conditions 0.356" diameter pellets of slab lengths of 0.07", 0.11" and 0.14" were produced for pellet weights of 0.15, 0.225 and 0.30 g. A series of physical characterizations including nitrogen adsorption/desorption, mercury porosimetry and X-ray diffraction showed little difference between the Ni-0104P and the final pellets employed in the SPDR (Au, 1992). These pellets had BET surface of 100 m\textsuperscript{2}/g, pore volume of ca. 0.20 cm\textsuperscript{3}/g (N\textsubscript{2} adsorption/desorption), micropore radius of 35 Å, and macropore radius of 240 Å.
Nonuniform pellets

A schematic of the catalyst profiles has already been given in Fig. 1. In order to compare distributions on a consistent weight-loading basis for the 13.3 wt% mixture (actually 0.02 g Ni-0104P/0.13 g kieselguhr) all pellets were normalized to a standard overall content of 0.1724 g Ni-0104P/cm³ of pellet. Thus, for the example of a second-order shell-active pellet:

\[ w(y) = cy^2 \]

where \( y \) is the distance from the center-plane, \( w(y) = g \) Ni-0104P/cm³ pellet and \( c \) is the proportionality constant.

The normalization constraint requires that

\[ \int_0^1 w(y) \, dy = 0.1724 \]

or

\[ \int_0^1 cy^2 \, dy = 0.1724 \]

\[ c = 0.517. \]

For the five power-law profiles studied here, the activity functions determined in this manner are:

- \( 2^+ : w(y) = 0.517 \, y^2 \); second-order, shell-active
- \( 1^+ : w(y) = 0.345 \, y \); first-order, shell-active
- \( 0^+ : w(y) = 0.172 \); uniform
- \( 1^- : w(y) = 0.345 \,(1 - y) \); first-order, core-active
- \( 2^- : w(y) = 0.517(1 - y)^2 \); second-order, core-active.

In preparation of the actual experimental pellets, these continuous power-law profiles were discretized by dividing each pellet into five equal-sized zones of uniform activity based on the median \( w(y) \) in each zone. These distributions are given in Table 1. To generate each activity function, the five layers of appropriate concentrations were compressed at 30,139 psi sequentially, starting with the center-plane layer.

**Table 1. Active ingredient distribution functions for the nonuniform catalyst pellets**

<table>
<thead>
<tr>
<th>Profile</th>
<th>Center → Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( w_1 )</td>
</tr>
<tr>
<td>( 2^+ )</td>
<td>0.005</td>
</tr>
<tr>
<td>( 1^+ )</td>
<td>0.035</td>
</tr>
<tr>
<td>( 0 )</td>
<td>0.172</td>
</tr>
<tr>
<td>( 1^- )</td>
<td>0.310</td>
</tr>
<tr>
<td>( 2^- )</td>
<td>0.423</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Kinetic model and analytical formulation**

As stated before, the kinetics of benzene hydrogenation under the conditions employed here appear well-correlated by an Eley–Rideal-type rate equation:

\[ k K_{BPB} x^q \]

\[ (-r) = \frac{k K_{BPB} x^q}{1 + K_{BPB}} \]

It should be noted that we claim no fundamental mechanistic significance for this; the rate data fit the mathematical form. The values of the model parameters are reasonable from a physicochemical point of view, however.

At low temperatures \( K_{BPB} > 1 \) and, for these experiments, the reaction becomes essentially zero order since the change in \( x \) in the SPDR is small.

The conservation equation for the pellet in the SPDR, if our design has been successful, is that of diffusion and reaction in a symmetric slab:

\[ D_x \left( \frac{d^2 C_x}{dz^2} \right) = (-r) \]

Define the nondimensional variables \( y \) and \( \alpha \):

\[ y = \left( \frac{z}{L} \right); \quad \alpha = \left( n_{HH}/n_H \right) \]
and substitute these definitions and the rate equation into eq. (7). When everything is expressed in terms of \( y, \alpha, \) and the conversion, \( X, \) we have for the rate

\[
(-r) = \frac{[k_s \alpha w(y)] K_B P_B x_H}{1 + K_B P_B}
\]

and for the pellet:

\[
\left[ \frac{d^2 X}{dy^2} \right] + \frac{6}{1 + \alpha - 3X} \frac{dX}{dy} = \left[ \frac{L^2 K_s \alpha e RT K_B}{D_s(2 - \alpha)} \right]
\]

\[
\times \left\{ \frac{w(y)(1 - X)(\alpha - 3X)(1 + \alpha - 3X)}{[1 + \alpha - 3X + K_B P(1 - X)]} \right\}
\]

with boundary conditions

\[
y = 0, \quad \frac{dX}{dy} = 0 \quad \text{(center-plane)}
\]

\[
y = 0, \quad X = X^* 
\]

\[
y = 1, \quad X = X_s, \quad \text{(surface)}. \quad (11)
\]

