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NOTES

Time-Dependent Pore-Mouth Poisoning of Catalysts

Recently, Weisz and Goodwin (*1*), in their report on diffusion-controlled combustion of "coke" deposited upon porous catalysts, noted that the "shell-progressive rate mechanism" (diffusion of reactant through a growing nonreactive shell) should have general applicability in a wide variety of fluid–solid rate phenomena. Levenspiel's text (*2*) treats fluid–solid reactions in terms of this moving boundary model (pseudo-steady approximation), while White and Carberry (*3*) present a general treatment of the shell-progressive mechanism for non-catalytic gas–solid reaction where particle size changes with extent of reaction. The work of Weisz and colleagues (*1*, *4*) demonstrates the validity and utility of the model as applied to regeneration.

If the shell-progressive mechanism is applicable, then catalyst poisoning via deposition of site deactivating agents is a phenomenon which can be treated in terms of diffusion through a progressively growing shell of poisoned catalyst. Coking of a porous catalyst under diffusion-controlled conditions is clearly a special case of a general diffusion-controlled poisoning process. The rate of the poisoning or coke-producing reaction may be finite so that the process cannot, *a priori*, be viewed *solely* in terms of diffusion to the reaction interface through a growing shell of poisoned or coked catalyst. More commonly, mass transfer through the boundary layer surrounding the catalyst pellet exists in series with the intraparticle diffusion step through the growing shell, followed by chemical reaction which in the limit occurs at the poisoned–unpoisoned boundary within the particle at a radial position, r. It will here be demonstrated, within the limits imposed by the shell-progressive mechanism, that a general relationship between the time and degree of catalyst contamination (or regeneration) can be readily fashioned for the case in which rates of interphase and intraparticle diffusion and first order chemical reaction are all finite.

NOMENCLATURE

A	Cross-sectional area
b	Stoichiometric coefficient
B	Solid reactant
C	Concentration of gaseous species
C_0	Bulk gas-phase concentration
C_s	External surface concentration
C_1	Concentration at reaction boundary
$\mathfrak{D}$	Intraparticle diffusivity
k	First order surface rate constant
k_g	Gas-phase mass transfer coefficient
L	Half-thickness of flat plate
N_{Da}	Damkohler number, $kR/\mathfrak{D}$
N_{Nu}	Nusselt number, $k_gR/\mathfrak{D}$
R	Particle radius
r	Radial position of reaction interface
S	Surface area per unit catalyst volume
t	Time
X	Flat-plate distance coordinate
X_1	Position of flat-plate reaction interface

Greek Letters

α, β	Defined by Eq. (21)
γ	Reduced radial position of reaction interface, r/R or X_1/L
$\bar{\gamma}$	Normalized flat-plate distance coordinate, X/L
ρ	Saturation concentration of poison, or coke
η	Effectiveness factor
θ	Total time $= t_{\mathrm{D}} + t_{\mathrm{m}} + t_{\mathrm{c}}$

τ Defined by Eq. (22)
σ Fraction of particle reacted
ψ Effectiveness factor (Thiele) modulus $= L(kS/\mathfrak{D})^{1/2}$ (flat plate)

CRITERION FOR THE APPLICATION OF THE SHELL-PROGRESSIVE MECHANISM (SPM)

If a sharp reaction boundary, which moves with time towards the center of the particle, is to exist it must be shown that the chemical reaction rate of poisoning, coking, or regeneration proceeds at a rate such that a rather sharp concentration gradient exists over a narrow zone of reaction at the solid product–reactant interface. For if the surface reaction rate is very slow relative to diffusion in both the fluid and porous solid phase, reaction occurs throughout the particle and in consequence a progressively moving shell of contaminated or reacted solid product cannot exist. Diffusion and reaction then occur simultaneously rather than in series.

