Coking and Activity of Porous Catalysts in Supercritical Reaction Media

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A mathematical model is presented to describe coking and activity characteristics of porous catalysts in supercritical reaction mixtures. These characteristics are determined by the way in which temperature and pressure affect the simultaneous physicochemical rate processes involving the effective diffusion of reactants in the pore, coke formation, and coke extraction. For a parallel coking reaction, the model predicts that when the reaction mixture density is isothermally increased from subcritical to low-to-moderate values, the ensuing higher reaction rates and restricted diffusion lead to pore-mouth plugging and decreased catalyst effectiveness factors. At dense supercritical conditions, however, the enhanced coke solubilities in the reaction mixture alleviate pore-mouth restrictions, resulting in a recovery of catalyst activity and increased effectiveness factors. The model predicts an optimum supercritical density at which catalyst activity is maintained at a maximum value. At smaller than optimum density values, the reaction rate is limited by coke extraction and at larger than optimum values, the rate is subject to pore diffusion limitations. These predictions are qualitatively consistent with reported experimental observations.

Introduction

Many catalytic hydrocarbon reactions (such as the catalytic reforming of naphthas to produce gasoline) are accompanied by simultaneous formation of undesirable heavy hydrocarbons or "coke." The primary reasons for coke buildup are the relatively low volatilities of the coke compounds that are formed and the low subcritical densities (and hence low coke solubilizing power) of the gas-phase reaction mixture. The coke buildup eventually plugs the pores of the support matrix, in which the catalyst particles reside, and causes total deactivation of the catalyst. Detailed reviews on the subject of coke formation on metal catalysts may be found elsewhere (Gates et al., 1979; Franck and Martino, 1985; Biswas et al., 1988; Butt and Petersen, 1988; Bartholomew and Butt, 1991).

In recent years, supercritical reaction media have been employed to extract heavy hydrocarbon or coke compounds *in situ* from porous catalysts (Tiltscher et al., 1981; Saim and Subramaniam, 1990; Yokota and Fujimoto, 1991; Adschiri et al., 1991). Supercritical fluids (SCFs) display unique solvent and transport properties. While the SCF solvent has liquid-like density and solvent power, the diffusivity and viscosity are more gas-like. The increased desorption of heavy hydrocarbons in dense supercritical reaction mixtures has been exploited to control both catalyst activity and product selectivity. Tiltscher et al. (1981) demonstrated that it is indeed possible to extract heavy hydrocarbon byproducts *in situ* with supercritical reaction mixtures and thereby maintain catalyst activity. One of the reactions they studied was the *cis-/trans*-isomerization of 1-hexene on a low surface area (5 m^2/g), low activity, α-Al_2O_3/Al metal catalyst. Low surface area catalysts are macroporous in nature with pore sizes in the order of thousands of angstroms. Restricted diffusion of reactants in macropores is not a major concern. In sharp contrast, industrial catalysts are often micro- to mesoporous with a majority of the surface area resident in pores of diameter 100 Å or less. Configurational diffusion effects in liquid-filled pores are known to be significant when the effective size of the diffusing solute is one-tenth the size of the pore (Lee et al., 1991). It seems plausible that the increased viscosity and decreased solute diffusivity in near-critical reaction mixtures in combination

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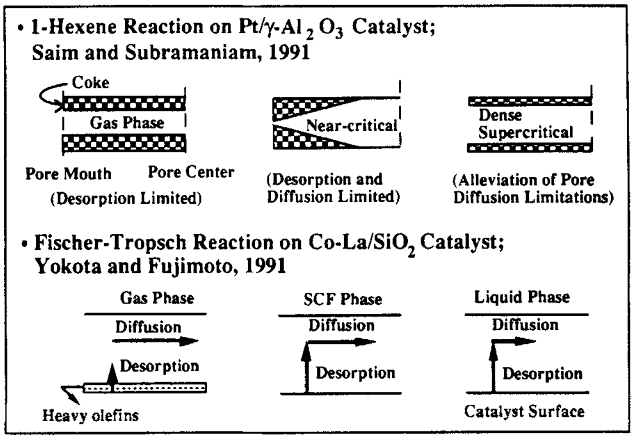

Figure 1. In situ extraction of heavy hydrocarbons in subcritical and supercritical reaction mixtures.

with increased coke deposition rates at the higher pressures can cause restricted diffusion in micro- to mesoporous catalysts. On such catalysts therefore, the reaction rates may actually be lowered at supercritical conditions relative to subcritical conditions.

Our research group has been investigating 1-hexene reaction at subcritical and supercritical conditions on a porous, high-activity industrial Pt/γ-Al$_2$O$_3$ catalyst with a surface area of nearly 200 m^2/g. The reaction mixture (consisting of 1-hexene and product isomers) was employed as the solvent medium to extract the coke compounds. As shown in Figure 1, the reaction rate is limited by desorption of the coke compounds at subcritical conditions, and hence 1-hexene conversion decays with time. As the reactor pressure is isothermally increased to yield low to moderate supercritical densities, the reaction rates increase and the diffusion rates in the pore decrease. Hence, the reactions and coke buildup are confined to the vicinity of the catalyst pore mouth. This preferential coke buildup eventually leads to pore-mouth plugging and *indirect* suppression of the active sites in the pore. The decrease in coke laydown, yet a rather abrupt loss of activity observed at near-critical densities, is consistent with catalyst deactivation by indirect site suppression. When the reactor pressure is further increased, the dense supercritical reaction mixture is able to solubilize the coke compounds and thereby alleviate pore mouth restrictions. Analysis of the reactor effluent revealed the presence of alkylated mononuclear and polynuclear aromatics in yields that are typical of coke formation. The extraction of these "soluble" coke compounds leads to an increase in reaction rates *and* a longer sustainment of catalyst activity as compared to subcritical conditions. The pore-mouth plugging at near-critical densities and pore-mouth opening in dense reaction mixtures are corroborated by coked catalyst characteristics such as coke laydown, BET surface area, pore volume, and pore volume distribution (Saim and Subramaniam, 1991).

As shown in Figure 1, Yokota and Fujimoto (1991) were able to demonstrate a better balance between desorption (more liquid-like) and diffusion (intermediate between a gas and a liquid) when Fischer-Tropsch synthesis was carried out using supercritical *n*-hexane as the reaction medium. The "well-balanced" desorption and diffusion in the supercritical phase result in increased reaction rates *and* enhanced activity maintenance as compared to either gas-phase or liquid-phase reaction media. Based on their study of the catalytic reforming of coal tar pitch in a supercritical fluid, Adschiri et al. (1991) also report that there should exist optimum supercritical operating conditions for high reaction rates and low coke deposition. The optimum density for activity maintenance, however, is not reported in either study.

It is clear from the referenced studies that the physical buildup of coke and the mechanism of deactivation (active site suppression *vis-a-vis* indirect suppression by pore plugging) depend on the relative rates of the physical and chemical processes underlying coke formation and simultaneous extraction. Temperature and density of the reaction mixture affect the coke formation rate, the effective diffusivity of the reactants in the pore, and the solubility of the coke compounds in the reaction mixture. To gain a better understanding of the physicochemical processes that dictate coking and activity of porous catalysts in supercritical reaction mixtures, a single-pore model is developed in this article.

