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Performance of Fixed-Bed Catalytic Reactors with Poison in the Feed

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The theory of conversion in a fixed-bed catalytic flow reactor with adsorbable poison in the feed is developed in terms of four basic parameters. For the poisoning wave a Bohart-Adams type breakthrough equation is used. The equations are so chosen that exact integration into relatively simple results can be carried out. The theory is applied to experimental data on the poisoning of Pt-Pd catalysts by H_2S. It is shown that all four parameters can be abstracted from a single conversion vs. time curve, so that conversion at new linear velocities, new bed lengths, new poison concentrations, and new particle sizes can be predicted.

INTRODUCTION

The performance of a fixed-bed catalytic flow reactor with adsorbable poison in the feed has apparently received little attention, no doubt due to uncertainties in the shape of the poisoning wave which travels down the bed. In two papers, Anderson *et al.* (*1*, *2*) have considered this problem from a standpoint somewhat related to the present treatment. Froment and Bischoff (*3*, *4*) have considered the special case in which the main reactant itself can poison the catalyst, as in catalytic cracking of gas-oils. Masamune and Smith (*5*) have considered in detail the shape of the poisoning wave in a single catalyst pellet, and indicate how these results can be integrated into the bed equations to give conversions, but do not give general explicit results. As compared with the earlier theories, the present treatment gives relatively simple explicit results of some generality [e.g., Eq. (7)] which should be applicable to a large amount of experimental data.

In the present theory, performance at any time depends on four parameters:

(a) The first order rate constant, k_0 (units, sec^{-1}), for the unpoisoned catalyst.

(b) A dimensionless parameter, h_0. The decrease in k_0 as poison accumulates on a given catalyst pellet is a function of h_0 (i.e., the degree of selectivity of the poison is determined by h_0).

(c) The rate constant, k_A, for adsorption of poison on the catalyst (units, sec^{-1}). The shape of the poisoning wave is dependent on the magnitude of k_A. The poisoning wave may be defined as a plot of concentration of poison (say in grams of poison per gram of catalyst) vs. distance from bed inlet at a particular time t.

(d) The adsorption capacity of the catalyst for poison, which may be expressed by the parameter W_s, the weight of poison per gram of catalyst which causes activity to drop to zero. An alternative parameter to W_s is t_s, the so-called stoichiometric time for poisoning, which is the time for the flow system to completely poison the bed if all poison were adsorbed. The relation between W_s and t_s is

$$t_s = \rho_B W_s L / M V_L C_p{}^0 \qquad (1)$$

where ρ_B is the bulk density of catalyst; L, the bed length; M, molecular weight of poison; V_L, the superficial linear velocity (cm/sec) of gas flow; and $C_p{}^0$, the inlet concentration of poison. The quantity t_s is thus the ratio of the total adsorptive capacity of the bed (in g of poison) to the rate (g/sec) at which the flow system brings poison to the catalyst.

THE BASIC THEORY

Conversion in an isothermal fixed-bed reactor, neglecting axial diffusion and for irreversible first order reaction, is ruled by the equation of mass balance (e.g., ref. *6*):

$$-V_L(\partial C/\partial x) = kC \qquad (2)$$

where C is the concentration of reactant (moles/cm^3) at a point x cm from the inlet. Formal integration of Eq. (2) from $x = 0$ to $x = L$ (L is reactor length in cm) gives immediately for the exit concentration

$$\ln \frac{C}{C_0} = \frac{-1}{V_L} \int_0^L k \, dx \qquad (3)$$

where C_0 is the inlet concentration of reactant.

To integrate Eq. (3), k must be known as a function of the weight W of poison adsorbed (g per g of catalyst) and W must be known as a function of x and t from the poisoning wave equation. [Note: for the case of an unpoisoned reactor, k is constant, so Eq. (3) may be immediately integrated to give the usual simple first order equation.]