For low temperatures the rate expression is simplified as described above, and

\[
(-r) = k_s \alpha e w(y) x_H 
\]

and the conservation equation is

\[
\left[ \frac{d^2 X}{dy^2} \right] + \frac{6}{1 + \alpha - 3X} \frac{dX}{dy} = \left[ \frac{L^2 k_s \alpha e RT}{D_s(2 - \alpha)} \right]
\]

\[
\times \left\{ w(y)(\alpha - 3X)(1 + \alpha - 3X) \right\} 
\]

\[
= \frac{L^2 k_s \alpha e RT}{D_s(2 - \alpha)} \left[ w(y)(\alpha - 3X)(1 + \alpha - 3X) \right]. \quad (13)
\]

Now, the Thiele modulus for slab geometry is

\[
\phi = L \left[ \frac{k_s \alpha e \rho x_B RT x_H}{D_s(1 + K_B P_B)} \right]^{1/2}
\]

(14)

and the Weisz–Hicks (1962) modulus:

\[
\Phi = \frac{L^2 (-r)_{obs} RT}{D_s(P_B)}.
\]

(15)

For steady-state conditions the observed rate of reaction, \((-r)_{obs}\), is equal to the transport flux at the pellet surface, so

\[
AL(-r)_{obs} = D_e \left[ \frac{P}{RT L} \right] (2 - \alpha) \left( \frac{dX}{dy} \right)_{y=1}
\]

(16)

The observed rate in a single pellet experiment is evaluated directly from the conversion:

\[
(-r)_{obs} = \frac{n_0 X_s}{AL}
\]

(17)
Thus, for the Weisz modulus from eq. (15) we have

\[
\Phi = L \left[ \frac{n_B X L_{RT}}{AD_e(P_nh) \bar{X}} \right]
\]

and for the effective diffusivity from eq. (16):

\[
D_e = \left[ \frac{n_B X_{LRT}(1 + \alpha - 3X_s)^2}{AP(2 - \alpha)} \right] \left[ \left( \frac{dX}{dy} \right)_{y=1} \right]^{-1}
\]

Finally, for the effectiveness factor, \( \eta \):

\[
\eta = \frac{n_B X_s}{(1 + K_B P_nh(x_{nh}))} \left( \frac{1 + K_B P_nh(x_{nh})}{k_B \alpha_w P_B \alpha_B (x_{nh})_s} \right)
\]

This series of expressions, in addition to providing \( \Phi \) and \( \eta \) from experimental data, allows estimation of the parameters \( k_B \), \( K_B \) and \( D_e \). Note also that from experiments in the fixed-bed reactor with the Ni-0104P in powder form (no intraparticle diffusion effects), rates are obtained from conversion data as

\[
( -r_{hm}) = \frac{n_B X \rho_s}{W}
\]

under the conditions where \( X \ll 1 \).

The SPDR analysis above incorporates four major assumptions: (i) deactivation of the catalyst was not important, (ii) boundary layer diffusion (gas-phase mass transfer) was rapid compared to intraparticle diffusion, (iii) the pellets under reaction conditions were isothermal, and (iv) the effective diffusivity was the same for the various pellets investigated. Points (i) and (ii) were investigated in separate experimentation and experimental conditions set accordingly so these requirements were met (Au, 1992). For point (iii), calculation of the Prater (1958) maximum temperature

\[
\Delta T_{max} = \frac{(C_B)_0 X \lambda (-\Delta H)}{\lambda}
\]

using values of \( \lambda \) for Ni-0104P of \( 3.5-5 \times 10^{-4} \text{cal/cm}^3 \text{s K} \) (Kehoe and Butt, 1972; Satterfield, 1970) and \( D_e \) of order 0.04 cm/s (Kehoe and Butt 1972), see also later) yield \( \Delta T_{max} \) values ranging from 0.1 to 2.2°C for the various experiments, hence nonisothermality is not a problem. As a result, thermal expansion problems are also of no consequence. For point (iv), the overall pellet dilution ratio and the pelletizing pressure were kept constant for all experiments. The reproducibility of \( D_e \) using this procedure has been shown to be within about \( \pm 20\% \) (Kehoe and Butt, 1972).

