An isothermal fixed-bed reactor with nonuniformly active catalysts: Experiments and theory

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Abstract
An isothermal fixed-bed reactor packed with supported catalyst pellets, in which the active metal catalyst was deposited as a thin band within the support, was studied experimentally. The purpose was to support our previous related theoretical studies. The oxidation of CO with excess oxygen over Pt catalyst was used as the test reaction. The catalysts were prepared by sequential impregnation of chloroplatinic acid and citric acid on γ-alumina pellets. A thin layer of Pt was achieved within the support to simulate the Dirac delta distribution. A maximum of two steady states were obtained when only one type of catalyst was packed in the reactor. A 'jump' from the high conversion regime to the low conversion regime occurred when the CO feed concentration was increased from low to high values; as the CO concentration was decreased, a continuous transition from the low conversion regime to the high conversion regime resulted generally. For the reactor packed with two different types of catalysts in series, the importance of their order of packing was demonstrated; also, three stable steady states were observed in some cases. Excellent qualitative agreement between the experiments and the theory was obtained.

Keywords: Fixed-bed reactor; nonuniformly active catalysts; CO oxidation; multiple steady states

Introduction
Most of the work done in the area of nonuniformly active catalysts has been primarily theoretical (cf. Dougherty and Verykios, 1987; Komiyama, 1985), where the effectiveness, selectivity, yield and deactivation resistance have been investigated in either a single catalyst pellet or fixed-bed reactor context. Only a relatively few studies (cf. those of Hegedus and coworkers, summarized in Hegedus and McCabe, 1981; Kunimori et al., 1982 and 1986; Oh and Cavendish, 1985a and 1985b; Chemburkar, 1987) have shown the preparation of nonuniformly active catalysts, and tested them for conversion and/or poison resistance. Further, actual matching of the theory with experiments has only been done by Hegedus et al. (1977), Oh and Cavendish (1985a and 1985b), and Chemburkar (1987).

In this paper, an isothermal fixed-bed reactor packed with catalyst pellets having a thin band of Pt deposited within the support was studied experimentally. CO oxidation over Pt/γ-alumina was used as the test reaction. Several catalysts with different Pt band locations were prepared and tested. Experiments were conducted in a reactor packed with a single type of catalyst, as well as with two different types of catalysts. The observed multiplicity behavior is discussed. An isothermal, heterogeneous plug-flow reactor model, based on the model developed by Morbidelli et al. (1986) and the multiple zones reactor model of Lee et al. (1987) was used to compare with the experimental data. The main goal is to show that with a proper distribution of Pt metal within the catalyst pellets, and also with a proper sequence of catalysts packed along the reactor, the overall conversion of the reactor can be improved. Another goal is to provide a link of the theory with experimental observations.

Catalyst
Since the theory of optimal catalyst activity profile developed by Morbidelli et al. (1982) requires a Dirac delta function as the distribution function, it is crucial experimentally to be able to prepare catalysts with a narrow band of Pt deposited at the desired location within the support, in order to simulate a Dirac delta distribution. In this work, four Pt/γ-alumina catalysts with different Pt band locations were prepared by the technique of sequential impregnation with chloroplatinic acid and citric acid (see Lee, 1987 for details). One was externally coated (egg-shell) catalyst, while the other three were internally loaded (egg-white) catalysts with different locations of the Pt band (Fig. 1). In order to compare different catalysts for their total catalytic activity, Pt loading and its fraction of exposed atoms (dispersion) must be determined. Table 1 shows the dispersion for all four catalysts, as measured by CO chemisorption using dynamic pulsing technique. 13 catalyst has significantly higher dispersion than the other three. This is probably because I3 had the longest impregnation time for citric acid, which made the Pt band closest to the center of the support, and the Pt atoms had more time to disperse.

The total Pt loading of each type of catalyst was determined by atomic absorption spectroscopy, and the results are also shown in Table 1. Ex catalyst has the highest Pt loading, whereas I3 has the lowest. This is because after the initial impregnation step in chloroplatinic acid, Ex was then washed and dried, so it retained most of the Pt in the support. The other three batches of catalyst were further impregnated in citric acid for different lengths of time, which permitted some adsorbed PtCl4 ions to desorb and diffuse out of the support. As a result, the longer the second impregnation in citric acid solution, the smaller the amount of Pt left on the support.