For k as a function of W a family of curves is needed giving various degrees of "selective poisoning." A linear curve will be the classical case of "nonselective poisoning." Curves which fall faster than linearly correspond to selective poisoning, which may be due to poison accumulating first on the outer layers of a porous catalyst (*7*). The family of curves suggested here is represented by

$$k = k_0 \left[\frac{1}{1 + h_0 W/W_s} - \frac{W/W_s}{1 + h_0} \right] \qquad (4)$$

where h_0 is the parameter determining the degree of selective poisoning. When $h_0 = 0$, activity falls linearly with poison, corresponding to nonselective poisoning. When $h_0 = 100$, severe selective poisoning exists, and curve D of Fig. 7 of ref. (*7*) for poisoned pore mouths is reproduced exactly. For $h_0 = 10$ mildly selective poisoning exists and curve C of Fig. 7 of ref. (*7*) is almost exactly reproduced. For each curve, $k = k_0$ when there is no poison, and $k = 0$ when $W = W_s$. The parameter h_0 has physical meaning as described in (*7*). The great advantage of Eq. (4) is that it not only has physical meaning but is also easily integrable when used in Eq. (3) along with the poisoning wave equation.

For the poisoning wave equation the so-called Bohart-Adams equation is used (*8*):

$$\frac{W}{W_s} = \frac{1 - \exp(-N_T t/t_s)}{1 + \exp(-N_T t/t_s)[\exp(N_T x/L) - 1]} \qquad (5)$$

where

$$N_T = k_A L/V_L \qquad (6)$$

Thus N_T is a useful defined quantity, dimensionless, equal to the product of rate, constant for adsorption times contact time, and is proportional to bed length for a given flow rate. In engineering terminology, N_T is the number of adsorptive transfer units in the bed. Equation (5) gives a large variety of shapes for the poisoning wave depending on the values of the two reduced parameters: $\tau = N_T t/t_s$ and $\lambda = N_T x/L$. For small values of τ, Eq. (5) gives a poisoning wave which falls exponentially with distance in the bed. For large values of τ, greater than about 4.0, a sigmoid-shaped poisoning wave is obtained. Large values of N_T correspond to efficient "gettering" of poison by the bed. For example, when $N_T = 100$, it takes only a few percent of the bed length to remove all poison. For large values of N_T, after a short transient period the poisoning wave travels down the bed at constant shape and at a constant velocity, since $e^{-\tau}$ drops to zero after a short time, and the wave shape depends only on the difference $(x - t)$. Equation (5) is an exact solution for simplified bed dynamical equations [see also refs. (*9*), (*10*)], and hence accounts automatically for poison which passes out of the reactor. Thus at $t = t_s$, the bed is not completely poisoned. In fact the poisoning wave, Eq. (5), is characterized by having the exit end ($x = L$) just 50% poisoned at $t = t_s$, providing N_T is greater than about 4 [since under these conditions the numerator of Eq. (5) is unity and the denominator is just 2.0]. In Fig. 1, W/W_s is plotted against the reduced distance parameter λ for various values of the reduced time, τ. The last three curves for $\tau = 5$, 8, 10 show the steady

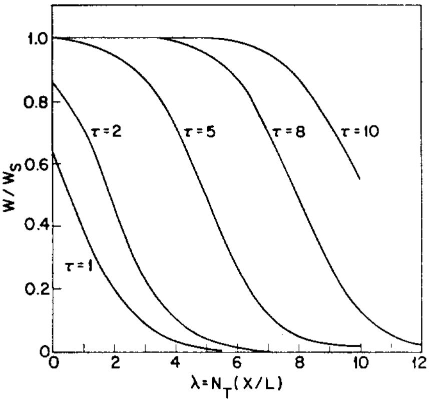

FIG. 1. Bohart-Adams generalized poisoning wave profiles: Plots of W/W_s vs. $\lambda = N_{\mathrm{T}}\, x/L$ for various reduced times, $\tau = N_{\mathrm{T}}\, t/t_s$

state shaped adsorption wave progressing down the bed at constant velocity.

