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Impurity Poisoning of Catalyst Pellets

B. VALDMAN,[1] P. A. RAMACHANDRAN, AND R. HUGHES

Department of Chemical Engineering, University of Salford, Salford M5 4WT, England

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A mathematical model has been developed for predicting the decrease in catalytic activity when an independent reversible poison is adsorbed on a catalytic surface. A Langmuir–Hinshelwood model is used for the reaction, and it is assumed that the poison in the gas phase is always in equilibrium with the adsorbed phase to which it is related by means of the Langmuir adsorption isotherm. The equations are solved for a slab and sphere both numerically and by a single point collocation approximation. A study of the dynamics of the process during deactivation and reactivation is presented and aspects of reactor performance in the presence of poison analyzed.

INTRODUCTION

The deactivation of a catalyst and the consequent decay of catalyst effectiveness is a very important and common problem in industry. Catalyst deactivation processes can be divided into three general classes (*1*): (a) poisoning, loss of activity caused by strong chemisorption of some impurity normally contained in the reacting mixture; (b) fouling, loss of activity caused by reactant or product impurity degradation on the catalyst surface, such as catalyst coking; (c) aging, loss of activity caused by sintering or decrease of active surface.

A number of theoretical studies of the process of catalyst fouling have been published in the literature, where parallel, series, or independent fouling has been considered (*2–6*). However, there are limited studies of the poisoning process where the poisoning is essentially caused by reversible adsorption of an impurity present in the feed stream. Gioia (*7*) and Gioia and Greco (*8*) have studied the problem of Langmuir adsorption of poison. The analysis is for the case where the main reaction is not under any diffusion limiting conditions. Further, the analysis is for an infinite slab geometry, and this depicts the actual case accurately only for small times of the poisoning process, because of the boundary conditions used. The situation where the main reaction is diffusion limited and follows Langmuir–Hinshelwood type of kinetics does not appear to have been studied.

It is the purpose of the present paper to study this last situation based on a model which assumes an isothermal catalyst pellet with uniform initial activity distribution. A uniform effective diffusivity which is unaffected by concentration gradients and by the poisoning process is also assumed, together with a diffusion controlled main reaction and Langmuir adsorption for the poisoning. External transport limitations are assumed to be negligible. An analytical solution is developed for calculating effectiveness factors. For the particular case of large times of poisoning, when new steady-state operating conditions are reached, an

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[1] On leave of absence from Department of Chemical Engineering, Universidade Federal do Rio de Janeiro, Brazil.

equation for calculating the effectiveness factor for the limiting cases of particles with large and low Thiele moduli is also presented. In the context of this analysis, the results presented by Gioia (7) can be obtained as a particular case of the present general model.

NOMENCLATURE

A, P	Concentration of reactant and poison, respectively, gram moles per cubic centimeter
B_{11}	Collocation constant for the Laplacian operator
C	Dimensionless concentration defined as A/A_0 and P/P_0
$\hat{C}$	Dimensionless concentration at the collocation point
$\hat{C}_P(0)$	Dimensionless concentration of poison at the collocation point at the instant of reactivation
D	Effective diffusivity, square centimeters per second
k	rate constant for main reaction, seconds^{-1}
K	Langmuir adsorption constant, cubic centimeters per gram mole
L	Particle half dimension, centimeters
$\bar{P}$	Adsorbed phase poison concentration, gram moles per cubic centimeter
$\bar{P}_{max}$	Maximum adsorbed phase poison concentration, gram moles per cubic centimeters
q	Dimensionless variable defined as $X/(\theta)^{\frac{1}{2}}$
r	Reaction rate of A, gram moles per cubic centimeter per second
t	Time, seconds
V	Dimensionless variable defined as $K_A A_0/(1 + K_P P_0)$
x	Distance into pellet, centimeters
X	Dimensionless distance defined as x/L
w_1, w_2	Dimensionless weight values