Fixed-bed reactor: Experimental
Each catalyst was first pretreated at 500°C (with flowing oxygen for 1 hr, followed by nitrogen flushing for 15 min and reducing with hydrogen for 3 hrs), then aged with the reaction mixture at 250°C for about 24 hrs. A quartz
reactor of 1 cm ID was used for all experiments. The catalytic zone was 18 cm long and an inert zone (12 cm long) was packed with_blank_y-alumina pellets before it. Thermocouples were placed both at the inlet (before the inert zone) and at the outlet of the reactor. The feed stream consisted of less than 2% CO, mixed with balance O2. With catalysts having different activities because of dispersion and/or loading, inert pellets were used to dilute the bed, so that the total Pt surface area for the whole reactor was constant. The four catalysts (Ex, I1, I2 and I3) were tested in the reactor at 100°C and 115°C under at least two flow rates each, which ranged from 152 cc/min to 544 cc/min. For the Ex catalyst, 50 active pellets were mixed evenly with 100 inert pellets, and packed in the reactor.

Dilution of reactor beds with inert pellets is a quite common practice (cf. Pirkle and Wachs, 1987; Buchanan and Sundaresan, 1987), in order to control the temperature (or catalytic activity profile) along the reactor for nonisothermal (or isothermal) reactors, so as to obtain an optimal temperature (or catalytic activity) profile and to prevent thermal runaway. In this study, there were several reasons for diluting the reactor bed; first, for an isothermal fixed-bed reactor, axial mixing can generally be ignored when the bed length to pellet diameter ratio is greater than about 50 (cf. Varma, 1981); here, a ratio of 57 was obtained, which provided plug flow behavior. Dilution of the reactor with inert pellets provides a larger bed length to pellet diameter ratio with lesser amount of Pt metal. Secondly, for an exothermic reaction, dilution minimizes nonisothermal effects in the reactor (cf. Votuba et al., 1976). Finally, as mentioned before, the total activity and length of the bed should be kept constant in order to compare the performance of different catalysts, and this can be achieved readily by adjusting the ratio of active to inert pellets.

Preliminary chemisorption runs conducted with pellets showed that for the same sample weight, the Ex catalyst absorbed roughly twice the amount of CO than the three internal catalysts. Since the active to inert pellets ratio for the reactor packed with Ex catalyst was 50/100, all internal catalyst reactors were packed with a ratio of 100/50. After all the experiments were conducted according to the above ratio, chemisorption was performed again on the used powdered catalysts, and Pt metal loading of each type of catalyst was also determined by atomic absorption spectroscopy. The final chemisorption data and loading are shown in Table 1, and the total surface area of Pt per unit volume of solid (A) for each catalyst is also included.

**FIXED-BED REACTOR: THEORY**

The fixed-bed reactor model presented here is an isothermal heterogeneous plug-flow model, with a bimolecular Langmuir-Hinshelwood kinetic expression, and is based on the model of Morbidelli et al. (1986). The fluid phase and solid phase mass balances in dimensionless form are given by

\[ \frac{dg}{dy} = - Da^* \frac{t^*}{u} \tag{1a} \]

with initial condition

\[ g(1) = 0 \]

and

\[ g - u - \alpha^* t^*(u) = 0 \tag{1b} \]

where

\[ t^*(u) = u/(1 + cu)^2 \]  
\[ \tilde{u} = u/s \tag{2} \]

The parameters \( Da^* \) and \( \alpha^* \) are defined in the Notation. Eqn 2 follows from the solution of diffusion-reaction equation in the solid phase, with a Dirac delta function located at \( s \) (Morbidelli et al., 1986).

Experimentally, feed concentration of CO was the main operating parameter, while all other parameters remained constant. Since CO feed concentration appears only in \( \sigma \), and \( K \) is constant during an experiment, \( \sigma \) changes linearly as CO feed concentration is changed. Therefore, bifurcation diagrams of conversion versus \( \sigma \) were made to predict the influence of CO feed concentration on reactor conversion, which might be observed experimentally.