Substituting Eq. (5) for W/W_s into Eq. (4) gives k as an explicit function of time t and distance x in the bed. Putting this expression for k into Eq. (3) leads to an expression which fortunately can be immediately integrated in closed form. The result is

$$\ln\frac{C}{C_0} = \frac{-r}{1+h_0} \times \left\{ \ln\left[1+\exp\left(\frac{-N_{\mathrm{T}}t}{t_s}\right)(\exp N_{\mathrm{T}} - 1)\right] + h_0 \ln\left[1+\frac{\exp(-N_{\mathrm{T}}t/t_s)(\exp N_{\mathrm{T}} - 1)}{1+h_0[1-\exp(-N_{\mathrm{T}}t/t_s)]}\right]\right\} \quad (7)$$

where

$$r = k_0/k_{\mathrm{A}} \quad (8)$$

For the case of nonselective poisoning, $h_0 = 0$, Eq. (7) greatly simplifies to:

$$\ln\frac{C}{C_0} = -r\ln\left\{1-\exp\left(\frac{-N_{\mathrm{T}}t}{t_s}\right) + \exp\left[N_{\mathrm{T}}\left(1-\frac{t}{t_s}\right)\right]\right\} \quad (9)$$

For the important case of reasonably long beds ($N_{\mathrm{T}} > 6$) and reasonably long times ($t/t_s > 0.6$), both Eq. (7) and Eq. (9) simplify somewhat since then $\exp(-N_{\mathrm{T}}t/t_s)$ is much less that unity. Thus the latter term may be dropped when it occurs alone (but not when it multiplies into a second exponential).

Equation (7) is clearly the general solution to the problem since it gives the fraction not converted, C/C_0, as a function of the four dimensionless reduced parameters: t/t_s, N_{T}, r, h_0. Equation (7) has four important asymptotic forms.

1. Conversion at zero time. When $t = 0$, the right-hand side of Eq. (7) becomes $-rN_{\mathrm{T}}$. This is the usual simple solution for first order reaction in an unpoisoned reactor since the quantity ($r\,N_{\mathrm{T}}$) (which we call N_{R}) is by definition:

$$N_{\mathrm{R}} = rN_{\mathrm{T}} = k_0L/V_{\mathrm{L}} \quad (10)$$

or the rate constant for reaction times contact time. In engineering terminology N_{R} is the number of reaction units in the reactor.

2. Conversion before breakthrough of poison. For a reasonably long reactor ($N_{\mathrm{T}} > 4$) there is a long period of time during which $\exp[N_{\mathrm{T}}(1 - t/t_s)]$ is much larger than unity. This is the period during which the bed is adsorbing all the poison [no significant breakthrough of poison in the exit stream, see Eq. (5)]. During this time, according to Eq. (7)

$$\ln\frac{C}{C_0} = N_{\mathrm{R}}\left(\frac{t}{t_s} - 1\right) + \frac{rh_0}{1+h_0}\ln(1+h_0) \quad (11)$$

which is a good approximation to Eq. (7) for the case when t/t_s lies between 0.2 and and 0.8 for long beds ($N_{\mathrm{T}} > 8$) and for h_0 not too large (say less than 10). Equation (11) is obtained from Eq. (7) by setting $\exp N_{\mathrm{T}} \gg 1$, $\exp[N_{\mathrm{T}}(1 - t/t_s)] \gg 1$, $\exp(-N_{\mathrm{T}}t/t_s) \ll 1$.