Solution of system equations and parameter estimation

The following system conditions are known: \( T, P, L, W, \rho_e, \rho_r, A, \alpha_w, n_B, n_B, \alpha \) and \( w(y) \). For the nonuniform pellets \( w(y) \) is dependent on the particular activity profile used [see eqs (5)], but the normalization constraint requires that the volume-averaged content of active ingredient be the same for all profiles (constant \( \rho_a \)). We have from experiment \( X \) and \( X^* \).

Low temperature regime. This regime is defined to be \( T = 60-120^\circ C, P_B > 0.02 \text{ atm.} \) The governing relationships are eqs (13) and (19). The following computational procedure is used:

1. With an estimated value of \( (k_s)/D_e \), eq (13) is separated into two simultaneous first-order equations and solved numerically with the given conditions at \( y = 0 \). This will yield two intraparticle profiles, \( X(y) \) and \( \text{d}X/\text{d}y(y) \). We then iterate on \( (k_s)/D_e \) until there is obtained \( X(y = 1, \text{computed}) = X_e(\text{experimental}) \). \( X_e(\text{experimental}) \) is not unity because there are well-mixed conditions in the volume above the pellet, and the conversion in the pellet is finite. Then

2. The solution of \( X(y = 1) \) and \( \text{d}X/\text{d}y(y) \) are substituted into eq. (19) and \( D_e \) evaluated. This, in turn, produces a value for \( k_s \).

3. The above procedure is repeated for the temperature range, giving \( k_s(T) \) and \( D_e(T) \). Both of these are taken to follow Arrhenius-type relationships:

\[
k_s = (k_s)_0 \exp(-E/RT)
\]

\[
D_e = (D_e)_0 \exp(-E_P/RT)
\]

and values of \( (k_s)_0, (D_e)_0, E \) and \( E_p \) are obtained from linear regression analysis of ln\( k_s \) and ln\( D_e \) vs \( 1/\text{RT} \). These values are taken to be invariant with temperature level.

High-temperature regime. These data are for experiments from 150-180°C here the governing relationships are eqs (10) and (19). An estimated value of \( k_s \) for this temperature region can be obtained from the \( (k_s)_0 \) and \( E \) determined above. There is, however, some difficulty associated with \( D_e \). As will be seen subsequently, there is significant scatter in estimated values from the low-temperature experiments, so \( D_e \) was recalculated from the higher-temperature data using the computed value from low temperature \( (k_s)_0 \) and \( E_P \) only as an initial approximation. This was done because it has been shown that the numerical simulation of intraparticle diffusion/reaction based on analysis of profiles is quite sensitive to the value of \( D_e \) (Downing et al., 1979). Accordingly, we start with estimated values of \( D_e \) and \( K_B \). Then,

1. Equation (10) is solved with the conditions at \( y = 0 \). We then search over \( D_e \) until \( X(y = 1, \text{computed}) = X_e \).

2. The values of \( X(y = 1) \) and \( \text{d}X/\text{d}y(y = 1) \) from (1) are then substituted into eq (19) to produce a new estimate of \( D_e \).

3. Steps 1 and 2 are then repeated for different \( K_B \) values until an optimum \( K_B \) is obtained which minimizes the difference in \( D_e \) from (1) and (2).
This will set the trend of $D_e$ with temperature, as well as that of $K_B$. The benzene adsorption constant, $K_B$, also follows an exponential temperature dependence

$$K_B = (K_B)_0 \exp(Q_B/RT).$$  \hspace{1cm} (26)

Thus linear regression of $K_B(T)$ vs $(1/T)$ yields values for $(K_B)_0$ and $Q_B$. The values so obtained are consistent with those so obtained from the analysis of eqs (20) and (21), and agree with those of Kehoe and Butt (1972).