Subscripts

A	Reactant
0	Surface
P	Poison

Greek letters

η	Effectiveness factor defined by Eq. (8)
τ	Characteristic time defined as $L^2 K_P \bar{P}_{max}/D_P$, seconds
θ	Dimensionless time defined as t/τ
λ	Dimensionless geometric shape parameter
ϕ	Thiele modulus defined as $(kL^2/D_A)^{\frac{1}{2}}$
ψ	Dimensionless concentration flux defined as dC_A/dX

GENERAL THEORY

A differential mass balance for the reacting component A in an isothermal flat slab is:

$$D_A d^2A/dx^2 = r, \qquad (1)$$

where D_A is an effective diffusivity and x a distance coordinate.

Assuming that the poison adsorbs independently of any other component, a mass balance for the poison component P yields:

$$D_P \partial^2 P/\partial x^2 = \partial \bar{P}/\partial t, \qquad (2)$$

with P as the gas phase concentration and $\bar{P}$ as the adsorbed phase concentration. If the adsorption of the poison is rapid, equilibrium conditions prevail and the concentrations P and $\bar{P}$ are related by means of the Langmuir adsorption isotherm:

$$\bar{P}/\bar{P}_{max} = K_P P/(1 + K_P P), \qquad (3)$$

where $\bar{P}_{max}$ is the maximum adsorbed phase poison concentration in equilibrium with the gas phase.

The model developed here is of validity for a diffusion limited general type of reaction rate expression of Langmuir–Hinshelwood kinetics, and the mathematical technique employed is of general applicability.

For the purpose of illustration only, we shall consider a particular case where the main reaction mechanism can be expressed by the following reaction rate equation:

$$r = kA/(1 + K_A A + K_P P), \qquad (4)$$

which represents the reaction rate of a component A when the adsorption of A is the controlling step and a certain number of active sites are occupied by a poison component P (*9*). The above reaction rate equation is also valid when the rate controlling mechanism is the surface reaction involving single active sites of the catalyst. This type of reaction rate occurs frequently in reactions of hydrogenation as, for example, in the hydrogenation of commercial benzene which contains small quantities of thiophene, where the thiophene acts as a poison by virtue of its preferential adsorption on the metallic catalyst used in the reaction (*10*).

Equations (1) to (4) can be combined and expressed in dimensionless form as:

$$\frac{\partial C_A}{\partial X^2} = \phi^2 \cdot \frac{C_A}{1 + K_A A_0 C_A + K_P P_0 C_P} \qquad (5)$$

and

$$\frac{\partial C_P}{\partial X^2} = \frac{1}{(1 + K_P P_0 C_P)^2} \cdot \frac{\partial C_P}{\partial \theta}, \qquad (6)$$

which are solved simultaneously with the following boundary conditions:

$$X = 0 \quad C_A = C_P = 1 \quad \text{for} \quad \theta > 0,$$

$$X = 1 \quad \frac{\partial C_A}{\partial X} = \frac{\partial C_P}{\partial X} = 0 \quad \text{for} \quad \theta > 0,$$

$$\theta = 0 \quad C_A = 1, C_P = 0 \quad \text{for} \quad 0 < X < 1.$$

For small values of dimensionless time, θ, Eq. (6) can be transformed to a total differential equation by using the transformation group

$$q = X \cdot \theta^{-\frac{1}{2}},$$

which yields the equation:

$$\frac{d^2 C_P}{dX^2} = -\frac{X}{\theta} \cdot \frac{1}{2(1 + K_P P_0 C_P)^2} \cdot \frac{dC_P}{dX}. \qquad (7)$$

Equation (5) represents the diffusion and chemical reaction in the catalyst. Since the poison concentration, C_P, depends on time, this equation represents an unsteady-state equation. Equation (6) represents the functional dependence of the poison penetration into the catalyst with time and on the poison concentration in the gas phase. For a particular value of dimensionless time, θ, the concentration profile of reactant and poison is obtained by solving these two equations simultaneously using numerical procedures.