For first order, steady state reaction in a flat plate

$$\frac{C}{C_0} = \frac{\sinh \psi\gamma}{\sinh \psi} \cong \exp\left[-\psi(1-\gamma)\right] \quad (1)$$

(approximation valid only for severe diffusional restriction). The analog of the shell-burning phenomenon in the steady state is the situation in which the reactant concentration drops to a small fraction, say $C/C_0 = e^{-4} = 0.0183$, of the external concentration within a "shell" near the plate surface which is small relative to the half-thickness of the plate, say $(1 - \gamma) = 0.02$. Use of these numbers in Eq. (1) reveals that the Thiele modulus, ψ, must be greater than about 200 to ensure a shell mechanism for the classical effectiveness factor situation. It is apparent that this same criterion can be extended to the quasi-steady coke burning or other "shell" situations provided the effectiveness factor is defined on the basis of the position of the moving interface, X_1. Since attention is confined to first order reactions, a concentration drop through the burned off catalyst or through the boundary layer does not influence whether or not a discrete interface is established. Thus,

$$L(kS/\mathfrak{D})^{1/2} > 200 \text{ for shell mechanism} \quad (2)$$

Expressing this inequality in terms of the Damköhler number

$$N_{\mathrm{Da}} = Lk/\mathfrak{D} > 4 \times 10^4/LS \text{ for shell mechanism} \quad (3)$$

For example, assuming an "average" catalyst for which

$$L = 0.1 \text{ cm and } S = 80 \text{ m}^2/\text{cc} = 8 \times 10^5 \text{ cm}^{-1}$$

we obtain

$$N_{\mathrm{Da}} > 1/2 \text{ for shell mechanism} \quad (4)$$

Of course, the critical Damköhler number depends on the particular catalyst, as shown in Eq. (3). The truly fundamental criterion is given by the Thiele modulus as shown in Eq. (2). Below the critical Damköhler number, the mechanism of coke burning or poison deposition goes over to the "transition region" as shown in Fig. 2 of the paper of Weisz and Goodwin (*1*). In the transition region, there is no clear-cut interface and the "shell" model *cannot* be applied rigorously.

The additional assumption implicit in the following treatment is that of pseudo-steady-state conditions. Bischoff's analysis reveals that this latter assumption is quite realistic for gas–solid systems (*5*).

CATALYST POISONING

Wheeler (*6*) directed attention to the poisoning of catalyst pores in terms of (a) uniform and (b) selective deposition of the poisoning agent upon catalytic sites. Selective or pore-mouth poisoning is defined as that deposition process which commences at the catalyst pellet exterior surface and progresses inward along pore walls until the center of the pellet is reached. Uniform poisoning involves indiscriminate deposition throughout the pellet, so that sites at the center of the pellet are exposed to poisoning simultaneously with those at the pellet surface. The rate of the poisoning reaction obviously dictates whether selective or uniform poisoning shall prevail, since a high rate [and low effectiveness (*10, 11*)] confines poisoning to the exterior portions of the pellet. Thus poisoning reactions intrinsically slow retative to diffusion will tend to prompt uniform poisoning while the more rapid transformations will invite selective poisoning. As Weisz has noted (*1*), the realization of uniform coke deposition follows the same generalization. Experimental criteria are given by Weisz (*7*), while the SPM criterion and its consequences have been specified above.

The distinction between these extremes of poisoning is of great practical import with respect to rate retardation (fouling). Clearly, uniform poisoning results in a rate arrestment which for first order reaction is linear in the fraction of sites unpoisoned. Pore-mouth or selective poisoning can lead to more drastic deactivation since only a small fraction of the pore mouth need be deactivated to create a "solid film" resistance in series with the chemical kinetic process. In the limit, as demonstrated by Wheeler, the catalytic process may become controlled by the slow diffusion of reactants through a deactivated "shell" surrounding the active sites lying within the pellet. A striking demonstration of these facts is to be found in a recent issue of this Journal. Anderson *et al.* (*8*) reported the details of an extensive study of sulfur poisoning of Fischer-Tropsch catalyst. Fouling data in an integral bed reactor were expressed in terms of sulfur content in the synthesis gas feed. Although not presenting poisoning rate kinetics for a single catalyst particle from these integral reactor data, the reference paper does declare that (a) resistance to poisoning increased with decreasing particle size and (b) that the poison is found to deposit in a thin layer near the external surface of the particles. Observations (a) and (b) are, of course, compatible and in accord with Wheeler's earlier assertions.

