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Consideration in Experimental Assessment of Effectiveness Factors for Porous Heterogeneous Catalysts with Nonuniformly Distributed Active Sites

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It is shown that the conventional experimental approach for assessing effectiveness factor by measuring catalytic rates over particles of different degrees of subdivision (but with conditions otherwise the same) can be used only with careful circumspection when catalytically active material is nonuniformly distributed within porous carrier materials. In particular, failure of subdivision to affect measured specific rates or rate constants (per unit mass) does not necessarily imply unity effectiveness factor when the distribution of active sites is nonuniform. It is shown how such particle size–activity tests can lead to an erroneous conclusion of negligible diffusional effects in cases where diffusional effects are actually quite large. In order to obtain the needed information as to diffusional effects, the subdivision experiments must be continued to the extent that the smallest particle sizes investigated are smaller than the size of the concentrated domains of active material within the original porous catalytic body. It is also shown how the pattern of specific activity as a function of particle size may actually be employed to suggest to the experimenter when he is dealing with inhomogeneous catalytic particles.

NOMENCLATURE

a	thickness of active layer of catalyst
A	parameter in Eq. (3)
C	concentration
D	diffusivity
h	modulus, $h = L\rho k/D$
J	parameter in Eq. (3)
k	specific, first order reaction rate constant per unit mass of catalyst
L	half thickness of slab of Fig. 1, thickness of slab of Fig. 2
X	distance
δ	fraction of slab thickness L that is catalytically active, $a \equiv \delta L$
ρ	density of porous catalyst

Subscripts

L	refers to fractional distance, $X_L \equiv X/L$
S	refers to gas–solid surface

INTRODUCTION

Although practitioners of the catalytic art have long appreciated the importance of uniformity in the distribution of a catalytic material within a three-dimensional carrier (*1*), interest in the implications of such distribution has heightened in recent years. Smith and Carberry (*8*) have shown that a partially impregnated carrier can improve yield selectivity and decrease thermal sensitivity in the oxidation of naphthalene to phthalic anhydride and Minhas and Carberry (*4*) have similarly shown the merits of such catalysts in SO_2 oxidation.

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Corbett and Luss (*2*) and Shadman-Yazdi and Petersen (*6*) have also investigated the influence of nonuniform distribution of active sites upon effectiveness factor, selectivity and deactivation. Kasaoka and Sakata (*3*) carried out analyses of catalytic effectiveness factors (as a function of a generalized Thiele modulus) for several linear and hyperbolic distribution models for intrinsic rate constant and diffusivity within porous catalysts.

The present paper addresses the problems inherent in an experimental assessment of the effectiveness factor of such nonuniform catalysts using the well-known ratio analysis [see for example, Satterfield (*5*) or Smith (*7*)] applied to specific rates or rate constants (usually measured in isothermal, differential, laboratory reactors) obtained using different particle size fractions of catalytic material produced by crushing and sieving such nonuniformly distributed catalytic pellets. That such problems may frequently arise is suggested by the facts that:

1. Concentrating catalytically active material near the outer periphery of a porous carrier pellet very frequently improves overall catalytic performance and selectivity (as compared to uniformly distributed catalysts of the same volume-averaged activity).
2. Manufacture of such catalysts by impregnation can frequently lead to such nonuniform distributions.
3. Routine laboratory testing procedures often include rate measurements made with different size fractions of crushed catalyst.

The approach is to represent such originally prepared nonuniform pellets by semi-infinite porous planes with catalytically active sites concentrated in a small region near the surface. The physical process of subdividing by crushing and size classification is simulated by repeatedly bisecting the planar bodies and the resulting planar bodies produced by the bisecting processes; the usual steady-state mathematical analysis is then carried out to give effectiveness factors for each mixture of planar bodies so produced.