It is implied in Eq. (11) that, in the early part of the conversion vs. time curve, when conversion first starts decreasing from 100%, the fraction not converted will increase exponentially with time. Therefore a plot of $\ln C/C_0$ vs. time will be a straight line of slope N_{R}/t_s. The intercept of the straight line depends on N_{R}, r, and h_0, but for $h_0 = 0$ is simply $-N_{\mathrm{R}}$. Clearly Eq. (11) can be used to get good estimates of N_{R} and t_s, and this will be discussed later. In a later publication it will be shown that the linearity of Eq. (11)

with time is quite independent of any assumed form for Eqs. (4) and (5), and depends only on a steady state shape of the poisoning wave. Anderson (*2*) has discussed this from a slightly different standpoint.

3. Shape of the tail of the conversion vs. time curves. The "tail" of the conversion vs. time curves at low conversions and long times corresponds to the quantity $\exp[N_T(1 - t/t_s)]$ being much less than unity. Using the usual Taylor expansion equation $\ln(1 + \epsilon) = \epsilon$ when ϵ is small, Eq. (7) becomes

$$-\ln \frac{C}{C_0} = \frac{r(1 + 2h_0)}{(1 + h_0)^2} \exp\left[-N_T\left(\frac{t}{t_s} - 1\right)\right] \tag{12}$$

If f is the fraction converted, then C/C_0 is $1 - f$ and $-\ln C/C_0 = -\ln(1 - f) = f$ for small conversions. Thus the fraction converted is given exactly by Eq. (12) for small conversions. Consequently it is implied in Eq. (12) that in the tail of the conversion vs. time curves the conversion will fall exponentially with time, and that the slope of a plot of $\ln f$ vs. time is N_T/t_s. This slope is exactly a factor r less than that of the plot of Eq. (11) so that the ratio of these slopes gives a simple way to determine the parameter r.

4. Conversion at $t = t_s$. A useful formula is obtained by setting $t = t_s$ in Eq. (7). Due to the particular form of Eq. (7), the conversion at $t = t_s$ does not depend on N_R or N_T but only on r and h_0, providing the bed is fairly long ($N_T > 4$). This is because the important quantity

$$\exp[N_T(1 - t/t_s)]$$

takes the absolute value of unity, independent of N_T, so that at $t = t_s$

$$\ln \frac{C}{C_0} = \frac{-r}{1 + h_0}\left[\ln 2 + h_0 \ln\left(\frac{2 + h_0}{1 + h_0}\right)\right] \tag{13}$$

This equation is useful for fitting constants to an experimental curve. Thus if t_s has been determined or estimated, a relationship is given in Eq. (13) between r and h_0 which must be fulfilled.

APPLICATION TO EXPERIMENTAL DATA

Some problems must be overcome in fitting a given experimental curve of percent conversion vs. time to a relationship involving four constants. Ideally all the parameters can and should be determined in specific experiments. For example, k_0 can be determined by measuring conversion with clean catalyst in a short bed in which conversions in the range 10% to 90% are obtained. The quantities k_A and t_s can be measured in the course of the regular long bed run by monitoring the exit concentration of poison, so that a poison breakthrough curve is obtained. This curve is then fitted to an equation almost identical to Eq. (5) (*1*, *2*, *5*). However, even in the absence of any such specific experiments, in many cases four constants can be determined from a single experimental curve, especially for the important case of reasonably long beds ($N_T > 4$). Because the basic equation (7) is exceedingly nonlinear in time, it is not suitable to use directly.

The general problem of fitting a given experimental curve to the four parameters will be discussed in a later paper. It is noted in passing, however, that the two linear plots of Eqs. (11) and (12) (made for short and long times, respectively) determine four quantities (two slopes and two intercepts) from which the four parameters can be determined. For the case of nonselective poisoning ($h_0 = 0$) the problem is greatly simplified since for this case the linear plot of Eq. (11) (for short times) immediately determines both N_R and t_s. The ratio r can then be determined from either Eq. (13) or Eq. (12).