Since the multiplicity behavior of the reactor depends on the solid-fluid interaction equation (eqn 2), the multiplicity of this equation can be easily analyzed by using Singularity theory (see Lee, 1987), to give a multiplicity master plot for the whole reactor. The highest order of singularity in this case is a cusp catastrophe, and the cusp point is given by \( g = 8, \alpha^* = 27, \sigma^* = 2 \). As studied by Morbidelli et al. (1986), the solution of the reactor can be found by first plotting the curve of \( u \) vs \( g \) according to eqn 2. Then at the inlet of the reactor (\( g = 1 \)), eqn 1a can be integrated along the curve to obtain the reactor profile. Fig. 2 shows the bifurcation set of the solid mass balance equation. It consists of the hysteresis variety (III) and boundary limit vertical set (BLV) (Balakotaiah and Luss, 1984), which divide the parameter space into three regions of different bifurcation diagrams of \( u \) vs \( g \). In region I, there is only one solution for the inlet of the reactor, and a unique branch gives a unique solution. In region II also, the reactor has only one solution, but there are still three branches in the diagram; this means that the solution jumps at the bifurcation point somewhere along the reactor, depending on \( Da^* \), but uniqueness still prevails. In region II, there are three possible inlet conditions for the reactor, which produce three different reactor profiles and exit conversions. The middle solution has been shown to be unstable (Morbidelli et al., 1986), while the top and bottom branches are stable, and are referred to as the 'low conversion branch' and the 'high conversion branch', respectively.

Fig. 3 shows a typical bifurcation diagram of conversion vs \( \sigma \). Basically, the diagram consists of three solution branches, where the unstable solution branch is drawn in dashed line. The top branch represents the high conversion regime, while the bottom one is the low conversion regime. When \( \sigma \) increases from small values and follows the high conversion regime, after a certain point, the high conversion regime ends and a jump to the low conversion regime occurs. However, when \( \sigma \) decreases from a high value following the low conversion regime, the reactor conversion increases continuously until it joins with the high conversion regime. This completes the hysteresis loop, with one jump from high to low regime, and the other a continuous transition from low to high regime. This type of bifurcation behavior has been previously reported by Puszynski et al. (1981) for a nonisothermal fixed-bed reactor. This hysteresis behavior can be explained by examining the reactor paths along the curves in the three bifurcation diagrams of Fig. 2. When \( \sigma \) starts at small values (region I), the reactor inlet (\( g = 1 \)) has a unique \( u \), and the reactor follows the only branch to yield the outlet concentration. As \( \sigma \) increases, the reactor inlet remains in the high conversion branch through region II; as it crosses to region III, the high conversion branch disappears, and the reactor inlet starts at the low conversion branch, which results in a much lower outlet conversion -- this explains the abrupt jump which occurs between regions II and III in Fig 3. When a reactor operates on the low conversion branch in regions II and III, it can ignite to the high conversion branch at the bifurcation point before the reactor ends, depending on the value of \( Da^* \). When \( \sigma \) starts at high values (in region III) and decreases, the reactor outlet conversion keeps increasing. The reactor inlet begins at the low conversion
branch, and remains there through region II until it crosses to region I; just before that point, the reactor outlet conversion from the low conversion regime is almost the same as that from the high conversion regime. This is so because at this stage, only the first layer of the reactor operates on the low conversion branch, while the rest of the reactor operates on the high conversion branch. Therefore, one observes the same outlet conversion as the reactor operated completely on the high conversion branch. When $\alpha^*$ is less than 27, a unique solution exists for all $\sigma$ values.

**RESULTS AND DISCUSSION**

Before presenting the experimental results, it is worthwhile to address the issue of isothermality in the catalyst and the fluid phases. Intraparticle temperature gradient in uniformly active catalysts is usually negligible (Carberry, 1976); for catalysts with nonuniform internal step distribution of CO feed concentrations and relatively low temperatures, inter- and intraparticle temperature gradients are again negligible. Since the maximum CO feed concentration used here was $\leq 2\%$; and the inlet (just before the inert zone) and the outlet (at the catalyst bed) reactor temperature measured in all steady-state experiments differed less than $10^\circ$C, it can be concluded that both inter- and intraparticle temperature gradients were negligible for all steady-state experiments conducted in this work.