METHODS

Mathematical Development

First-order chemical reaction combined with pore diffusion within the idealized catalytic slab of Fig. 1 is described in the steady state by the one-dimensional differential equation:

$$\frac{d^2C}{dX_L^2} - h^2C = 0, \qquad (1)$$

where

$$X_L = X/L,$$

and

$$h^2 = \rho k L^2/D \text{ (Thiele modulus).}$$

This equation is applicable for both the exterior, catalytically active, part ($h > 0$) of the slab and the interior inactive ($h = 0$) part. The boundary conditions are: for the interior part:

$$\text{at } X_L = 0, \quad \frac{dC_{\text{inactive}}}{dX_L} = 0,$$

and for the exterior active part:

$$1.\ \text{at } X_L = 1.0, \quad C = C_s,$$

$$2.\ \text{at } X_L = a/L, \quad \frac{dC_{\text{act}}}{dX_L} = \frac{dC_{\text{inact}}}{dX_L} = 0.$$

Solving this differential equation with the stated boundary conditions gives the following reactant concentration profiles: for the exterior, active region:

$$C = \frac{[\cosh(hX_L) - \tanh(ha/L)\cdot\sinh(hX_L)]}{[\cosh(h) - \tanh(ha/L)\cdot\sinh(h)]}\cdot C_s;$$

for the interior, inactive region:

$$C = \frac{[\cosh(ha/L) - \tanh(ha/L)\cdot\sinh(ha/L)]}{[\cosh(h) - \tanh(ha/L)\cdot\sinh(h)]}\cdot C_s.$$

The steady-state reaction rate per unit surface area of the slab is:

$$r = \frac{D}{L}\cdot\left.\frac{dC}{dX_L}\right|_{X_L=1.0},$$

while the rate per unit area without transport resistance is given by:

$$r' = \rho L\delta k C_s.$$

The effectiveness factor is then obtained in the usual way:

$$\eta = \frac{r}{r'} = \frac{\left\{1 - \dfrac{\tanh[h(1-\delta)]}{\tanh(h)}\right\}}{h\delta\left\{\dfrac{1}{\tanh(h)} - \tanh[h(1-\delta)]\right\}}. \quad (2)$$

The slab of Fig. 2 is now used to portray the slab of Fig. 1 broken in half, i.e., the slab of Fig. 1 is axially bisected by a plane to produce two slabs each of thickness L as shown in Fig. 2. The mathematical analysis for such a slab is carried out in the usual way with the following results:

Concentration Profile in Active Region

$$C = A\sinh(hX_L) + C_s\cosh(hX_L).$$

Concentration Profile in Inactive Region

$$C = (C_s - J)X_L + J.$$

Effectiveness Factor

$$\eta = \frac{1 - J/C_s - hA/C_s}{\delta h^2}, \quad (3)$$

where

$$\frac{A}{C_s} = \frac{[1 + h(\delta - 1)\sinh(h\delta) - \cosh(h\delta)]}{[\sinh(h\delta) - h(\delta - 1)\cosh(h\delta)]},$$

and

$$\frac{J}{C_s} = \left(\frac{A}{C_s}\right)[\sinh(h\delta) - h\delta\cosh(h\delta)] + \cosh(h\delta) - h\delta\sinh(h\delta).$$

Note that the modulus h is defined in the same way (dimenion L) for both the slab of Fig. 1 and that of Fig. 2.

It should be noted that Eq. (3) and the associated expressions are applicable not only to the slab of Fig. 2 but also to the active member of the two slabs formed by splitting the slab of Fig. 2 in half by a vertical plane, provided h is decreased and δ is increased each by a factor of two. The active slabs formed by similar subsequent splittings can then also be described by

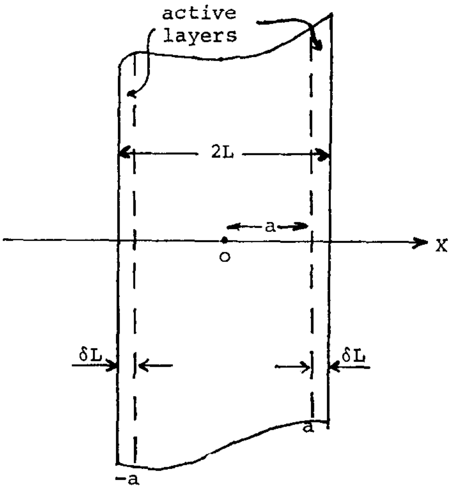

FIG. 1. Schematic diagram of planar catalyst with active sites concentrated in two outer layers of thickness $\delta L = a$.