The analysis presented here may provide a basis whereby the time-dependent selective poisoning kinetics may be explicity incorporated into integral fouling relationships such as those presented by Anderson *et al.* (*8*). Wheeler's treatment of pore-mouth or selective poisoning is readily extended to the time-dependent regime and the assumption of an infinitely rapid poisoning reaction rate relative to that of diffusion need not be retained. The elimination of these restrictions is important since Wheeler's treatment embraces only those circumstances in which a quantity of poison is imposed upon the system for a period of time sufficient to cause a fixed, and thereafter, time-independent deactivation. More commonly, a poison or coke-bearing agent is fed to the catalytic system in continuous though often small supply (*8*). Further, as mentioned above, the rate of the deactivation reaction between the agent and the surface may well be finite, and characterized by a Damköhler number conforming to the SPM criterion.

DETAILS OF ANALYSIS

In the general instance three processes occur in series during shell-progressive regeneration or selective poisoning.

1. Interphase mass transport of the reacting species from the bulk gas phase to the external surface of the catalyst particle.
2. Intraparticle diffusion of the species from the external surface through regenerated or contaminated pores to the narrow zone of reaction.
3. Chemical reaction or chemisorption of the species upon the surface within the zone at position *r*.

The time-on-stream vs. degree of particle regeneration or contamination relation can be easily derived without assuming any one of the above three steps to be rate-controlling.

Consider a flat porous catalyst of cross-sectional area A, half-thickness L, and poison concentration ρ. The weight of poison on the catalyst is $A\rho(L - X)$, where X is measured from the center line ($X = 0$) to the surface ($X = L$). Equating the rate of consumption to that of bulk mass transport, diffusion, and reaction, on the assumption that the shell-progressive mechanism prevails

$$\frac{1}{A}\frac{dA\rho(L - X)}{dt} = -\rho\frac{dX}{dt} = bk_g(C_0 - C_s)$$
$$= -b\mathfrak{D}\frac{dC}{dX} = bkC_1 \quad (5)$$

where b is the stoichiometric coefficient for the reaction

$$\mathrm{C} + b\mathrm{B} \rightarrow \text{product}$$

For example, in total regeneration, O_2 + coke $\rightarrow CO_2$ . . . , b is unity. while $b = 2$ if CO is the primary product. Letting $\gamma = X_1/L$ equating consumption to the gas-phase mass transfer rate, and integrating, the bulk concentration is obtained

$$C_0 = C_s + [\rho L(1-\gamma)/bk_g t] \tag{6}$$

If bulk mass transfer is rate-controlling, C_s (external surface concentration) is zero and,

$$t_m = \rho L(1-\gamma)/bk_g C_0 \tag{7}$$

Now solve for the concentration distribution across the reacted layer,

$$-b\mathfrak{D}\left.\frac{dC}{dX}\right|_{X=L} = \text{constant}$$

and

$$\begin{cases} X = X_1 & C = C_1 \\ X = L & C = C_s \end{cases} \tag{8}$$

$$C_s - C = \frac{(C_s - C_1)(1-\bar{\gamma})}{(1-\gamma)} \qquad \bar{\gamma} = \frac{X}{L}$$

then

$$-\mathfrak{D}\left.\frac{dC}{dX}\right|_{X=L} = \frac{\mathfrak{D}(C_s - C_1)}{L(1-\gamma)} = -\frac{\rho L}{b}\frac{d\gamma}{dt} \tag{9}$$

Integrating and solving for C_s

$$C_s = C_1 + [(1-\gamma)^2 L^2 \rho/2b\mathfrak{D}t] \tag{10}$$

If shell diffusion is rate-controlling $C_1 = 0$ and $C_s = C_0$

$$t_d = [L^2\rho(1-\gamma)^2/2b\mathfrak{D}C_0] \tag{11}$$

Equating chemical reaction with consumption and solving for C_1

$$\begin{aligned} -\rho L(d\gamma/dt) &= bkC_1 \\ C_1 &= [\rho L(1-\gamma)/bkt] \end{aligned} \tag{12}$$