The model predicts that the coke formation rate actually increases with coke extraction and that activity maintenance is achieved whenever the coke extraction rate equals the coke formation rate. The predicted variations of activity and coke buildup with reaction mixture density are qualitatively consistent with our experimental observations summarized in Figure 1. Furthermore, as hypothesized by Yokota and Fujimoto (1991) and by Adschiri et al. (1991), the model also predicts that there exists an optimum density at which catalyst activity is maintained at a maximum value. At smaller than optimum density values the reaction rate is limited by coke extraction, and at larger values the rate is limited by pore diffusion limitations. Model limitations and possible improvements are also discussed.

Model Development

Existing models for catalyst coking (Masamune and Smith, 1966; Haynes and Leung, 1983) are extended to describe coke deposition with simultaneous extraction. An isolated, cylindrical, isothermal catalyst pore is considered as shown in Figure 2. It was deemed that phenomenological information is more easily obtained from modeling this simplified geometry rather than the more complex pore structure in an individual pellet. Model assumptions are as follows:

- External mass-transfer limitations and radial concentra-

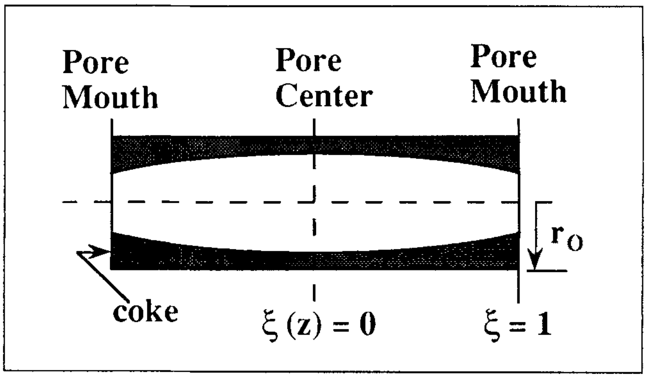

Figure 2. Pore model.

tion gradients in the pore are neglected as being insignificant. The latter assumption implies that transport of reactants to the catalyst surface through the porous coke layer is not rate-limiting.

- Coke forms via a parallel first-order irreversible reaction.
- The consumption of reactant A by the coke formation reaction is neglected as insignificant in the material balance for the main reactant. This is justifiable because experimentally observed yields of coke are two to three orders of magnitude lower than the yield of the isomers (Saim, 1990). For the latter reason, the main reactant (A) concentration profiles in the pore are assumed to develop rapidly relative to the coke growth rate (the so-called pseudo-steady-state assumption).
- The extraction of coke from the catalyst surface is described by an effective desorption rate constant.
- The amount of extracted coke neither significantly affects the reaction mixture density nor exceeds the solubility limits of the coke in the reaction mixture. This assumption is justified since only up to 0.50 wt. % of heavy hydrocarbons (C_{12}-C_{30} compounds) was observed in the reactor effluent during the isomerization of 1-hexene over a $Pt/\gamma\text{-}Al_2O_3$ catalyst at the highest supercritical density studied (Saim, 1990).
- All molecules are treated as hard spheres. The diffusion rate of the extracted coke molecules out of the pore is assumed to be fast as compared to the coke formation rate on the catalyst. In other words, the concentration profile of the extracted coke molecules is established rapidly relative to the coke growth so that there is no accumulation of the extracted coke in the fluid phase in the bulk. This assumption while valid at early times, is questionable when the pore is near plugging. Nevertheless, the qualitative trends predicted by the model should not be affected. Moreover, for catalyst activity maintenance, conditions that would lead to pore plugging are to be avoided.

The reactions are represented as follows:

$$A->B \quad \text{(main reaction)}$$

and

$$A->W \quad \text{(coking reaction)}$$

where A is the reactant, B the product, and W the surface coke. Since coke laydown results in a decrease in the activity of the catalyst, a linear activity function having the following form is included in the rate expressions.

$$a = 1-(W/W_S) \tag{1}$$

The rate expressions for the reaction of $A\,(-r_A)$ and the formation of coke on the surface (r_W) are as follows:

$$-r_A = a\,k_A\,C_A \tag{2}$$

$$r_W = a\,k_W\,C_A \tag{3}$$

The rate of extraction of the coke compounds from the catalyst surface is described by:

$$r_C = k_C\,W \tag{4}$$

where k_C is the effective desorption rate constant.

If D_i^e is defined as the effective diffusivity of species i, then the pore mass balances on the reactant (A) and the surface coke (W), respectively, yield:

$$\frac{\partial}{\partial z}\left(D_A^e\frac{\partial C_A}{\partial z}\right) - a(\rho_{\text{cat}}k_A)C_A = 0 \tag{5}$$

$$\frac{\partial W}{\partial t} = a\left(\frac{M_w k_w}{S_0}\right)C_A - k_C\,W \tag{6}$$

The boundary and initial conditions are as follows:

$$C_A(\pm L,\, t) = C_A^o \tag{7}$$

$$\frac{dC_A}{dz}(0,\, t) = W(z,\, 0) = 0 \tag{8}$$

The relationships among the coke laydown, the effective radius of the pore, and the effective diffusivity at any time are similar to those employed by Haynes and Leung (1983). The diffusivity depends on the effective radius of the pore, which in turn depends on the coke laydown at a position in the pore. The effective radius, r, is related to the initial radius, r_0, and the coke density, ρ_w, by the relation:

$$r^2 = r_0^2 - (2r_0W/\rho_W) = r_0^2 - (\alpha r_0^2\psi) \tag{9}$$

The effective diffusivity of i at any time, D_i^e, is related to the initial effective diffusivity, D_i^0, and the radius of molecule i, r_m, by the following relation:

$$\frac{D_i^e}{D_i^0} = \left(\frac{1-r_m/r}{1-r_m/r_0}\right)^4\left(\frac{r}{r_0}\right)^2 \tag{10}$$

A similar correlation was employed by Erkey and Akgerman (1990) to describe the effective diffusivity of naphthalene dissolved in supercritical carbon dioxide in alumina pores and by Biswas and Do (1987) to describe the effective diffusivity of gases in porous reforming catalysts that are subject to coke formation upon reaction.

The dimensionless forms of the material balance equations are as follows:

$$\frac{\partial}{\partial\xi}\left(\left(\frac{1-\lambda}{1-\lambda_0}\right)^4\left(\frac{\lambda_0}{\lambda}\right)^2\frac{\partial\zeta_A}{\partial\xi}\right) - a\,\phi^2\,\zeta_A = 0 \tag{11}$$

$$\frac{\partial\psi}{\partial\tau} = a\left(\frac{\phi_w^2}{\beta_0}\right)\zeta_A - \left(\frac{D_C^0}{D_A^0}\right)\phi_C^2\,\psi \tag{12}$$

with dimensionless boundary and initial conditions as follows:

$$\zeta_A(1,\tau) = 1 \tag{13}$$

$$\frac{d\zeta}{d\xi}(0,\tau) = \psi(\xi,0) = 0 \tag{14}$$

An alternate form of Eq. 12 is:

$$\frac{\partial\psi}{\partial\left(\tau\frac{\phi_w^2}{\beta_0}\right)}=a\,\zeta_A-\left[\left(\frac{D_C^0}{D_A^0}\right)\phi_C^2\Big/\left(\frac{\phi_w^2}{\beta_0}\right)\right]\psi \tag{15}$$

The dimensionless pore radius is given by:

$$\lambda=\lambda_0/\sqrt{1-\alpha\psi},\ \alpha\psi\le 1-\lambda_o^2 \tag{16}$$

Note that the term ($\tau\phi_w^2/\beta_0$) in Eq. 15 represents a modified form of dimensionless time. The dimensionless parameter $P=\phi_C^2(D_C^0/D_A^0)/(\phi_w^2/\beta_0)$ is an "extraction" parameter and provides a measure of the coke extraction rate relative to the coke formation rate on the catalyst. Clearly, our model should reduce to: the Haynes and Leung model (1983) when $P=0$; the Masamune and Smith model (1966) when $P=0$ and $\alpha=0$. The reliability of our model simulations may thus be readily verified.