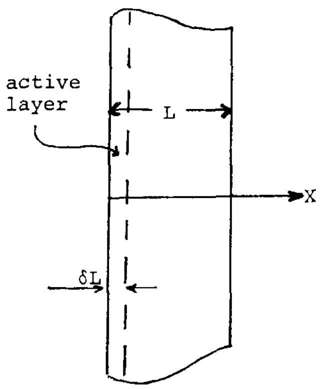

FIG. 2. Schematic diagram of planar catalyst resulting from bisection of the catalytic body of Fig. 1.

Eq. (3) provided h is properly adjusted to account for decrease in L with δ properly adjusted to maintain $\delta L = L - a$. Of course the inactive portions formed by each split contain no active sites, are inactive catalytically, and hence make no contribution to the numerator or denominator of the effectiveness factor relationship (nor would they influence related experimental measurements of η) even though the inactive pieces may be retained in the mixture to which η applies.

RESULTS AND DISCUSSION

In order to demonstrate the influence of the fractional thickness δ of the active catalytic layer of a given particle having the structure of the slab of Fig. 2, Eq. (3) is plotted versus modulus h in Fig. 3 for various constant values of δ. From Fig. 3 it is evident that the influence of the fractional thickness δ of an outer layer of catalytically active material is most pronounced at high values of h (large particles). This may be understood as an increase of the effectiveness of catalytic sites within a large particle as they are moved toward the surface to form a peripheral layer less influenced by diffusion of the gaseous reactant. Even at values of modulus h less than 10, however, the effect of changing δ from 1.0 to 0.5 is not insignificant.

Starting with the slab of Fig. 1 with modulus h_0 and initial fractional active layer thickness δ_0, and splitting it vertically into two slabs as shown in Fig. 2, and then successively splitting the slabs vertically produces a series of active slabs of decreasing modulus h, increasing δ and increasing effectiveness factor, η; these values are shown plotted in Figs. 4–7 as η vs h/h_0 for different values of the original modulus h_0 and the original fractional thickness δ_0. It should be pointed out that $h = h_0$ is the same for the slabs of Figs. 1 and 2, by definition. Only slight differences in effectiveness factor are obtained for these two slabs [Eq. (2) for Fig. 1 and Eq. (3) for Fig. 2]; the difference is evident graphically only for $h_0 = 10$ and $\delta_0 = 0.1$ (Fig. 4). From Figures 4–7 it is evident that if δ_0 is sufficiently small (<0.1) and h_0 is sufficiently large, the first several splittings of the slabs cause very little change in effectiveness factor η, even when the initial value of η (at h_0 and δ_0) is significantly less than unity. The implication of this result is that the conventional method of estimating effectiveness factor, by forming ratios of specific reaction rates measured isothermally for different particle sizes of a crushed and sieved catalyst, can produce erroneous results in the event the catalytically active material is not uniformly distributed throughout the original catalyst pellet. As a particular example (and referring to Fig. 5), the kinetic testing of several different size fractions, obtained from a starting pellet with $h_0 = 100$ and $\delta_0 = 0.01$, could produce values of the specific rate not very different, thereby erroneously implying unity effectiveness factor.

It is evident from Fig. 4 that when the starting values of both h_0 and δ_0 are small, then the starting value of the effectiveness factor is essentially unity and does not