Overall. The procedure detailed above decomposes the parameter estimation problem into a series of one-dimensional searches. It has been assumed that the objective functions (normally, the current estimate minus the prior estimate) are unimodal in the variable being searched (i.e., $D_e$, $K_B$, etc.). A Golden Section search (Wilde and Beightler, 1967) is a reasonably efficient way to do this.

The values of the reaction rate, adsorption and diffusion parameters determined from the analysis are given in Table 2. Excellent reproducibility of $(k_i)_0$ and $E$ values were obtained between the fixed-bed and SPDR results, with both parameters within 10% of each other. The values given in Table 2 are those obtained from the SPDR analysis, and are in good agreement with previous reports (Kehoe and Butt, 1972; Marangozis et al., 1979). The effective diffusivity, $D_e$, was found as expected to be only a weak function of temperature, and is of order 0.03 cm$^2$/s for the experimental conditions used here, compared to values of 0.052 cm$^2$/s (pure Ni-0104P) and 0.035 cm$^2$/s (25% Ni-0104P, 25% graphite, 25% $\gamma$-Al$_2$O$_3$) reported by Kehoe and Butt (1972). The estimated $K_B$ values were found to be very sensitive to even small variations in $k$, or $D_e$ and scattered over a wide range. Widely divergent values of $K_B$ have also been reported by other investigators, and this is probably just a reflection of the fact that $K_B$ is not very significant in the rate expression. The $\pm 0.5$ kcal/mol uncertainty in $Q_B$ given in Table 2 is an estimate; a better idea of the uncertainty involved in this correlation is given by visual inspection of Fig. 4.

**Experiments**

**Effect of activity profile on rate.** The effect of activity distribution on observed rate as a function of temperature is shown in Figs 5 and 6 for diffusion (pellet) lengths of 0.07 and 0.14", respectively. The following observations pertain:

(1) All profiles with the shorter diffusion length have higher activities due to the smaller $L$.

(2) In each case the conversion trend correlates directly with the amount of shell activity, such that in order of performance:

$$2^+ > 1^+ > 0 > 1^- > 2^-.$$

This is to be expected since overall the reaction over a wide range of conditions behaves as positive-order. In a diffusion-limited regime, the best distribution is the most surface-active one. Note, however, that in some regions of the results shown in Figs 5 and 6, the reaction is effectively zero-order, as shown particularly by the 0.07" pellet at low temperatures where all profiles have similar performance. However, as the temperature increases the difference between the five profiles also increases. At 180°C, there is a 30% rate enhancement by changing from a uniform to a second-order shell-active distribution. The same is observed with the 0.14" pellet, except, now that we are dealing with a reaction at much higher Thiele modulus the activity improvement from uniform to second-order shell-active profile is almost 80%.

**Effect of diffusion length on rate.** The dependence of overall rate of reaction on the diffusion length for the different profiles is shown in Figs 7–11. Some observed trends are expected: since the reaction is either

![Fig. 4. Correlation of experimental values of $K_B$ vs. $(1/T)$.](image)
near zero-order to first-order in the experimental regime, the $2^-$ and $1^+$ profiles give higher overall rate than uniform or core-loaded profiles. Indeed, the rates for the $2^-$ profile are very low. The more diffusion-limited a pellet is the higher is the rate increase from halving the diffusion length; for example, for the $2^-$ pellet the rate increase as we increase the diffusion length from $L = 0.4''$ to $0.07''$ is about 60%, whereas it increases by about 100% for the uniform pellet and 180% for the $2^-$ pellet. However, the magnitudes of the rates of reaction for the core-loaded pellets are always smaller than for the uniform or externally loaded samples. Upon comparison of Figs 7–9 it can also be seen that the $(2^-, 0.14'')$ and $(1^+, 0.14'')$ rates appear between those of $(0, 0.14'')$ and $(0, 0.07'')$. If this indeed is so, then it would imply that in systems where it is impractical to reduce particle size (normally due to pressure-drop limitations), shell-concentrated active ingredient even deposited on larger particles may improve conversion substantially. In general, it is not surprising that, given the combination of
nonuniform activity profiles and complex kinetics, there is no direct proportionality between diffusion length and rate even in the region of strong diffusion limitation.