Figs. 4a - d show the reactor outlet conversion of CO versus CO feed concentration (in volume %) at various temperatures and flow rates, for I3, I2 and Ex catalysts. The lines were drawn by hand to join the data points together. As expected, larger flow rates gave smaller residence times, which in turn produced lower overall conversions. Therefore, the curve for the higher flow rate always appears on the left side of the lower flow rate curve. Basically, these response curves have qualitative features similar to those calculated for the plug flow reactor model discussed above. Two conversion curves can be found generally for intermediate values of CO feed concentration, which comprise the hysteresis phenomenon. As CO feed concentration increased from zero to higher values, the reactor outlet conversion was about 85 to 90 percent on the high conversion regime, for all flow rates, temperatures and catalysts, which was the result of external mass transfer dominating the overall reaction rate. After CO feed concentration increased to a certain point, reactor outlet conversion jumped to the low conversion regime, which was affected mainly by kinetics control (cf. Keil and Wicke, 1980). At intermediate CO feed concentration values, multiplicity occurred, which was caused by the interactions of mass transport and reaction kinetics. The exact point in the temperature curve where CO feed concentration crosses the low CO conversion and catalyst used; this bifurcation point became the distinct feature of each reactor operated at certain conditions with a certain catalyst, which could be used as a guide for reactor performance comparisons. When the CO feed concentration started at high values (above 2%), all reactors were at the low conversion regime; as the concentration decreased, the conversion slowly increased until it joined with the high conversion solution smoothly to complete the hysteresis loop. This was the case most of the times. However, oscillations occurred often at this transition point from the low to the high regime, as also observed by Wicke and Onken (1986) for the adiabatic reactor. On the other hand, oscillations occurred less often at the other transition point where the high conversion regime ended with a jump to the low conversion regime. Temperature fluctuations were also observed during these oscillations, which actually drove the conversion to oscillate further.

**Comparison of different catalysts**

Fig. 5 shows a comparison of the four reactors at 115°C and 152 cc/min flow rate (results from the dual-zone reactor are discussed later). Lines were drawn to show the maximum conversion exhibited by each set of experimental data. II reactor has the widest range of high conversion regime; it jumped to the low conversion regime at about 1.6% CO feed concentration, while all other reactors encountered jumps down to the low conversion regime at smaller CO feed concentrations. I2 reactor gave the second widest range of high conversion branch, followed by I3 and Ex. Although Ex had about 35% more total activity than all the internal reactors, it still did not perform as well as them. This shows that under certain conditions, egg-white catalysts provide higher conversion than egg-shell catalysts. At higher CO feed concentrations, when all reactors operated in the low conversion regime, all four catalysts gave roughly the same conversion.

**Theoretical predictions**

Attempts were made to fit the experimental data with the fixed-bed reactor model discussed earlier. An exact qualitative match is not possible here, since right cylindrical catalyst pellets were used experimentally, while infinite cylinders were simulated for simplicity in the reactor model. Another complication arises because of the true representation of kinetics of CO oxidation over Pt. Although this reaction has been studied extensively, the exact reaction mechanism is not yet fully understood. Various researchers (cf. Voltz et al. 1973) have suggested the bimolecular Langmuir-Hinshelwood kinetic expression. However, others (Herz and Marin, 1980; Chemburkar, 1987) have found that the bimolecular Langmuir-Hinshelwood kinetics does not fit their intrinsic kinetic data. They have instead used a mechanistic surface reaction model, which involves solving the equations of the adsorption and reaction steps, with no specific elementary step as the rate determining step. Since this type of model is relatively more complicated, the bimolecular Langmuir-Hinshelwood kinetic model was used here to predict the qualitative behavior of the experimental data. A wide range of kinetic parameters $k$ and $K$ of the bimolecular Langmuir-Hinshelwood expression have been reported in the literature. Thus, $k$ and $K$ could be used as adjustable parameters, as long as they were within the range of reported values.

Fig. 6 shows the results of temperature variation on the reactor model, where the temperature of curve (a) is lower than that of curve (b). Good qualitative agreement is obtained between the model and the experiments (Figs. 4a,b), where the higher temperature curve always gives a wider high conversion regime, and the jump occurs at a higher CO feed concentration. In order to relate $\sigma$ to CO feed concentration, note that the jumps for the higher flow rate data in Figs. 4a,b occur at $0.5\%$ CO (i.e. $1.63 \times 10^{-7}$ g mol/cm$^3$ at $100^\circ$C), while in Fig. 6 they occur at $\sigma = 50$. This implies $K = 3.1 \times 10^8$ cm$^3$/g mol, which is a value within the range reported in the literature (Lee, 1987). Note that temperature affects both model parameters $\alpha^*$ and $D^*$ through $k$, and higher temperature gives higher $\alpha^*$ and $D^*$ values.