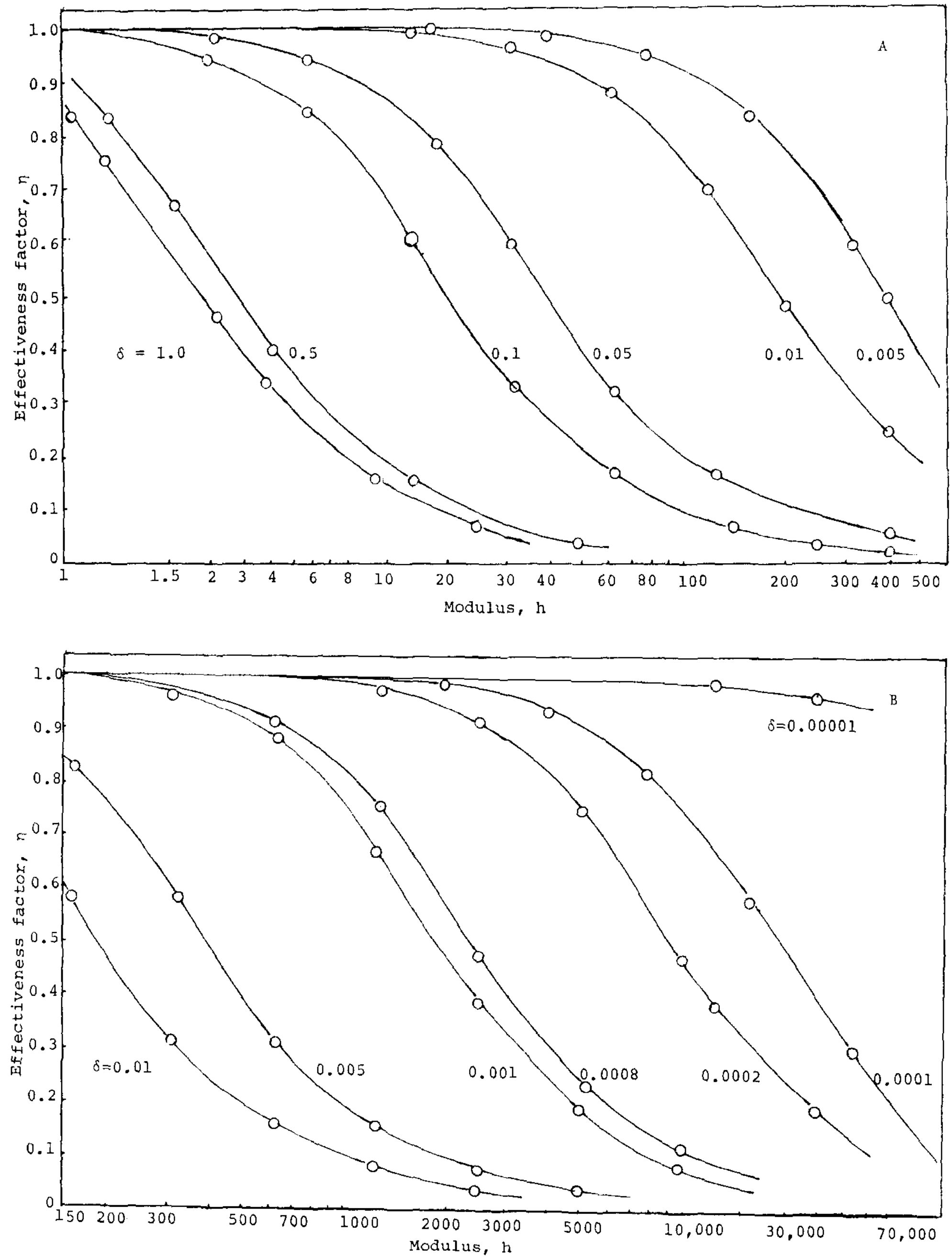

FIG. 3A and B. Effectiveness factor plotted versus modulus for slabs of Fig. 2 of constant values of δ. Equations (3).

change perceptibly as the original particle is fractured because the active material is near the particle periphery and works effectively regardless of particle size. Figure 4 (for $h_0 = 10$) shows, however, that even for $\delta_0 = 0.05$ and larger the effectiveness factor for the unfractured particle is less than unity. Nevertheless Fig. 4 indicates that the "particle size test" will be successful even for $\delta_0 = 0.1$—viz, breaking up such par-