Other dimensionless parameters that characterize the problem include the Thiele (diffusion-reaction) modulus (ϕ) and the pore-accessibility factor (α). The parameter α may be viewed as a relative measure of deactivation by active site suppression *vis-a-vis* pore-mouth plugging. If $\alpha<1$, the coke is dense enough to fully deactivate the pore before pore-mouth plugging can occur. If $\alpha\ge 1$, the pore mouth can plug in the absence of extraction at sufficiently large values of Thiele modulus.

Results and Discussion

The dimensionless equations (Eqs. 11, 15, and 16) along with the initial and boundary conditions (Eqs. 13 and 14) were solved by a modified Crank-Nicholson scheme developed by Douglas (1958, 1961) and described by von Rosenberg (1969). The pseudo-steady-state equations describing the main reaction are cast into the form:

$$\frac{d^2\zeta_A}{d\xi^2}-F\frac{d\zeta_A}{d\xi}-G\zeta_A=0 \tag{17}$$

where

$$F=\left(\frac{4}{1-\lambda}+\frac{2}{\lambda}\right)\frac{d\lambda}{d\xi} \tag{18}$$

$$G=\phi^2\left(\frac{\lambda}{\lambda_0}\right)^2\left(\frac{1-\lambda_0}{1-\lambda}\right)^4(1-\psi) \tag{19}$$

Equation 17 is cast into finite-difference form, where F and G are evaluated at a time between successive time steps. The resulting equations are then solved and the ζ values obtained for the new time step are used to solve for ψ at the new time step. The effectiveness factor is then evaluated. The effectiveness factor is defined as the reaction rate in the presence of catalyst deactivation by coking to that in the absence of coking *and* transport limitations, and is given by:

$$\eta=\frac{D_A^e(L,t)\,\frac{\partial C_A}{\partial z}(L,t)}{L\,\rho_{\text{cat}}\,k_A\,C_A^0} \tag{20}$$

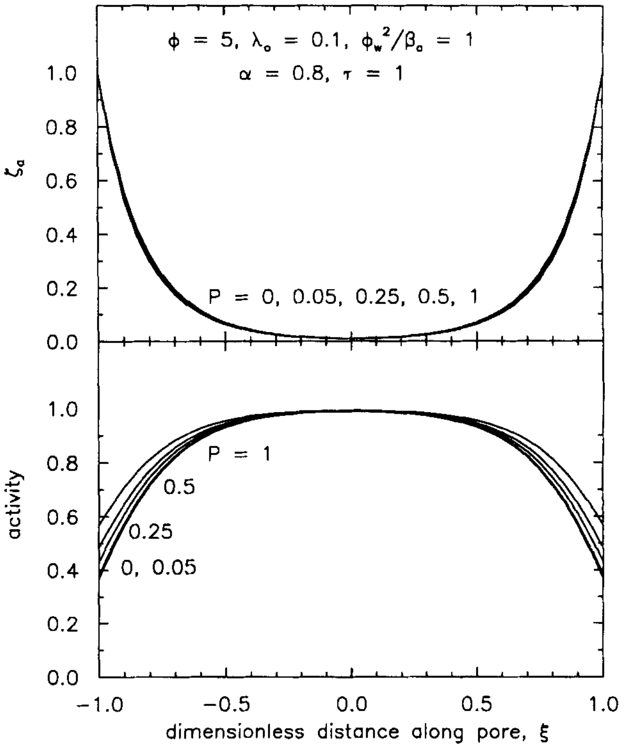

Figure 3. Effect of simultaneous coke extraction on early concentration and activity profiles.

The effects of concurrent coke extraction on the temporal—(a) catalyst activity profiles, (b) reactant concentration profiles, (c) coke growth and coke extraction rates, (d) coke laydown profiles, and (e) the catalyst effectiveness factor—are simulated for varying degrees of coke extraction. In addition, the model was also employed to predict temporal catalyst effectiveness factor and coke laydown behavior with isothermal increases in pressure.

Activity and concentration profiles

Figure 3 demonstrates the effect of coke extraction on the concentration and activity profiles within the pore for a given time ($\tau=1$) and for pore accessibility parameter (α) value equal to 0.8. The rather steep gradients in the main reactant concentration with very little reaction in the center of the pore are due to pore-diffusion limitations (initial Thiele modulus $\phi=5$). Since coke formation depends on the main reactant concentration, the corresponding activity profiles display a maximum at the center of the pore. As expected, increased coke extraction (that is, increasing P values) results in increased activities, with the maximum increases occurring at either pore mouth.

Figures 4a and 4b show the concentration and activity profiles for $\tau=4.5$ and α values of 0.80 and 1.0, respectively. At the later time, the coke formation rate continues to be greater than the coke extraction rate (see Figure 5), resulting in continued buildup of coke. However, there are more marked differences in the activity profiles upon coke extraction as compared to those at the earlier time ($\tau=1$). As the propensity for pore-mouth plugging increases (that is, at larger α values), the pore-diffusion limitations increase rather rapidly with coke buildup, resulting in steeper concentration profiles (see Figure