EFFECTIVENESS FACTOR

The overall effectiveness factor of a catalyst pellet can be characterized by the ratio of the actually observed reaction rate to the reaction rate based on the surface conditions in absence of any poisoning or external mass transfer resistance and is mathematically expressed for the case under consideration as:

$$\eta = \frac{1 + K_A A_0}{\phi^2} \cdot \left. \frac{dC_A}{dX} \right|_{X=0}. \qquad (8)$$

The value of dC_A/dX at the surface is determined by integrating Eq. (5) and taking its value at $X = 0$. As the reaction rate of A is a function of the concentration of reactant A and poison P, this integration can normally be performed only by numerical methods as a two point boundary value problem, except for the limiting case of uniform distribution of poison. Thus, the numerical integration must be carried out by a trial and error procedure.

An alternative way to calculate the effectiveness factor is by the orthogonal collocation polynomial approximation (*11*) using a single parameter trial function. The effectiveness factor becomes:

$$\eta = \frac{(\lambda + 1)}{r(X = 1, \theta = 0)} \cdot [w_1 r(X = X_1) + w_2 r(X = 1)], \quad (9)$$

where λ is a geometric factor and $w_{1,2}$ are weight values.

The reaction rate at a single internal collocation point, $r(X_1)$, can be determined by calculating the poison, $\hat{C}_P$, and reactant, $\hat{C}_A$, concentrations at this point by the equations:

$$\frac{1}{B_{11}} \cdot \frac{1}{(1 + K_P P_0)^2} \cdot \left[\ln \frac{1 - \hat{C}_P}{1 + K_P P_0 \hat{C}_P} - K_P P_0 \cdot (1 + K_P P_0) \cdot \frac{\hat{C}_P}{1 + K_P P_0 \hat{C}_P} \right] = -\theta \quad (10)$$

and

$$1 + \frac{\phi^2}{B_{11}} \cdot \frac{\hat{C}_A}{(1 - \hat{C}_A)(1 + K_A A_0 \hat{C}_A + K_P P_0 \hat{C}_P)} = 0, \quad (11)$$

where B_{11} is a constant dependent on the pellet geometry (Table 1), and θ any selected value of time. The effectiveness factor at this value of time can then be calculated by the following expression:

$$\eta = \frac{(\lambda + 1)(1 + K_A A_0)}{1 + K_A A_0 + K_P P_0} \cdot w_2 \left[1 + \frac{w_1}{w_2} \cdot \frac{\hat{C}_A (1 + K_A A_0 + K_P P_0)}{1 + K_A A_0 \hat{C}_A + K_P P_0 \hat{C}_P} \right]. \quad (12)$$

TABLE 1

Matrices for Single Point Orthogonal Collocation Approximation

Geometry	λ	B_{11}	w_1	w_2
Planar	0	−2.5	0.833	0.167
Cylindrical	1	−6.0	0.375	0.125
Spherical	2	−10.5	0.233	0.100

Table 1 gives values of λ, B_{11}, w_1, and w_2 for slab, cylinder, and spherical geometries.

Equation (10) shows that the time necessary for a concentration of poison to reach a given value at the collocation point is inversely proportional to the parameter B_{11}, which is directly related to the shape of the particle. From Table 1 it can be seen that for a sphere this parameter has a larger value than for a slab, and hence the time necessary for a sphere to become poisoned is less than for a slab. This result was also reported for the case of a system poisoned by a precursor P in the feed, which reacts with the active surface according to an irreversible and nonlinear mechanism (*6*).

LIMITING CASES

1. *Large Values of Thiele Moduli*

At larger times when the poison can be considered uniformly adsorbed over the entire catalyst, $C_P = 1$, and using Petersen's (*12*) approximation for large values of Thiele moduli, the effectiveness factor can be calculated by the expression:

$$\eta = \frac{(1 + K_A A_0)}{\phi} \times \left\{ \frac{2}{K_A A_0} \left[1 - \frac{\ln(1 + V)}{V} \right] \right\}^{\frac{1}{2}}, \quad (13)$$

where $V = K_A A_0 / (1 + K_P P_0)$.