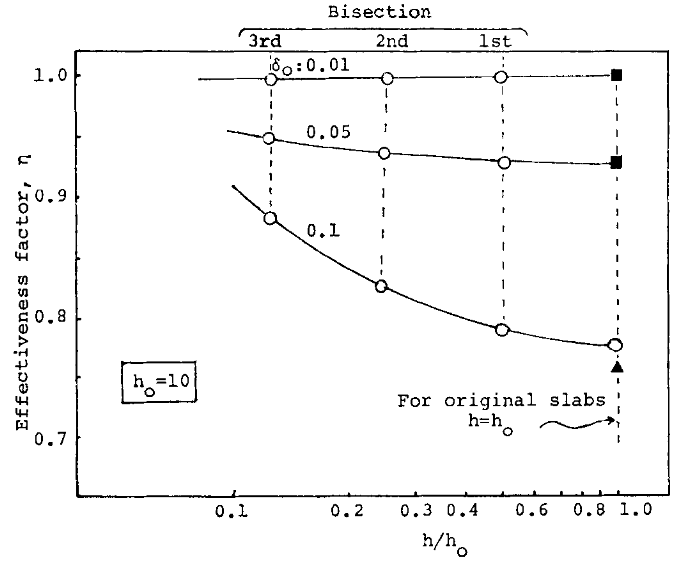

FIG. 4. Change in effectiveness factor due to repeated sequential bisection of slabs, $h_0 = 10$. (■) η for either slab of Fig. 1 or slab of Fig. 2; (▲) η for slab of Fig. 1 only; (○) η for slab of Fig. 2 only.

ticles will lead to increases in effectiveness factor.

Similar behavior (i.e., reliable "particle size tests") is *not* predicted, however, for $h_0 = 100$ as shown in Fig. 5. In Fig. 5 for $h_0 = 100$ and $\delta_0 = 0.05$ the starting value of the effectiveness factor is only 0.2 but halving the particle size does not percep-

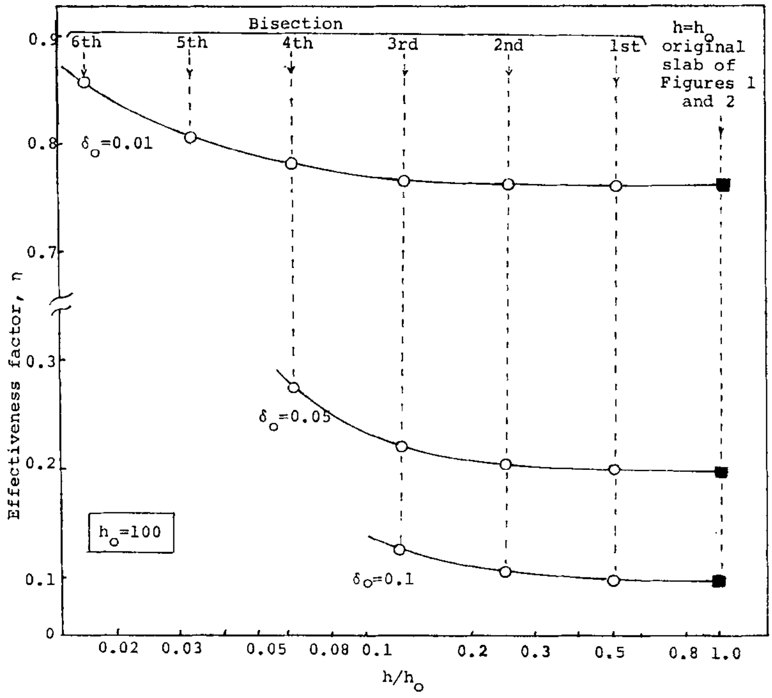

FIG. 5. Change in effectiveness factor due to repeated sequential bisection of slabs, $h_0 = 100$. (■) η for either slab of Fig. 1 or slab of Fig. 2; (○) η for slab of Fig. 2 only.

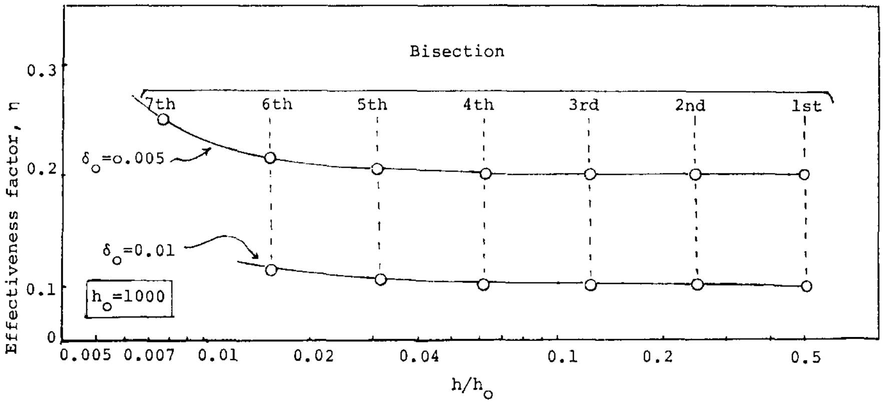

FIG. 6. Change in effectiveness factor due to repeated sequential bisection of slabs, $h_0 = 1000$. (O) Slab of Fig. 2 only; η not shown for $h = h_0$.