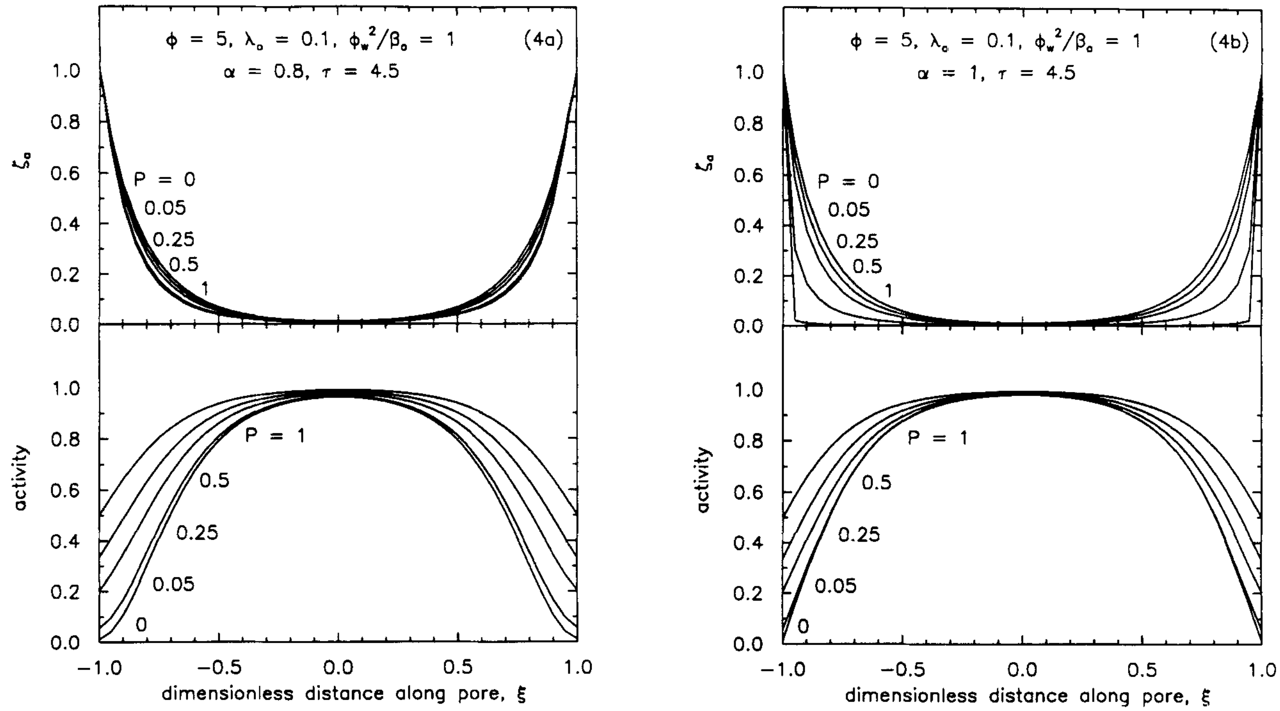

Figure 4. Effect of simultaneous coke extraction on concentration and activity profiles.

4b). For $\alpha = 1.0$, note that the extraction of the coke compounds alleviates pore-mouth choking by widening the pore mouth and thereby sustains catalyst activity for longer periods of time.

Coke formation and extraction rates

Figure 5 demonstrates the effect of the extraction parameter on the temporal coke growth and coke extraction rates at the pore mouth. In the absence of extraction, the coke growth rate continuously decreases with time due to catalyst deactivation. For $\alpha = 0.8$, coke growth ceases when the active sites in the pore are fully deactivated. For $\alpha = 1.0$ and $\alpha = 1.5$, the coke growth rate declines rapidly and ceases rather abruptly beyond the discontinuity (Figure 5), where the effective pore radius approaches the molecular radius. The point of discontinuity corresponds to the occurrence of pore-mouth plugging resulting in total deactivation of the catalyst by *indirect site suppression*.

When coke extraction occurs, the coke growth rate increases due to an increase in catalyst activity ($a = 1 - \psi$). When the extraction rate is high enough to prevent the catalyst from total deactivation either by active site suppression or by pore-mouth plugging, the extraction and coke growth rates eventually become equal; thereafter, the pore maintains constant activity. Note in Figure 6 that the effectiveness factor reaches a steady state when the coke growth and extraction rates equal each other.

The model predicts that pore-mouth plugging can be not only delayed, but actually prevented, by a high enough extraction rate. For $\alpha = 1.5$, it is apparent from Figure 5 that pore-mouth plugging is delayed in the presence of extraction. For $\alpha = 1.0$, while the pore mouth plugs in the absence of extraction, it is possible to avert pore-mouth plugging and maintain catalyst activity even with an extraction parameter as low as 0.05. Even when pore-mouth plugging is not a possible deactivation mechanism (as in the case where $\alpha = 0.80$), concurrent coke extraction proves useful in significantly improving the catalyst effectiveness factors, as shown in Figure 6. When

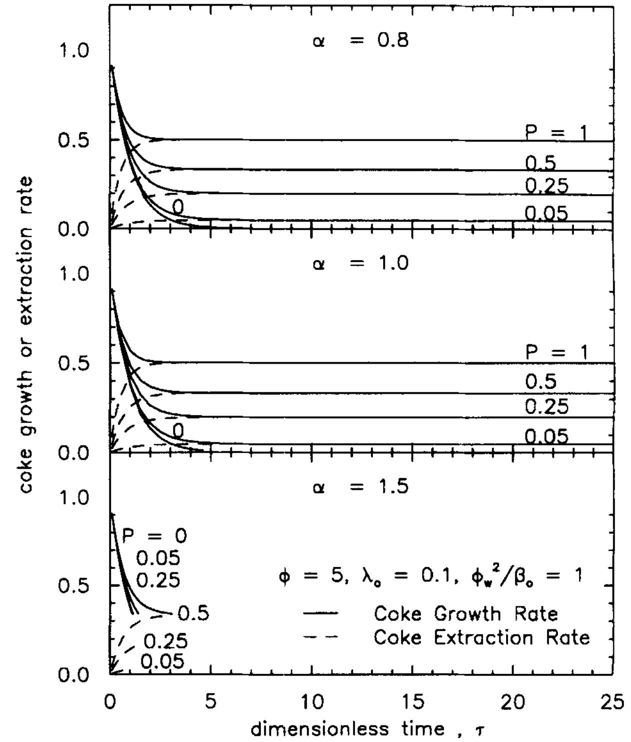

Figure 5. Effect of extraction on temporal coke growth and extraction rates.

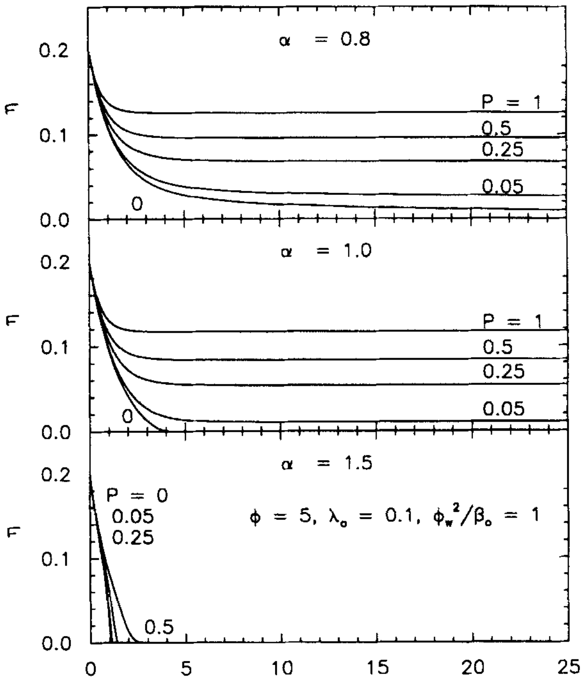

Figure 6. Effect of extraction on temporal catalyst effectiveness factor, τ.

$\alpha = 0.80$, there is a greater than tenfold increase in catalyst effectiveness factor at extraction parameter values of one. As discussed later, these extraction parameter values are indeed practically achievable.

Coke laydown profiles

The temporal coke laydown profiles provide a clear picture of catalyst deactivation by either active site suppression or pore-mouth plugging at the various reaction mixture densities. Figures 7a-7c demonstrate the effect of extraction on coke laydown profiles for $\alpha = 0.8$, 1.0 and 1.5, respectively. For $\alpha = 0.8$ and *no* extraction $[\phi_C^2\ (D_C^0/D_A^0) = 0]$, the simulated coke laydown profiles are identical to those reported by Haynes and Leung (1983). The increased extraction serves to widen the pore mouth, and the resulting coke laydown profiles eventually reach a steady state. The time at which steady state occurs corresponds to the time at which the coke growth and extraction rates become equal (Figure 5) or equivalently when the effectiveness factor becomes constant (Figure 6). With increased extraction, the coke buildup is primarily confined to the vicinity of the pore mouth with an inert inner section. This is reflected in the approximately tenfold increase in the steady-state effectiveness factor. Note that while the general trend of coke buildup is from the pore mouth to the pore center, the amount of the buildup depends on the magnitude of the extraction parameter.