The value of the parameter V ranges between $K_A A_0 / (1 + K_P P_0)$ and $K_A A_0$ for time infinity and time equal to zero, respectively. For unpoisoned catalyst, ($P_0 = 0$), the above formula is generally valid for Thiele moduli larger than 3. For a poisoned catalyst, the value of Thiele moduli which correspond to the beginning of the asymptotic region is larger and depends on the amount of poison adsorbed in the catalyst.

2. *Low Values of Thiele Moduli*

For low values of Thiele moduli the concentration profile of C_A tends to unity, and Eq. (12) can be used to calculate the effectiveness factor as a function of the concentration at the collocation point, $\hat{C}_P$, which changes with time, as related in Eq. (10).

For uniform poison distribution Eq. (12) yields:

$$\eta(\theta = \infty) = \frac{1 + K_A A_0}{1 + K_A A_0 + K_P P_0}. \tag{14}$$

This equation is valid for any value of $K_P P_0$ and for particles with Thiele moduli less than 0.5. As the value of $K_P P_0$ increases this upper limit also increases.

REACTIVATION OF CATALYST

The orthogonal collocation method can be used to follow the increase of the effectiveness factor when the poison is removed from the gas phase, corresponding to a negative step in the concentration of poison at the catalyst surface. For a single collocation point Eq. (7) is solved subject to the conditions that at time equal to zero the concentration of poison at the surface is zero and at the collocation point is equal to a value $\hat{C}_P(0)$. For this case the concentration of poison at the collocation point is related to time by the equation:

$$\theta = \frac{1}{B_{11}} \cdot \left[\frac{1}{1 + K_P P_0 \hat{C}_P} - \frac{1}{1 + K_P P_0 \hat{C}_P(0)} + \ln\left(\frac{1 + K_P P_0 \hat{C}_P(0)}{\hat{C}_P(0)} \cdot \frac{\hat{C}_P}{1 + K_P P_0 \hat{C}_P} \right) \right]. \tag{15}$$

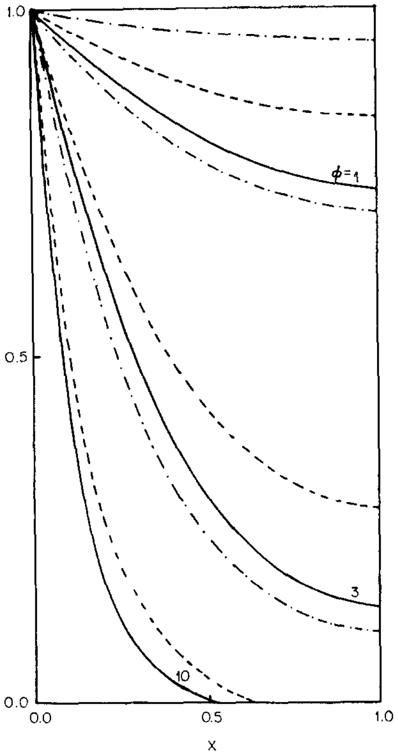

FIG. 1. Steady-state distribution of reactant, in a flat slab catalyst pellet, at different levels of poison concentration. Key: The solid curves are for $K_P P_0 = 0$, the broken for $K_P P_0 = 1$, and the dotted for $K_P P_0 = 10$.

Once the poison concentration is known at a fixed value of time, θ, Eqs. (11) and (12) can be used to calculate the effectiveness factor at this particular time during the process of reactivation of the particle.