If chemical reaction is rate-controlling, $C_1 = C_0$ and

$$t_c = \rho L(1-\gamma)/bkC_0 \tag{13}$$

Substituting (12) into (10) and that result into (6), there results, on solving for time,

$$t = \theta = \frac{\rho L(1-\gamma)}{bk_g C_0} + \frac{\rho L^2(1-\gamma)^2}{2b\mathfrak{D}C_0} + \frac{\rho L(1-\gamma)}{bkC_0} \tag{14}$$

In view of Eqs. (7), (11), and (13), it follows that

$$\theta = t_m + t_d + t_c \tag{15}$$

which result simply verifies that in the case of consecutive first order events, the total time per cycle is simply the sum of the time constants for each step of the series. Thus Eq. (14) could be written directly in terms of Eqs. (7), (11), and (13). It follows that the well-known expressions for t_m, t_0, and t_c for the spherical case permit one to state the general sphere solution immediately. In the case of a spherical catalyst (*2, 3*)

$$t_m = \rho R(1-\gamma^3)/3bk_g C_0 \tag{16}$$

$$t_d = (\rho R^2/6b\mathfrak{D}C_0)(1 - 3\gamma^2 + 2\gamma^3) \tag{17}$$

$$t_c = \rho R(1-\gamma)/bkC_0 \tag{18}$$

therefore

$$\theta = \frac{\rho R^2}{b\mathfrak{D}C_0}\left[\frac{(1-\gamma^3)}{3}\left(\frac{1}{N_{\mathrm{Nu}}} - 1\right) + \frac{(1-\gamma^2)}{2} + \frac{(1-\gamma)}{N_{\mathrm{Da}}}\right] \tag{19}$$

where

$$\gamma = \frac{R}{r_1} \qquad N_{\mathrm{Nu}} = \frac{k_g R}{\mathfrak{D}} \qquad N_{\mathrm{Da}} = \frac{kR}{\mathfrak{D}}$$

N_{Nu}, the Nusselt number is the ratio of bulk mass transfer to intraparticle diffusion (*9, 10*) while N_{Da}, the Damköhler number, expresses the ratio of chemical reaction rate to that of intraparticle transport.

Equation (14) may be expressed in terms of N_{Nu} and N_{Da} for a plate equivalent to a sphere where $L = R/3$

$$\theta = \frac{\rho R^2}{18b\mathfrak{D}C_0}\left[6(1-\gamma)\left(\frac{1}{N_{\mathrm{Nu}}} + \frac{1}{N_{\mathrm{Da}}}\right) + (1-\gamma)^2\right] \tag{20}$$

For the flat plate, the fraction reacted σ is $1 - \gamma$, thus (20) can be solved to yield an explicit relation between σ and time, θ

$$\sigma = -\alpha + (\alpha^2 + \beta^2)^{1/2} \tag{21}$$

where

$$\alpha = 3\left(\frac{1}{N_{\mathrm{Nu}}} + \frac{1}{N_{\mathrm{Da}}}\right) \text{ and } \beta = \left(\frac{18b\mathfrak{D}C_0\theta}{\rho R^2}\right)^{1/2}$$

For large values of N_{Nu} and N_{Da} (shell-diffusion control) α approaches zero and σ varies as the square root of time.

The general sphere solution [Eq. (19)] does not yield an explicit σ–time relation. Since $\sigma = (1 - \gamma^3)$ for a sphere, the relation is readily displayed graphically. In Figs. 1, 2, and 3, σ is plotted against

$$\tau = \frac{1}{R} (b\mathfrak{D}C_0\theta/\rho)^{1/2} \qquad (22)$$

for various values of N_{Nu} and N_{Da} for a spherical catalyst. The range of usefulness of the flat-plate approximation, Eq. (21), is indicated by the dashed portion of the curves. Evidently the flat-plate approximation is a rather accurate description of the spherical case up to σ values of about 0.4. That is, virtually 40% of the SPM regeneration, coking, or poisoning process for a spherical catalyst is accurately described in terms of a flat plate of half-thickness equal to one-third the sphere radius. Early stages of regeneration, coking, or poisoning may, therefore, be readily described by Eq. (21), the explicitness and simplicity of which relative to Eq. (19) is obvious.