Figure 7b illustrates the prevention of pore plugging with extraction for an α value of 1.0. Although the temporal coke laydown pattern does not change, the amount of coke laydown at a given time decreases as the extraction parameter increases. For $\alpha = 1.5$, while pore-mouth plugging is not prevented, it is indeed delayed by the concurrent extraction of coke.

In the foregoing sections, it has been demonstrated that for parallel coking, extraction significantly enhances catalyst activity by reducing coke laydown. The greatest loss of activity occurs during early times, when the catalyst activity is at its maximum and the coke growth rate is near its maximum. As coke extraction occurs, the catalyst activity and therefore the coke growth rate are prevented from continually declining. When the coke growth rate equals the extraction rate, the effectiveness factor and coke laydown profiles reach a steady state. For $\alpha \geq 1$, the pore mouth may plug before this steady state is reached. In all cases, however, it is possible to maintain catalyst activity for longer periods of time in the presence of extraction. The uniform buildup of coke in the pore under kinetically controlled main reaction rate and the progressive buildup of coke from the pore mouth to the center under diffusion-controlled main reaction rate are consistent with a parallel coking mechanism.

Prediction of catalyst effectiveness factor and coke buildup profiles at various reaction mixture densities

The coking of Pt/γ-Al_2O_3 catalyst in 1-hexene/product iso-

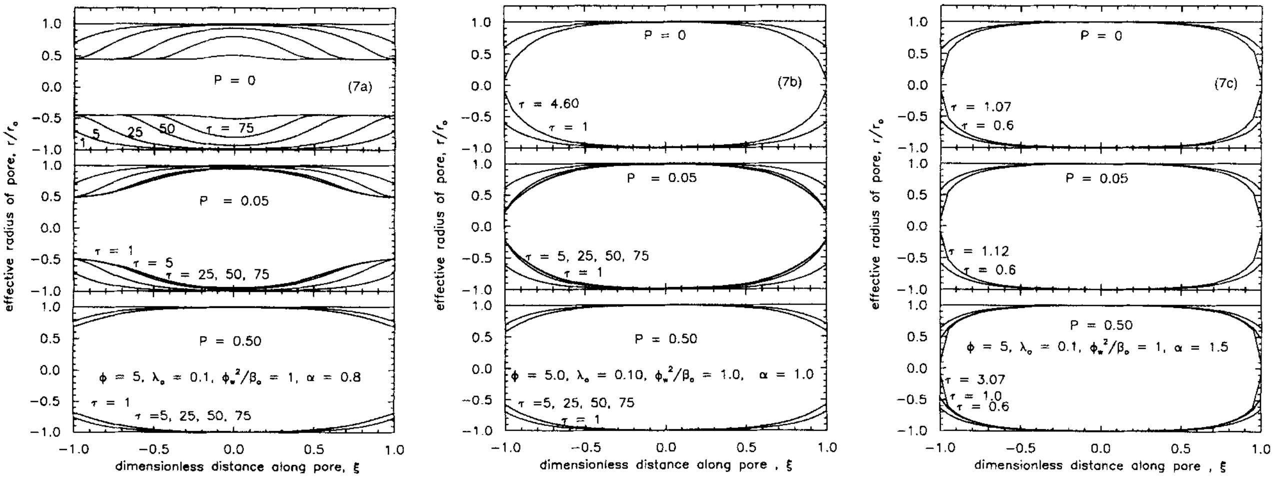

Figure 7. Effect of extraction on temporal coke laydown profiles in the pore.

Table 1. Physical and Thermodynamic Property Data Used in the Simulations

Property	Value	Source*
Z_c	0.26	(a)
T_c	504.0 K	(a)
P_c	31.7 bar	(a)
v_c	$350\ \mathrm{cm^3 \cdot mol^{-1}}$	(a)
ρ_c	$0.24\ \mathrm{g \cdot cm^{-3}}$	(b)
T (triple point)	113.4 K	(c)
v_0	$104.4\ \mathrm{cm^3 \cdot mol^{-1}}$	(d)
W_s	$2.37 \times 10^{-7}\ \mathrm{g \cdot cm^{-2}}$	(e)
r_0	30 Å	(e)
ρ_w	$0.52\ \mathrm{g \cdot cm^{-3}}$	(b)
ρ_{cat}	$1.19 \pm 0.14\ \mathrm{g \cdot cm^{-3}}$	(f)
k_A	$2.46 \times 10^3 \exp(-16.63/RT)\mathrm{m^3 \cdot g\ cat^{-1} \cdot h^{-1}}$; T in K, R in $\mathrm{kcal \cdot mol^{-1} \cdot K^{-1}}$	(b)
L	0.0709 ± 0.0073 cm	(f)
S_0	$140\ \mathrm{m^2 \cdot g\ cat^{-1}}$	(b)
M_w	$128.74\ \mathrm{g \cdot mol^{-1}}$	(a)
k_w	$0.33\ \mathrm{cm^3 \cdot g\ cat^{-1} \cdot h^{-1}}$ at 238°C	(e)
r_m	2.95 Å	(g)
V	$300\ \mathrm{cm^3}$	(b)
v	$209\ \mathrm{cm^3 \cdot h^{-1}}$	(b)

* (a) Reid et al. (1987); (b) Saim (1990); (c) McCullogh et al. (1957); (d) calculated from Batschinski (1913); (e) calculated from data of Saim (1990); (f) measurements on Engelhard E-302 Catalyst used by Saim (1990); (g) calculated by method of Bondi (1964).

mer reaction mixtures at 238°C ($1.01 T_c$) was simulated. The temporal catalyst effectiveness factor and coke buildup profiles at various reaction mixture densities were predicted with the model. Table 1 lists the values of the physicochemical property and rate data corresponding to the chosen system and operating conditions. Since more than 70% of the aged Pt/γ-Al_2O_3 catalyst surface area resides in pores with diameter 100 Å or less, a 60-Å-diameter pore was chosen for modeling purposes. The bulk reaction mixture composition was assumed to be constant with 1-hexene comprising 95% of the mixture, and 2- and 3-hexenes comprising the other 5%.

The effective molecular radius of 1-hexene was calculated by determining the molecular volume via the method of Bondi (1964). Because the physical properties of the hexenes are similar, and the extracted coke compounds were in such low concentrations, the diffusivity of 1-hexene in the reaction mixture is well approximated by the self-diffusivity of 1-hexene. The correlation of Lee and Thodos (1983), which was obtained by fitting data in both supercritical and subcritical regimes, was used in the bulk diffusivity estimation. The solid volume at the triple point was determined using the correlation of Sharma (1980) as described by Lee and Thodos (1983). To use this correlation, an intrinsic volume, v_o, described by Hildebrand (1971) and Hildebrand and Lamoreaux (1972), had to be found. Hildebrand notes that v_o corresponds to the value of $M_W \omega$, which is well approximated by the sum of the volumes of the component atoms of the molecule (Batschinski, 1913). The value of v_o needed for calculating the solid volume was determined by summing the volumes of the component molecules.