This procedure is illustrated using experimental data obtained in this laboratory for the poisoning of a catalyst containing 1% platinum plus 1% palladium supported on activated alumina. The feed to the reactor was oxygen containing 13 parts per million of hydrogen sulfide (as a poison) plus 83 parts per million of carbon monoxide. The reaction under investigation was the oxidation of carbon monoxide to carbon dioxide at 25°C and 0.5 atm pressure. (The above concentrations were chosen to correspond to

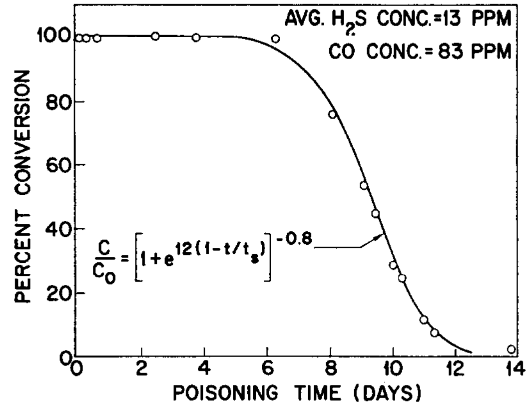

FIG. 2. Comparison between calculated and experimental catalytic activity history for CO oxidation at 25°C. Curve is calculated and points are experimental. Catalyst, 1% Pt–1% Pd supported on alumina.

a probable space cabin environment.) The superficial linear velocity was 2.0 cm/sec and the bed length was 9.3 cm.

The plot of conversion vs. time is shown in Fig. 2. Conversion of CO was complete for about 6 days, but between the 6th and 12th day it fell virtually to zero. Conversion of CO was measured by gas chromatography.

In analyzing this curve the first step is to replot it according to Eq. (11): ln C/C_0 vs. time. The resulting plot is linear up to about 8.6 days (35% conversion) with a slope of 1.00 per day and an intercept of −9.6. If now it is assumed that $h_0 = 0$ (i.e., that poisoning is nonselective) then this fixes $N_{\mathrm{R}} = 9.6$, since according to Eq. (11), when $h_0 = 0$ the intercept is $-N_{\mathrm{R}}$. The stoichiometric poisoning time t_s is also fixed at 9.6 days since the slope (1.0) is N_{R}/t_s for the case $h_0 = 0$. Thus, using the hypothesis that $h_0 = 0$, N_{R} and t_s are determined as 9.6 and 9.6 days, respectively.

The ratio r can now be conveniently determined from Eq. (13). When $h_0 = 0$ and $t = t_s$,

$$r = \frac{-\ln(C/C_0)}{\ln 2} \tag{14}$$

Since the percent conversion at $t = t_s = 9.6$ days is 43%, then C/C_0 in Eq. (14) is 0.57 (i.e., 1 − fraction converted) so that $r = 0.559/0.693 = 0.80$. The quantity N_{T} is immediately determined from Eq. (10) as $N_{\mathrm{T}} = N_{\mathrm{R}}/r = 12.0$. This completes the curve-fitting since, assuming $h_0 = 0$, all four constants have been determined. Substituting these values into Eq. (9) results in the breakthrough curve of Fig. 2:

$$\begin{aligned} C/C_0 &= 1 - \text{Fraction converted} \\ C/C_0 &= \{1 - \exp(-12t/9.6) \\ &\quad + \exp[12\,(1 - t/9.6)]\}^{-0.80} \\ &= \{1 + \exp(-12t/t_s) \\ &\quad \times (\exp[12 - 1])\}^{0.80} \\ &\cong \{1 + \exp[12(1 - t/t_s)]\}^{-0.80} \end{aligned} \tag{15}$$

In Fig. 2 the points are experimental and the curve is calculated from Eq. (15). Clearly the fit is within the experimental error, which justifies *a posteriori* the hypothesis that $h_0 = 0$. There is no guarantee that the above values for the four parameters are unique, since possibly other combinations will also fit the data. As mentioned earlier, special experiments should be performed to fix further the parameters, such as experiments with a short clean bed to fix k_0 and hence N_{R}.