**Dual-zone reactor**

Previous theoretical studies have shown that reactor conversion could be improved by packing the reactor with two zones of different catalysts, where the second zone has a larger $\alpha$ value than the first zone (Lee et al., 1987). Thus experiments were conducted for reactors packed with two different types of catalysts in series. I3 and Ex catalysts were chosen to test the performance of the dual-zone reactor. In one case, the first half of the reactor bed was packed with I3 catalyst with the active to inert pellet ratio of 50/25, while the second half was packed with Ex catalyst and an active to
inert pellet ratio of 25/50, so that the total number of pellets and the total activity in the whole bed were still the same as in the single-zone reactors studied previously. Fig. 5a shows a comparison of the I3/Ex (first zone/second zone) dual-zone reactor with the Ex and I3 single-zone reactors at 115°C and 152 cc/min flow rate. As can be seen, the high conversion regime of the dual-zone reactor extended past 2% CO feed concentration, while the I3 and Ex reactors jumped from the high to the low regime at less than 1.3% CO feed concentration. Thus at high CO feed concentrations, the dual-zone reactor composed of I3 and Ex catalysts was superior to either the I3 or the Ex reactor alone. Because of limitations of the CO and CO2 analyzers used, the experimental data could be taken only up to 2% CO concentration. For the dual-zone reactor, the low conversion regime was obtained by a temperature perturbation. Perturbations in flow rate could also be used for this purpose.

In order to show the importance of the order of catalysts in a dual-zone reactor, the results of the I3/Ex reactor were compared with the results of the reactor packed with the very same catalyst pellets, but in the reverse order (Ex/I3). According to the theory (Lee et al., 1987), the I3/Ex reactor should perform better than the Ex/I3 reactor. Figs. 7a,b show results at 100°C and 152 cc/min flow rate. For the I3/Ex reactor, just as at 115°C (Fig. 5a), the high-conversion regime extends past 2% CO feed concentration, while for the Ex/I3 reactor, a jump from the high to the low conversion regime occurs at less than 1.1% CO feed concentration. Thus the I3/Ex reactor gave a wider range of high conversion regime, and it also gave higher conversion when both reactors operated in the low conversion regime.

In the case of the Ex/I3 reactor (Fig. 7b), there was also a third solution branch which emanated from the low conversion regime, as the low conversion regime increased to join with the high conversion regime. As the CO feed concentration was increased, the conversion of this third branch also decreased, and finally, it jumped to the low conversion regime just like the high conversion regime, but it had a smaller jump. Experimentally, the third conversion regime was obtained by first following the low conversion regime while decreasing CO feed concentration; however, just before the low conversion regime joined with the high conversion regime, the CO feed concentration was increased instead, and the reactor then followed the third conversion regime. As a result, three stable solution branches were found in this dual-zone reactor, where two jumps occurred upon increase of CO feed concentration, one from the high to the low conversion regime, and the other from the middle to the low conversion regime.

Fig. 7c shows a simulation from the dual-zone reactor model plotted as reactor conversion vs. σ. There is a different α* for each zone because of the different catalysts used. This diagram shows features very similar to the experimental results observed in Fig. 7b, where there are three stable solution branches at intermediate values of σ. This calculation shows that the bifurcation behavior observed experimentally is also obtained qualitatively from the reactor model.

A knowledge of the theoretical results was most helpful in guiding the experimental work, since the middle stable conversion branch could be easily missed if only increasing (on the high conversion branch) and decreasing (on the low conversion branch) CO feed concentrations were investigated during the experiment. The theoretical existence of the stable middle conversion branch prompted us to study increasing CO feed concentrations also on the low conversion branch.

CONCLUDING REMARKS

An isothermal fixed-bed reactor packed with supported catalyst pellets, in which the active metal catalyst was deposited as a thin band within the support, was studied experimentally. The objective was to show that with a proper distribution of Pt metal within the catalyst pellets, and also with a proper sequence of different catalysts packed along the reactor, the overall conversion of the reactor could be improved. The oxidation of CO over Pt/alumina was used as the test reaction. Three different egg-white and one egg-shell catalysts were tested. In order to obtain constant total activity in reactors with different catalysts, dilution of the active catalyst with inert pellets was employed. Dilution of the reactor bed was also effective in order to achieve higher bed length to pellet diameter ratio with smaller amount of Pt, and to minimize nonisothermal effects.

A maximum of two steady-states were observed in the reactor packed with one type of catalyst. A 'jump' from the high conversion regime to the low conversion regime occurred when the CO feed concentration increased from zero to high conversion. As the CO feed concentration decreased, a continuous transition from the low branch to the high branch resulted generally. This is consistent with the predictions of the plug-flow reactor model. Conversion obtained from the high conversion regime changed very little for different flow rates and temperatures, which was due to mass transfer control; on the other hand, the low conversion regime was largely kinetic controlled. Oscillations were also observed frequently just before the transition from the low conversion regime to the high conversion regime. Temperature fluctuations were also observed during these oscillations, which might have actually driven the conversion to oscillate further. When comparing the performance of different catalysts, the reactor packed with 11 catalyst had the widest range of high conversion regime, while the Ex reactor had the shortest; this result was observed in all the experiments.