Coke compounds formed from olefinic precursors are often polynuclear aromatic hydrocarbons (Myers et al., 1961; Appleby et al., 1962). In this work, naphthalene was chosen as the representative coke compound. The coking rate constant, k_W, was estimated from data on the composition of the product stream (Saim, 1990), assuming the coke extraction rate to be equal to the formation rate at the highest density investigated ($2.53\ \rho_c$). The value of the mass of coke per unit surface area at total deactivation, W_S, is of the same order as reported by Biswas and Do (1987).

Due to a lack of sufficient data on the solubility and effective desorption constants for supercritical hexene-naphthalene-Pt/γ-Al_2O_3 systems, the adsorption equilibrium constant (K_A) data of Erkey and Akgerman (1990) for the CO_2-naphthalene-Al_2O_3 system were used to obtain the effective desorption coefficient k_C. Implicit is the assumption that K_A values for 1-hexene are similar to that for CO_2 at similar reduced densities and reduced temperatures. The K_A values reported by Erkey and Akgerman (1990) at a reduced CO_2 temperature of 1.01 was correlated with reduced density as follows:

$$\ln(K_A) = a + b\rho_r \tag{21}$$

The effective desorption coefficient k_C is approximately given as follows:

$$k_C = 1.0/[K_A \rho_{\mathrm{cat}} (V/v)] \tag{22}$$

The values of V and v correspond to the reactor volume and the effluent flow rate (Saim, 1990). Because the reported K_A values are based on particle density, it is necessary to multiply the K_A values by the density of the catalyst particles in the system being modeled. Since $[\rho_{\mathrm{cat}} (V/v)]$ is of order unity, the variation of k_C with reaction mixture density is dictated primarily by the corresponding variation in K_A.

The model was employed to predict temporal catalyst effectiveness factor and coke buildup profiles corresponding to the parameter values summarized in Table 2 for various reaction mixture densities. Note that the initial Thiele modulus and extraction parameter increase with density. Since $\alpha > 1$, the pore mouth can plug and cause indirect site suppression at sufficiently large values of Thiele modulus. Figure 8 shows the variation of effectiveness factor (defined as the reaction rate in the presence of deactivation relative to that in the absence of deactivation *and* transport limitations) vs. reduced

Table 2. Parameter Values Used to Simulate Pt/γ-Al_2O_3 Catalyst Activity at 238°C in Subcritical and Supercritical Reaction Mixtures

Parameter	Reduced Density			
	$\rho_r=0.45$	$\rho_r=1.56$	$\rho_r=2.01$	$\rho_r=2.53$
λ_0	0.098	0.098	0.098	0.098
α	3.043	3.043	3.043	3.043
ϕ_o	0.59	1.09	1.33	1.78
$P=\phi_c^2(D_c^0/D_A^0)/(\phi_w^2/\beta_0)$	0.31×10^{-6}	0.480	1.04	2.68

density for two early dimensionless times. The dimensionless time parameter is normalized with respect to the reduced density to ensure that the pores are being viewed at the same real time. Note that as reduced density increases, the effectiveness factors first decrease, pass through a minimum, and then increase.

At the subcritical density ($\rho_r=0.45$), there is virtually no coke extraction ($P\approx0$). Furthermore, the initial Thiele modulus of 0.59 indicates that the main reaction is in a transition between surface reaction rate control and pore-diffusion control. Consequently, coking occurs more or less uniformly in the pore as shown in the inset. As the density is increased into the supercritical region ($\rho_r=1.56$), the increase in coke extraction is offset by the accompanying increase in coke formation rate and a decrease in the effective diffusivity of the reactant molecules. This introduces pore-diffusion limitations (initial $\phi=1.09$) and the effectiveness factor decreases. Note that coke buildup occurs preferentially near the pore mouth, eventually resulting in total deactivation by pore mouth plugging. A further increase in density to 2.01 ρ_c aggravates the pore-diffusion limitations (initial $\phi=1.33$). The concomitant increase in extraction parameter ($P=1.04$) is not sufficient enough to thwart pore-mouth plugging. However, at a density of 2.53 ρ_c, the increase in the coke extraction parameter ($P=2.68$) alleviates pore-diffusion limitations due to catalyst coking and thwarts pore-mouth plugging. This results in a recovery of catalyst activity and an increase in catalyst effectiveness factor.

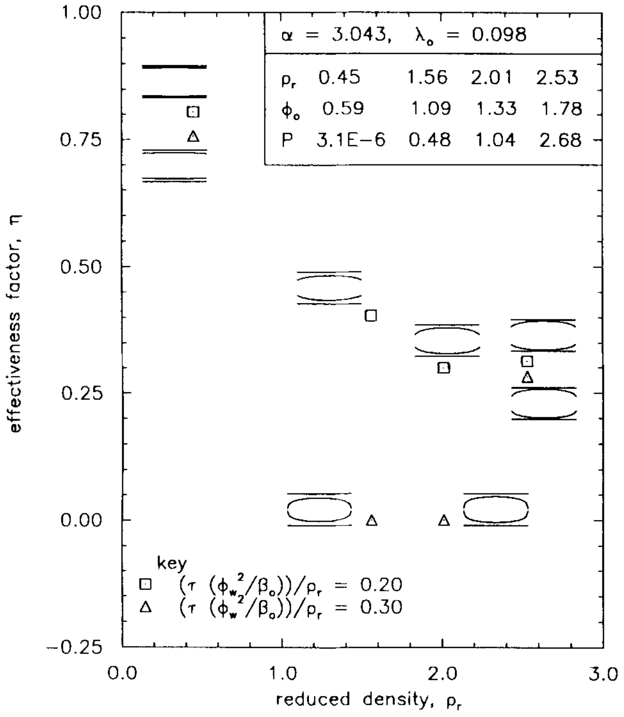

Figure 8. Variation of early catalyst effectiveness factor and corresponding coke laydown profile with reduced density.

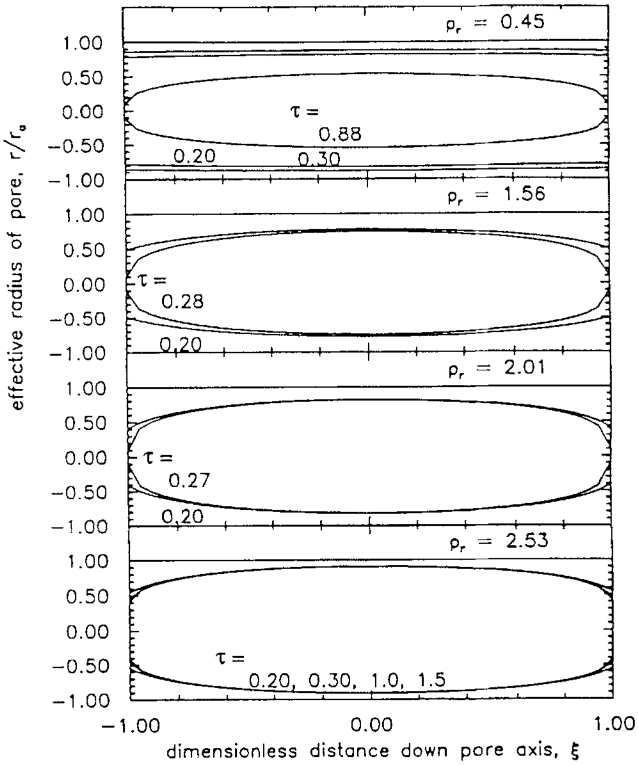

Figure 9. Temporal coke laydown profile in the pore at various reduced densities.