In the above theory three advances have been made. First, from the practical design standpoint one is now in a position to predict the conversion–time curve for any new space velocity, bed length, or concentration of poison in the feed, since N_{T} (or N_{R}) and t_s depend linearly on these variables, as defined by Eqs. (1), (6), and (10). Secondly, from the fundamental standpoint, the absolute values of the rate constants k_0 and k_{A} can immediately be calculated from Eqs. (6) and (10). Thirdly, with the absolute value of k_0 in hand, the usual analysis (7) for effect of mass transfer and pore diffusion on the rate can be made, so that the effect of catalyst particle size can be predicted. Without the above theory, these predictions appear rather difficult.

The above treatment can be elaborated by using other families of curves for Eq. (4) and other adsorption breakthrough curves for Eq. (5). This will be investigated in a later paper, in which it will also be pointed out that the shape of the "tail" of the conversion vs. time curves is mainly determined by the shape of the tail of the basic poisoning curves, of which Eq. (4) is one possible family.

The treatment of Anderson and Whitehouse (*1*) has much in common with the foregoing. However, in place of Eq. (4) they use four empirical curves giving various degrees of selective poisoning, and in place of Eq. (5) they use four empirical curves giving various poisoning wave shapes. Thus instead of one "master equation" [Eq. (7)], their treatment concludes with a number of special cases, which are somewhat unwieldy to apply to experimental data. Since Anderson and Whitehouse do not consider the kinetics of adsorption of poison [i.e., do not use a "breakthrough equation," our Eq. (5)], time does not explicitly enter into their equations, and no account is made of poison passed out of the reactor after breakthrough of poison. Hence for a flow system it is difficult, if not impossible, to apply their treatment of the later stages of poisoning (e.g., for $t > t_s$), since the amount of poison adsorbed is not known, unless one assumes a breakthrough equation such as Eq. (5), or alternatively has extensive analytical data on the amount of poison adsorbed as a function of time.

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APPENDIX

Some explanation of Eq. (5) is likely in order. When a fixed bed of catalysts is adsorbing poison from a flowing gas stream, the distribution of poison in the bed, as well as the gas-phase concentration of poison throughout the bed, is ruled (*9*, *11*) in the absence of axial diffusion by the two equations:

$$V_L \frac{\partial C_p}{\partial x} = \rho_B \frac{\partial W}{\partial t} \qquad \text{(A1)}$$

$$\rho_B \frac{\partial W}{\partial t} = R(C_p, W) \qquad \text{(A2)}$$

where C_p is the gas-phase concentration of poison at time t and at point X, while $R(C_p, W)$ is the function which describes the kinetics of poison adsorption. The function R is in general determined by mass-transfer rates from the flowing gas stream to the external catalyst surface, or by the rate of diffusion into the catalyst pores. The actual adsorption step from gas to solid surface is usually much faster than either of the other two processes. Equation (A1) is an equation of mass balance which states the rate of adsorption on the solid equals the rate of loss from the gas stream.

The exact solution of Eqs. (A1) and (A2) for even the simplest R function is most difficult and much mathematical effort has been expended on this (*11*). Equation (5) is probably the only known exact solution given in terms of elementary functions, and is, for the adsorption kinetics;

$$R(C_p,W) = k_A C_p(1-W/W_s) \qquad \text{(A3)}$$

The kinetics of Eq. (A3) do not exactly correspond to any particular physical situation except irreversible Langmuir type adsorption. However, the general property of an adsorption rate proportioned to gas-phase concentration which diminishes to zero as saturation is reached roughly describes all situations. For present purposes, Eq. (5) can best be looked upon as a semi-empirical equation which gives a variety of physically likely poisoning wave shapes as the two parameters τ and λ are varied. The gas-phase concentration of poison throughout the bed is also given by Eq. (5) for reasonably long times and reasonably long beds, due to the condition that after a poison wave has reached a constant pattern (*11*) then $C/C_0 = W/W_s$.

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