Reactors packed with two types of catalysts in series were also studied experimentally. Significant improvement over the single reactor was obtained. In one case, a stable intermediate conversion state was discovered; this observation shows the validity of the theoretical prediction from the dual-zone reactor of a possible third solution branch.

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NOTATION

A specific activity, Pt surface area per unit pellet volume
\( B_{in} \) Biot number for mass transfer, \( \frac{K_{g}R_{p}}{D_{e}} \)
\( D_{ac}^{*} \) Damkohler number, \( Kl (1 - \epsilon/N) \)
\( D_{e} \) effective diffusion coefficient
\( g \) dimensionless fluid phase reactant concentration with respect to the fluid feed concentration
\( k \) volume averaged reaction rate constant
\( k_{g} \) mass transfer coefficient
\( K \) adsorption equilibrium constant
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\[ L \] reactor length

\[ n \] pellet geometry; \( n = 0 \) for infinite slab, \( n = 1 \) for infinite cylinder, \( n = 2 \) for sphere

\[ R_p \] pellet dimension; half thickness for \( n = 0 \), radius for \( n = 1, 2 \)

\[ \zeta \] dimensionless location of the active catalyst within the pellet with respect to the pellet radius

\[ v \] dimensionless solid phase reactant concentration with respect to the fluid feed concentration

\[ \Omega \] velocity of fluid phase

\[ Y \] dimensionless reactor axial coordinate, \( z/\Omega \)

\[ z \] axial coordinate along the reactor

Greek Letters

\[ \alpha^* \] dimensionless group, \( \phi_0^2(\psi_n(\zeta) + 1)/Bi_{\infty}/(n+1) \)

\[ \epsilon \] void fraction

\[ \sigma \] dimensionless adsorption equilibrium constant, \( KQ_0^2 \)

\[ \phi_0^2 \] Thiele modulus, \( \phi_0^2 = kR_p^2/De \)

\[ \psi_n(\zeta) = 1 - \zeta, n = 0; = \ln(1/\zeta), n = 1; = 1/\zeta - 1, n = 2 \]

REFERENCES


TABLE 1

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<th>Characteristics of Pt/γ-Alumina Catalysts</th>
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<tr>
<td>Support: 1/8&quot; x 1/8&quot; right cylinder γ-alumina, surface area = 100 m²/gnm</td>
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<td>Pt Loading (wt %)</td>
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<td>Dispersion (%)</td>
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<td>A (cm²/cm³)</td>
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<td>Thickness of Catalyst Band (cm)</td>
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Fig. 1: Cross-sections of the four catalysts studied.

Fig. 2: Bifurcation set of the solid-fluid interaction equation (eqn 2) in the $\alpha^* - \sigma$ space.

Fig. 3: Typical bifurcation diagram of reactor conversion vs $\sigma$ which exhibits multiplicity. ($\alpha^* = 220$, $Da^* = 500$).

Fig. 4: Experimental results. I3 ($\bar{s} = 0.27$) reactor at (a) $100^\circ$C and (b) $115^\circ$C; (c) I2 ($\bar{s} = 0.5$) reactor at $115^\circ$C; (d) Ex ($\bar{s} = 1$) reactor at $115^\circ$C.

Fig. 5: Comparison of the four single-zone reactors at $115^\circ$C and 152 cc/min flow rate. (a) Ex and I3, (b) I2 and I1. In (a), results for the dual-zone (I3/Ex) reactor are also shown.

Fig. 6: Model simulation of temperature variation in the reactor; curve (a) $\alpha^* = 150$, $Da^* = 400$, curve (b) $\alpha^* = 250$, $Da^* = 600$.

Fig. 7a,b: Comparison of the (a) I3/Ex and (b) Ex/I3 dual-zone reactors at $100^\circ$C and 152 cc/min flow rate.

Fig. 7c: Model simulation of a dual-zone reactor [$\alpha^*$ (first zone) = 300, $\alpha^*$ (second zone) = 200, $y_1 = 0.8$, $Da^* = 500$] to show the bifurcation phenomena observed in Fig. 7b.