Parameter values are summarized in Table 2.

As shown in the immediate vicinity of each plotted point in Figure 8, the coke laydown pattern in the pore changes with increasing reduced density, going from flat layers of coke deposition ($\rho_r=0.45$) to high coke concentrations near the pore mouth ($\rho_r=1.56$) to laydown in a pore that has been widened by coke extraction ($\rho_r=2.53$). The qualitative trends of effectiveness factor versus reduced density *and* the physical coke buildup in the pore at the various densities are consistent with those reported previously (Saim and Subramaniam, 1991). It may therefore be also concluded that the observed coking of the Pt/γ-Al_2O_3 catalyst in 1-hexene/product isomer reaction mixtures occurs by a predominantly parallel coking reaction.

The temporal coke laydown profiles at the four reduced densities are seen more clearly in Figure 9. While total deactivation by pore-mouth plugging occurs at the lower three densities, pore-mouth plugging is averted at the highest density where the coke laydown profile attains a steady state with a finite catalyst activity. Hence, the temporal effectiveness factor profiles eventually become invariant with time (see Figure 10). Note that increased pore-diffusion limitations cause the pore mouth to plug roughly three times faster in 1.56 ρ_c and 2.01 ρ_c reaction mixtures as compared to subcritical reaction mix-

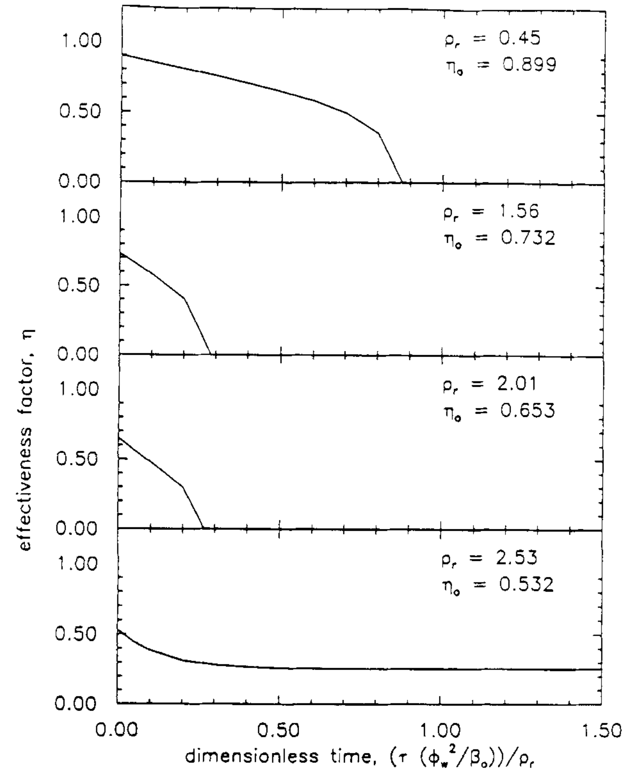

Figure 10. Temporal variation of catalyst effectiveness factor at various reduced densities.

Parameter values are summarized in Table 2.

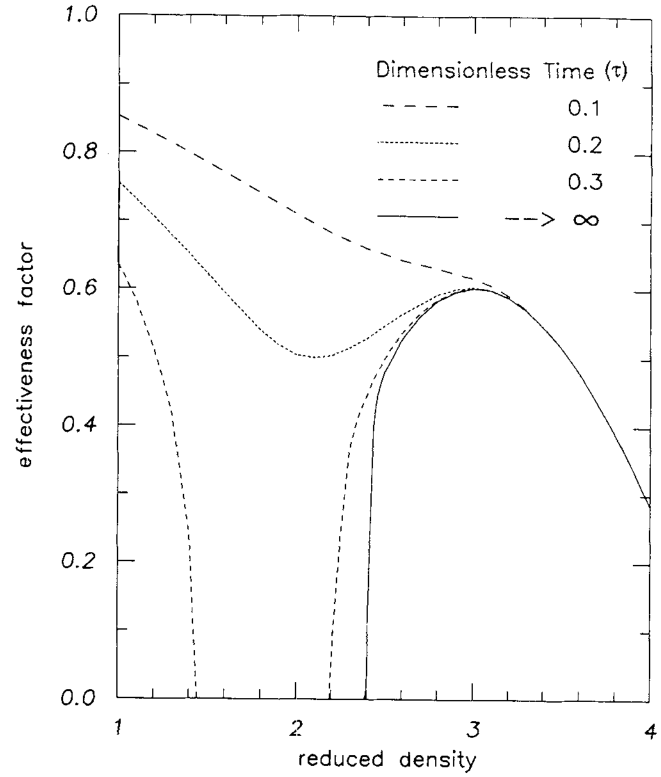

Figure 11. Variation of temporal catalyst effectiveness factor with reaction mixture density.

Parameter values are summarized in Table 2.

ture. Furthermore, the amount of coke laydown is generally lower in the pores which plugged rapidly. As seen in Figure 10, pore-mouth plugging is accompanied by an abrupt loss of activity leading to total deactivation.

The activity and coke laydown at various reaction mixture densities are dictated by the values of the dimensionless groups that characterize the problem: the Thiele modulus (ϕ), the pore-accessibility factor (α), and the extraction parameter (P). Hence, the effect of uncertainties in parameter values (Table 1) on model simulation may be inferred from how these parameters affect the magnitude of the dimensionless groups. Two necessary (but *not* sufficient) conditions for observing the minimum in activity vs. density are the possibility of pore plugging ($\alpha \geq 1$) *and* the existence of pore diffusion limitations (initial $\phi > 0.3$). The additional requirement is the recovery of catalyst activity at the higher densities due to increased values of the coke extraction modulus (P). Except for the value of pore diameter, all other values in Table 1 are reliable for the system under study, either taken from the literature or obtained experimentally by us. Assuming 10% uncertainty in each of the variables affecting the Thiele modulus, the corresponding uncertainty in the Thiele modulus is roughly 25%. Even with this uncertainty, the ϕ values are such that the main reaction will still be subject to pore diffusion limitations, especially at the supercritical densities. Furthermore, if we had chosen a less realistic average pore diameter (r_o) of 100 Å, instead of 60 Å, α value will remain greater than unity, implying that the pore will still plug. Hence, both of the conditions necessary for premature pore-mouth plugging (initial $\phi > 0.3$ and $\alpha \geq 1$) are preserved in the uncertainty range of the parameter values.

The recovery of catalyst activity at dense supercritical conditions is due to alleviation of pore-mouth restrictions as a result of enhanced extraction of the coke deposits at liquid-like densities (Saim and Subramaniam, 1991). The empirical correlation used in our simulations does indeed predict increased coke extraction at higher densities. Thus, even though the correlation may not be accurate (due to a lack of reliable information on the exact nature of the coke compounds and their extractabilities), the *qualitative* trends of activity variation with density are indeed reliable for coking of micro- to mesoporous catalyst addressed in our study. The *quantitative* effects of varying P (the extraction parameter) on catalyst activity may be inferred from Figures 3–7.