Another feature of Figs. 1, 2, and 3 is worth noting: the apparent linearity of the σ–τ relation over a significant range of σ values and for wide variations in N_{Da} and N_{Nu}. Since τ is a square root function of time-on-stream, then a linear σ–τ relation

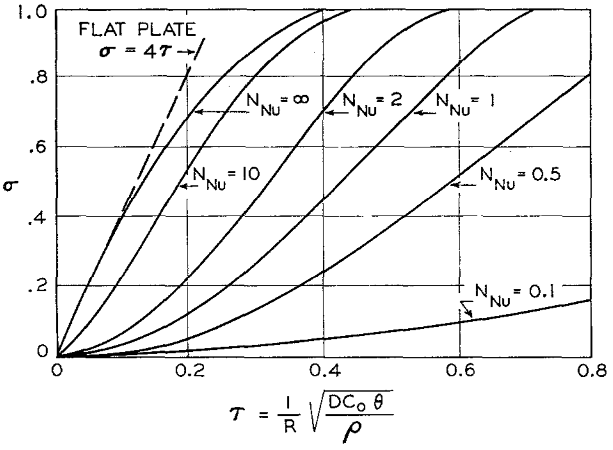

FIG. 1. Fraction of spherical catalyst poisoned or regenerated vs. dimensionless time, $N_{\mathrm{Da}} = \infty$ first order reaction.

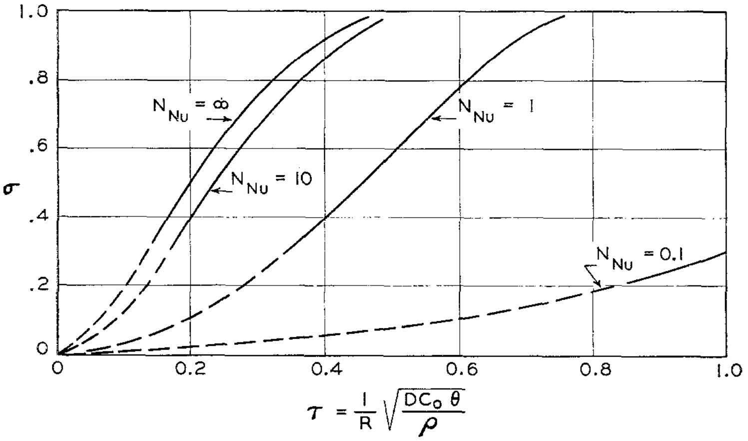

FIG. 2. Fraction of spherical catalyst poisoned or regenerated vs. dimensionless time, $N_{\mathrm{Da}} = 10$ first order reaction.

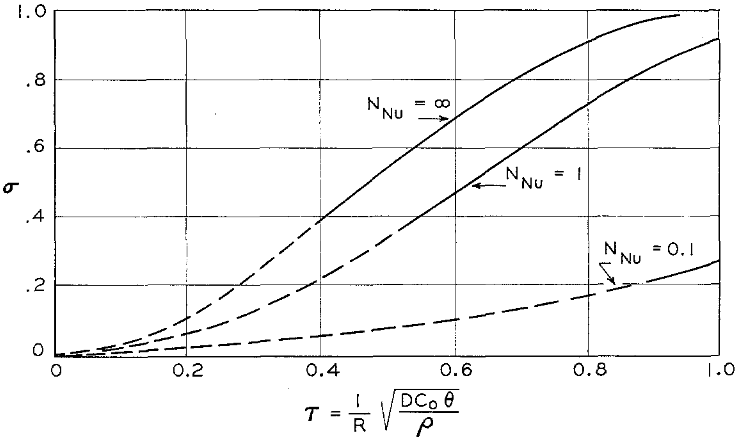

FIG. 3. Fraction of spherical catalyst poisoned or regenerated vs. dimensionless time, N_{Da} = 1 first order reaction.