tibly alter the effectiveness factor. Such an experiment would produce no observable change in specific catalytic activity when the particle size was halved and could lend to an erroneous deduction regarding diffusional effects. The reason is that for $h_0 = 100$ and $\delta_0 = 0.05$ the active layer itself is diffusion limited and is not affected by fracturing the particle until the particle is reduced to sizes of the same order as the thickness of the active layer (i.e., until $h \approx 0.05\ h_0$). Thus for $h_0 = 100$ and $\delta_0 = 0.05$ one could perform the particle size test over a tenfold size range, see essentially no change in specific activity and thereby erroneously conclude that the original effectiveness factor was unity. As is evident from Figs. 4–7, the larger the modulus h_0 of the starting particles, the greater the chance for an erroneous conclusion from the particle

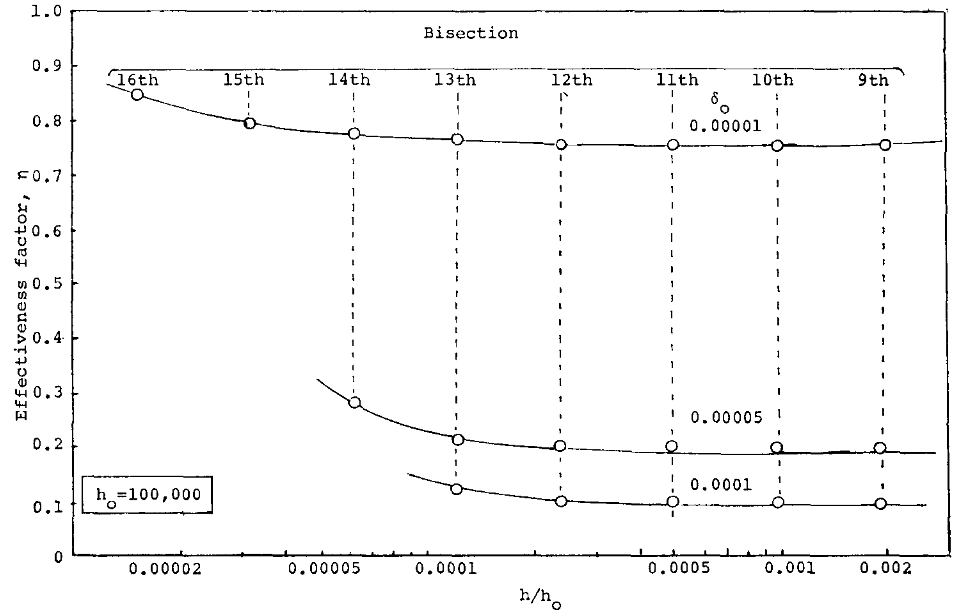

FIG. 7. Change in effectiveness factor due to repeated sequential bisection of slab, $h_0 = 10^5$. Results for η shown only for 9th through 16th bisection of slab of Fig. 2.