With increasing densities in the supercritical region, one would expect the reaction rate to eventually become limited by pore diffusion. Figure 11 shows model predictions of the temporal effectiveness factor over a wide range of densities. Note that the catalyst undergoes progressively rapid deactivation with increasing densities up to roughly 2.4 ρ_c. The rather sharp increase in activity just beyond 2.4 ρ_c is due to the alleviation of pore-mouth restrictions following onset of coke solubilization in the dense supercritical reaction mixture. As hypothesized by Yokota and Fujimoto (1991) and by Adschiri et al. (1991), the model predicts an optimum density ($\sim 3\ \rho_c$) in the supercritical region at which catalyst activity is maintained at a maximum value. Note that at smaller than optimum density values the reaction rate is limited by coke extraction, while beyond this optimum density the effectiveness factors are nearly those obtained in the absence of deactivation, implying that the reaction rate (or catalyst activity) is limited only by pore-diffusion limitations. Hence, *regardless* of whether coking occurs by a series or parallel mechanism, the overall reaction rate will eventually be limited by pore diffusion limitations at liquid-like densities.

The excellent qualitative agreement between predictions of the single-pore model (with an initial pore diameter of 60 Å) and experimentally observed trends should not be surprising considering that more than 70% of the surface area of the aged Pt/γ-Al_2O_3 catalyst used in our experiments resides in pores with diameter 100 Å or less. For the latter reason, it would be unreasonable to expect a quantitative match with experiments. A drawback with the model, however, is that it predicts steady states in catalyst effectiveness factor that are not always observed. While Tiltscher et al. (1981) observed constant activity during supercritical 1-hexene isomerization on a *macroporous* catalyst, Saim and Subramaniam (1991) observed a gradual decrease in activity for the same reaction on a *micro-* to *mesoporous* industrial catalyst. The temporal decrease in catalyst activity may be modeled by considering a coking network, where different coke compounds with varying solubilities in the reaction mixture are formed.

The model may be improved by considering a porous pellet with a distribution of randomly oriented pores and by accounting for the different effective diffusivities of the reactant and coke molecules in the pores (see, for example, Yortsos and Sharma, 1986). Even so, for accurate quantitative predictions, reliable supercritical desorption data for the 1-hexene-coke compound-Pt/γ-Al_2O_3 system and accurate data on coking kinetics are needed.

Summary

Existing models, which account for catalyst deactivation by either active site suppression or pore-mouth plugging, have been extended to describe coke deposition with simultaneous extraction in subcritical and supercritical reaction mixtures. In addition to the Thiele modulus and the pore-accessibility factor, a dimensionless coke extraction parameter (that provides a measure of the coke extraction rate relative to the coke formation rate) also characterizes the model. Simultaneous coke extraction enhances catalyst activity by alleviating coke buildup. The reduced coke accumulation lowers pore-diffusion resistances and leads to increased effectiveness factors as compared to the case of negligible coke extraction. The increased activity leads to a greater coke growth rate. Hence, the coke growth and extraction rates approach each other and eventually become equal if pore plugging is averted. In the latter case, the catalyst effectiveness factor eventually attains a constant value.

The model was employed to predict the variation of catalyst activity with reaction mixture density for the Pt/γ-Al_2O_3 catalyzed reaction of 1-hexene in a CSTR. As the density is isothermally increased from subcritical to near-critical values, the ensuing higher reaction rates and restricted diffusion result in a sharp reduction in catalyst effectiveness factor, eventually leading to total deactivation by pore-mouth plugging. At sufficiently dense supercritical conditions, however, the enhanced coke solubilities in the reaction mixture avert pore-mouth plugging, resulting in a recovery of catalyst activity and increased catalyst effectiveness. The model predictions are qualitatively consistent with those observed experimentally for this reaction system. It may therefore be concluded that the observed coking occurs by a predominantly parallel coking mechanism. The model also predicts an optimum density in the supercritical region at which catalyst activity is maintained at a maximum value. At smaller than optimum density values, the reaction rate is limited by coke extraction and at larger than optimum values, the rate is subject to pore-diffusion limitations. The model thus provides a useful framework for future theoretical and experimental investigations aimed at determining optimum conditions for continuous *in situ* maintenance of catalyst activity.

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Notation

a = activity function the catalyst, dimensionless
A = reactant for main reaction
B = product of main reaction
C_i = concentration of species i, mol·cm^{-3}
D_i^e = effective diffusivity of component i in the pore at time t, cm^2·s^{-1}
D_i^o = effective diffusivity of component i in pore in the absence of coke laydown, cm^2·s^{-1}
k_c = effective desorption constant for coke on surface, s^{-1}
k_i = rate constant for reaction i, cm^3·(g cat.)$^{-1}$ s^{-1}; $i=A$, W
K_A = adsorption equilibrium constant, m^3·kg cat.$^{-1}$
M_W = molecular weight of coke, g·mol^{-1}
P = $(k_C W_S S_0)/(M_W k_W C_A^0)$ = ratio of coke extraction to coke formation rates, dimensionless
r_C = rate of extraction of coke, g·cm^{-2}·s^{-1}
r_i = rate of formation of species i, kmol·(g cat.)$^{-1}$·s^{-1}; $i=A$, W
S_o = original surface area of pore per unit mass of catalyst, m^2·g^{-1}
t = time, s
v_o = intrinsic volume as described by Hildebrand (1971), cm^3·mol^{-1}
V = volume of reactor, m^3
W = coke laydown on catalyst, kg·cm^{-2}
W_S = coke laydown corresponding to total deactivation of catalyst, kg·cm^{-2}
z = axial coordinate, ranging from L to $-L$, cm

Greek letters

α = $(2W_S)/(r_0\rho_W)$ = pore accessibility factor, dimensionless
β_0 = $(W_S S_0 \rho_{\text{cat}})/(C_A^0 M_W)$ = maximum yield of coke at total deactivation, dimensionless
ζ_A = C_A/C_A^0, dimensionless
η = effectiveness factor: ratio of reaction rate of entire pellet to initial reaction rate at surface of pellet, dimensionless
λ_o = r_m/r_o, ratio of molecular radius to pore radius in the absence of coke laydown, dimensionless
λ = r_m/r, ratio of molecular radius to pore radius at time t, dimensionless
ξ = z/L = dimensionless distance along pore axis measured from the center of the pore
ρ_{cat} = bulk density of catalyst, g·cm^{-3}
ρ_W = density of coke, g·cm^{-3}
τ = $(tD_A^0)/L^2$, dimensionless time
υ = volumetric flow rate of reactants to reactor, cm^3·s^{-1}
ϕ = $L\sqrt{(\rho_{\text{cat}}k_A)/D_A^0}$, Thiele modulus for main reaction before coke laydown, dimensionless
ϕ_C = $L\sqrt{k_C/D_C^0}$, Thiele modulus for coke extraction, dimensionless
ϕ_W = $L\sqrt{(\rho_{\text{cat}}k_W)/D_A^0}$, Thiele modulus for coking reaction, dimensionless
ψ = W/W_S = dimensionless coke laydown

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