Effectiveness factors. Figures 12 and 13 show the effectiveness factor plots for the five activity profiles and the two pellet lengths of 0.07" and 0.14". As expected, there is no differentiation in performance at low $\phi$ ($\eta \to 1$ in all cases). Differences among the profiles begin to appear in the region $0.5 < \phi < 2$, and at higher values the effectiveness also corresponds with activity profile in the order $2^+ > 1^+ > 0 > 1^- > 2^-$. The small region of $\eta > 1$ shown in Fig. 12 is most probably the result of uncertainty in the value of $K_B$.

The differences among the five profiles continue to increase as $\phi$ increases. Such a trend, for example, is observed upon comparison of Figs 12 and 13 for $\phi \geq 2$. Differences in $\eta - \phi$ are substantially greater for the 0.14" pellets than for their 0.07" counterparts.
CONCLUSIONS

The single pellet diffusion reactor provides a direct means for investigation of the effect of nonuniform activity profiles on diffusion-limited catalytic reactions. The catalyst pellet itself is also of a convenient size for special preparation, inspection and characterization both before and after use. With benzene hydrogenation on supported Ni as a model reaction we have been able to evaluate reaction kinetic parameters, effective diffusivities and profile distribution influences in a single experiment. Since the Eley-Rideal kinetic correlation behaves overall as positive fractional-order, overall effectiveness correlates directly with the amount of active ingredient located in the catalyst shell and highest activity is always observed for preferential loading near the surface (2 $^\circ$ profile). The relationship between diffusion length and overall rate of reaction is influenced by both the nature of the activity profile and the fractional-order kinetics, and is complex. However, the differentiation in performance among the various nonuniform profiles does appear to increase with pellet length, while at low $\phi$ the same performance is obtained with all profiles.

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NOTATION

\( A \) cross-sectional area of catalyst, cm\(^2\)

\( a_e, a_r \) surface areas of pellet, powder Ni-0104P, cm\(^2\)/g

\( C_B, (C_B)_0 \) concentration of benzene; feed concentration of benzene, mol/cm\(^3\)

\( D_e \) effective diffusivity, cm\(^2\)/s

\( (D_e)_0 \) pre-exponential factor, effective diffusivity, cm\(^2\)/s

\( E \) reaction activation energy cal/mol

\( E_D \) activation energy, effective diffusivity, cal/mol

\( \Delta H \) heat of reaction, cal/mol

\( k \) reaction rate constant, eq. (6)

\( k_e, k_r \) volumetric rate constants of pellet, powder catalyst, mol/cm\(^3\) pellet-s

\( \bar{k}_e \) volume-averaged rate constant of nonuniform pellet, mol/cm\(^3\) pellet-s

\( k_i \) intrinsic rate constant of active catalyst, mol/cm\(^2\) Ni-0104P-s

\( (k_i)_0 \) pre-exponential factor of intrinsic rate constant, mol/cm\(^2\) Ni-0104P-s

\( K_B \) adsorption constant of benzene, (1/atm)

\( (K_B)_0 \) pre-exponential factor of benzene adsorption constant, 1/atm

\( L \) length of pellet, cm

\( n_{\text{H}}, n_B \) feed rates of benzene, hydrogen, mol/s

\( P \) total pressure, atm

\( P_B \) partial pressure of benzene, atm

\( Q_B \) heat of adsorption, cal/mol

\( R \) gas constant, 82.06 cm\(^3\) atm/mol K

\( (r-s)_h \) local, observed rates of reaction, mol benzene reacted/cm\(^3\) pellet-s

\( (r-s)_{\text{obs}} \) position of square wave

\( s \) dimensionless pellet heat rise

\( \phi \) Thiele modulus

\( \psi \) Weisz-Hicks modulus

\( \eta \) effectiveness factor

\( \lambda \) catalyst pellet thermal conductivity, cal/s cm K

\( \rho_e, \rho_r \) overall activity densities of pellet, powder catalysts, g Ni-0104P/cm\(^3\) bulk volume

Greek letters

\( \alpha \) molar feed ratio of hydrogen/benzene; n_H/n_B

\( \beta \) dimensionless pellet heat rise

\( \phi \) Thiele modulus

\( \Phi \) Weisz-Hicks modulus

\( \eta \) effectiveness factor

\( \lambda \) catalyst pellet thermal conductivity, cal/s cm K

\( \rho_e, \rho_r \) overall activity densities of pellet, powder catalysts, g Ni-0104P/cm\(^3\) bulk volume