RESULTS AND DISCUSSION

In the following numerical results the values used for the various parameters were (7):

$$D_P = 10^{-2}\ \text{cm}^2/\text{sec},$$
$$L = 0.6\ \text{cm},$$
$$K_P = 10^9\ \text{cm}^3/\text{gmol},$$
$$\bar{P}_{\max} = 10^{-5}\ \text{gmol/cm}^3,$$
$$K_A C_A = 1\ \text{dimensionless},$$

which leads to a characteristic time of the system, τ, equal to 100 hr.

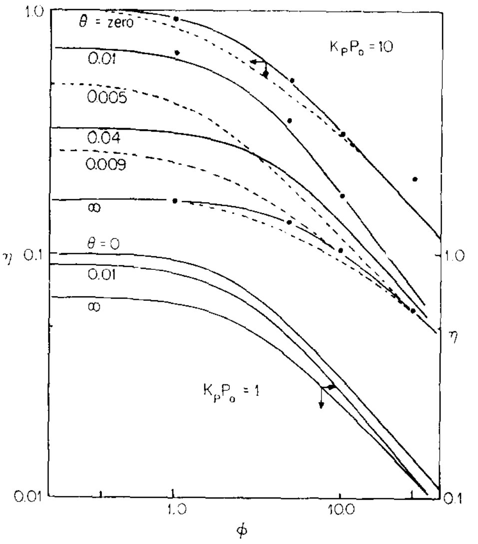

FIG. 2. Effectiveness factor versus Thiele modulus, for slab and sphere, at various times of poisoning. Key: The solid curves are for a flat slab and the broken for a sphere; the dots are effectiveness factor calculated by a single point collocation approximation for a flat slab.

1. Concentration Distribution of Reactant

Figure 1 compares the concentration distribution of reactant A in a finite slab when no poisoning is present to the distribution in the presence of poisoning at time equal to infinity, at two levels of poison concentration characterized by K_PP_0 equal to 1 and 10 and for three values of Thiele moduli equal to 1, 3, and 10. As can be seen from this figure, there is a large spread on the concentration profiles at intermediate values of the Thiele modulus ($\phi = 3$). At Thiele moduli equal to 1 and 10 the change of concentration profile due to poisoning is much less pronounced.

2. Effectiveness Factor

The variation of effectiveness factor, η, as a function of Thiele modulus at different values of dimensionless time, θ, is shown in Fig. 2 for slab and spherical geometry. For convenience, the results for a sphere are plotted on the basis of the Thiele modulus for a sphere of radius R, being defined as the same as a slab of thickness equal to $3L$. The curves for sphere and flat plate agree closely in the absence of poison, $\theta = 0$ and for the steady state reached in the presence of poison, $\theta = \infty$. For intermediate values of θ, the effectiveness factor for a flat plate and sphere do not coincide, indicating that the poisoning is faster in the case of a sphere.

The value of the effectiveness factor calculated by using a single collocation point approximation is compared with the numerical solution of the differential equation in Fig. 2. It can be seen that the single collocation point approximation gives accurate predictions of the effectiveness factor for Thiele moduli less than 5 in the absence of poisoning. For larger values of Thiele moduli, a single collocation point predicts higher effectiveness factors than the numerical solution. Hence it is necessary to use two point collocation which is sufficient for all practical ranges of Thiele moduli (*12*). The failure of the single collocation point for Thiele modulus larger than 5 is due to the fact that, the concentration profile of the reactant being very steep, the concentration at the collocation point has a small value close to zero. When poisoning takes place, the concentration of reactant at various points is larger than in the absence of poison as already shown in Fig. 1. Therefore, the single collocation point is sufficiently accurate up to a Thiele modulus of about 10 in the presence of poisoning.