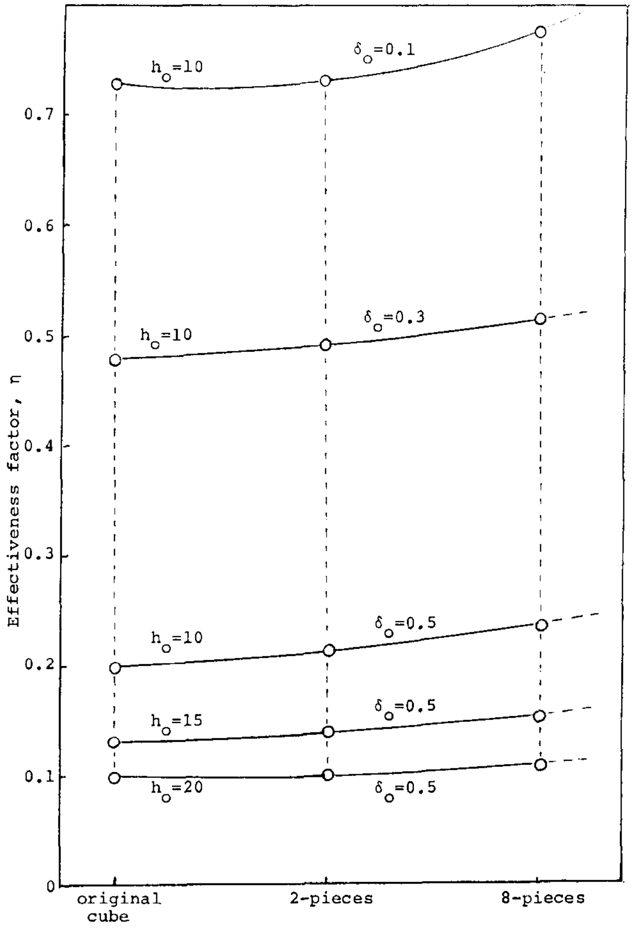

FIG. 8. Effectiveness factor shown for original cubic catalyst pellet, for the two pieces from a single-plane bisection, and for the eight pieces resulting from subdivision by two orthogonal planes.

size test because the larger h_0 the greater is the extent to which the particles must be subdivided to show an increase in measured catalytic activity per unit mass.

Aside from serving as a caveat against performing routine particle size activity tests with inhomogeneous particles Figs. 4–7 also suggest how an experimenter might use the particle size test to discover whether he is dealing with inhomogeneous catalytic particles. Figures 4–7 show that when the particle size test indicates little or no change in catalytic specific activity until the particle size is very greatly reduced, with a gradual rise in activity thereafter, then inhomogeneous particles are implied. This test is of course a sufficient condition but not a necessary one. For example, if h_0 is small, the particles may be inhomogeneous but be completely effective ($\eta = 1$) and therefore, show no change in specific activity no matter how far they are subdivided.

Three-Dimensional Models

In order to approach more closely to catalytic reality than do the slabs of Figs. 1 and 2, the governing differential equations and boundary conditions can also be written for spheres, cylinders and cubes containing active catalytic layers surrounding inactive cores. Because there is some question as to whether closed-form analytical solutions can be obtained for such situations, it was decided to approximate a cube by neglecting edge effects and assuming the behavior at each face to be described by Eq. (3) for Fig. 2. The original cube of edge L was then regarded as divided into two identical pieces by a plane parallel to two of its facts; each of these new pieces would have five faces active to a depth δL and one inactive face. Another case was considered whereby the original cube was cut into eight identical pieces by three orthogonal planes passing through its center; each of the eight cubes would have three active faces and three inactive faces. The effectiveness factor has been computed for such cases and various starting values of h_0 and δ_0 and the results are shown plotted in Fig. 8. The results are similar to those obtained for bisecting the slab (Fig. 7) and again demonstrate small changes in η due to fracturing for various starting values of h_0 and δ_0.

CONCLUSIONS

The foregoing computational results suggest that experimenters should be loath to draw conclusions about effectiveness factors from the results of kinetic experiments using various size fractions of crushed catalyst unless they are sure that the catalytic active sites or the catalytic material is deposited homogeneously within the porous 3-dimensional catalytic body. The importance of investigating the spatial distribution of active material (e.g., by an electron microprobe) is evident. In particular, kinetic experiments with sieved size fractions should cover a particle size range which extends to sizes smaller than the thickness dimension of any domain of catalytically active material deposited nonuniformly on a porous support. That unity effectiveness factor must obtain when size reduction of catalytic particles produces negligible changes in observed reaction rates is a notion that does not necessarily apply to such nonuniform catalysts. To insure that particles are sufficiently small to operate with unity effectiveness factor, the particles themselves should be of sizes on the order of the dimension of the domain of high concentration of active sites. The specific rates or rate constants obtained isothermally with particles of various sizes, but at least as small as the active domain dimension, can then be tested for diffusional artifacts by the usual procedures.

It has been demonstrated that the first few subdivisions of severely diffusion-resistant, inhomogeneous particles will often show no change in measured specific catalytic activity thereby possibly leading to erroneous conclusions. On the other hand an investigation of specific activity that encompasses a wide range of particle sizes can be used as a clue to particle inhomogeneity if a pattern of constant measured specific activity begins to rise only after the particles are subdivided to very small sizes.

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