might tempt one to infer diffusion control of the process. However, no conclusions concerning the nature of the regeneration or coking rate are permissible unless accurate data over the entire range of reaction variables are at hand. For example, in Fig. 3, at $N_{Da} = 1$ and $N_{Nu} = 1$, an apparent $\sigma \propto \theta^{1/2}$ dependence exists over a significant range of σ (~20% to 80%); yet it certainly cannot be inferred that shell diffusion controls in this case. Indeed for the values of N_{Nu} and N_{Da} prevailing in this example, both chemical reaction and bulk mass transfer limit the rate process. This demonstrates the point that the square root of time-extent of reaction relation does not necessarily indicate diffusion control.

An excellent case in point is provided by Voorhies (*11*) treatment of coking of cracking catalysts. These data were empirically assembled by expressing coke content (proportional to σ) in terms of approximately the square root of time-on-stream. This finding was assumed to suggest an intraparticle diffusional process as rate-controlling. However, it is clear that when mass transfer, shell diffusion, and reaction all proceed at finite, comparable rates, a fortuitous dependency upon the square root of time may prevail and in consequence no mechanistic inference is permissible. Only an exhaustive investigation of the rate process in terms of key variables as illustrated by the coke-burning work of Weisz and Goodwin (*1*) can establish the precise nature of rate control.

A further illustration of the pertinence of this analysis is provided by Schwab's data (*12*) on the effect of catalyst particle size upon the catalyst activity–poison dosage relationship. In that work a linear relation is found for the smallest particles (uniform poisoning) while an apparently unexpected nonlinearity is manifest for larger particles. This particle size effect is clearly suggestive of a selective, diffusion influenced phenomena, in accord with the model set forth here.

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Determination of the Nature of Catalyst Acid Sites by Infrared Spectroscopy

This note aims to report a new possibility for the evaluation of Lewis acidity of high alumina catalysts and carriers. The method is founded on the measurement of the infrared *symmetrical* deformation band of ammonia. Up to now, only the N–H stretching or the asymmetrical deformation bands of ammonia had been used (*1–3*).

Silica-alumina catalysts were prepared by hydrolysis of aluminum isopropoxide and ethyl silicate, according to the procedure described by Leonard *et al.* (*4*) and calcined at 500°C for 16 hr in a muffle oven. The sample film, held in a cell fitted with NaCl windows, was heated under high vacuum ($\leqslant 10^{-5}$ mm Hg) at 400°C for at least 2 hr. Ammonia was introduced at this temperature and the sample was slowly brought to room temperature, while a constant ammonia pressure of 50 mm Hg was maintained in the cell. After equilibrium was established, the film was evacuated overnight at 25°C. The sample was then heated successively at 100°, 200°, and 300°C, and finally water vapor from the atmosphere was admitted into the cell. The spectra were obtained by a Beckman I.R. 4 spectrophotometer fitted with sodium chloride or calcium fluoride optics.

The asymmetrical deformation bands are observed for ammonia at 1630–1620 cm^{-1}, for ammonium at 1480–1475 cm^{-1} in alumina-rich samples, and at 1450–1440 cm^{-1} in substances of low alumina contents. For example, the ammonium deformation band is centered at 1444 cm^{-1} for a silica-alumina containing 85% silica, whereas for pure alumina it is situated at 1478 cm^{-1}. At increasing silica content the shoulder at 1444 cm^{-1} which is very small for samples containing 5% silica, becomes more important, so as to present a single band for 85% silica catalysts.

In the 1350–1200 cm^{-1} spectral range, a strong and rather broad band appears in samples rich in alumina and exposed to NH_3. The frequency of this band shifts to higher values when the catalyst is heated. It may also be present in substances of high silica content, but the overlapping with Si–O vibrations does not permit its characterization. This band coincides with that of the symmetric deformation of ammonia reported for ammine coordination complexes (*5*) which is known to be very sensitive to the electronic character of the metal. Wilmshurst (*6*) has established a linear relationship between the electronegativity of the metal in the ammine complexes and the square of the symmetric