For studying the effect of size and other characteristics of catalyst pellets, it is convenient to plot the variation of effectiveness factor as a function of real time, t. The ratio η/η_0 which represents the ratio of the effectiveness factor at any time to that for an unpoisoned catalyst is shown in Fig. 3 for five values of Thiele moduli. This ratio signifies the relative drop in the reaction rate caused by poisoning as a function of time. For small values of the Thiele modulus the poisoning is completed in much less time than for the larger ones,

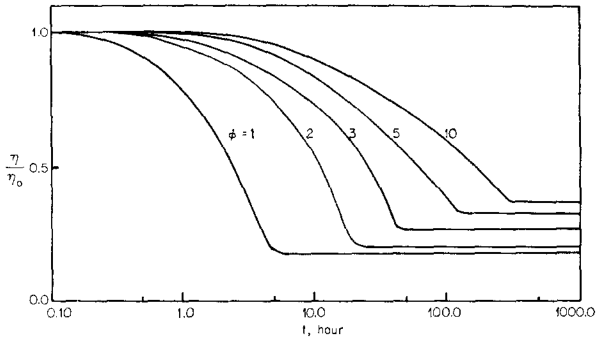

FIG. 3. Time-dependent variation of the ratio η/η_0 during poisoning, for various values of Thiele moduli, of flat slab catalyst pellets.

and it is also accompanied by a larger relative drop in activity. The reverse is true for a large Thiele modulus. For example, a system with Thiele modulus equal to 1 drops to 18% of its original activity at the steady state, and this takes less than 10 hr, while a system of Thiele modulus equal to 10 drops only to 37% and this takes more than 300 hr. A similar trend is also seen at any given time. For example, 3 hr after the introduction of poison into the system, the relative drops in activity are equal to 58 and 2% for Thiele modulus equal to 1 and 10, respectively.

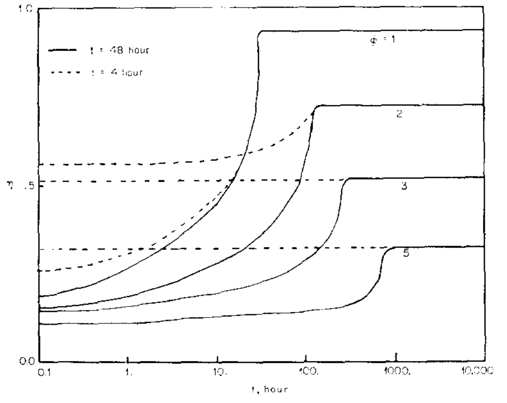

FIG. 4. Time-dependent variation of the effectiveness factor during poison desorption, for various values of Thiele moduli. Key: The solid curves are for 48-hr contact of poison, and the broken are for 4-hr.

3. Dynamics of Poison Desorption

If the poison is removed from the feed stream, the catalyst will recover its original activity, since it is assumed that the adsorption is reversible. Figure 4 represents the dynamics of desorption of poison from the active sites (reactivation), for two situations. One is when the poison remains a long time in the feed and hence equilibrium will be achieved between the adsorbed phase and the gas phase concentrations. This equilibrium is achieved after 48 hr for all systems with Thiele moduli smaller than 10, for K_PP_0 equal to 10 and other catalyst parameters cited earlier. The continuous lines in Fig. 4 represent the dynamics of catalyst reactivation for the system in which the poison is present in the gas phase for times larger than this. A comparison of Figs. 3 and 4 shows that the time necessary for the catalyst to recover the original activity is much longer than the time necessary for poisoning. For example, for a Thiele modulus equal to 2, Fig. 3 shows that the poisoning is completed in approximately 25 hr, and Fig. 4 shows that the time necessary for the system to recover its original activity level is approximately equal to 150 hr, that is, the time for reactivation is roughly sixfold that for deactivation. These theoretical predictions support the experimental results published by Gioia (*7*) for the study of ethylene

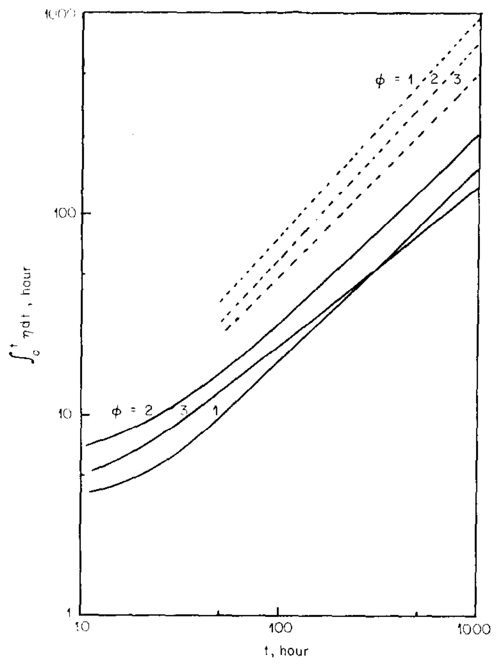

FIG. 5. Effect of Thiele modulus on catalyst productivity. Key: The solid curves are for 48-hr contact of poison, and the broken are for 4-hr.

hydrogenation in which water vapor was the reversible poison. For a value of K_PP_0 equal to 10 the poisoning was completed in 11 min, while the reactivation took 60 min. Therefore, it can be said that the dynamics of poisoning of catalyst is very fast during the process of deactivation and very slow during reactivation.

If the poison is not present in the gas phase for sufficient time to reach equilibrium, the dynamics of reactivation of systems with different Thiele moduli will be different. The broken lines in Fig. 4 illustrate how the poison is removed from the feed stream after 4 hr of operation. For this duration of poisoning the activity decrease for systems with a Thiele modulus greater than 3 is very small (Fig. 3), and therefore the time required for reactivation is also small, as is shown in Fig. 4. Conversely, for Thiele moduli equal to 1 and 2 the activity is 25 and 55%, respectively, and for these values significant reactivation periods namely, 40 and 150 hr, are necessary.

4. Reactor Performance in Presence of Poisoning

It is interesting to examine the performance of a reactor for systems subject to continuous and intermittent poisoning for long periods of operation. The productivity of the reactor can be measured as the area under the curve of effectiveness factor versus time for a given total period of operation. Figure 5 provides a direct measure of the value of productivity for a continuous operation time, *t*, for three cases (Thiele moduli equal to 1, 2, and 3). The broken lines in Fig. 5 show the reactor performance when the poison is present only for the first 4 hr in the feed stream, corresponding to the case of intermittent poisoning. It can be seen from this figure that a system with a smaller Thiele modulus gives a better productivity. However, if the poison is present continuously along with the feed, the behavior is different. This is shown by the continuous lines of Fig. 5, where a system with an intermediate value of the Thiele modulus equal to 2 gives better productivity than that with a Thiele modulus equal to 1 or 3. Figure 5 also shows that a system with a Thiele modulus equal to 1 gives a better performance than a Thiele modulus equal to 3 only if the time of operation is more than 300 hr. These results can be easily explained on the basis of the plot of effectiveness factor versus time for various Thiele moduli (Fig. 3).

These results indicate that higher mass transfer resistances increase the lifetime of the pellets, while lower mass transfer increases the effectiveness factor. The combined effects of these opposing factors result in an optimum value of Thiele modulus for which the productivity is maximum for a given period of continuous operation.

CONCLUSIONS

The problem of the decrease in catalyst activity due to a reversible adsorption of poison was solved both numerically, solving the differential equations for the system, and using a single point collocation approximation. The latter is shown to be sufficiently accurate for many practical situations. It was found that for small Thiele moduli the poisoning is rapid and also accompanied by a large drop in effectiveness factor compared to the initial value. The reverse was found to be true for large Thiele moduli. The dynamics of poison desorption indicates that the time for reactivation is much larger than the time for deactivation, which is in agreement with the experiments of Gioia (7). The analysis of reactor performance for the case where the poison is continuously present in the feed stream shows that the use of an intermediate value of the Thiele modulus in many cases gives an improved productivity compared with low or large values of Thiele moduli. For the case of intermittent poisoning, the catalyst with no diffusion limitation is shown to yield the maximum productivity.

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