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On the Relative Importance of Intraparticle and Interphase Transport Effects in Gas–Solid Catalysis

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Criteria expressed in terms of several new dimensionless groups are derived to assess the relative importance of intraparticle and interphase heat and mass transport effects in gas–solid catalysis. An overall criterion incorporating all the effects is also presented. Evaluation of the criteria for typical cases shows that in experimental reactors with low flow rates the relative importance of the effects frequently fall in the order: interphase heat transport > intraparticle mass transport > interphase mass transport > intraparticle heat transport.

NOMENCLATURE

Bi_h	thermal Biot number, $= hd_p/\lambda$
Bi_m	mass Biot number, $= k_cd_p/D_e$
C	concentration
C_p	heat capacity
d_p	diameter of catalyst particle
D	bulk diffusivity
$\mathrm{Da}_{\mathrm{II}}$	second Damköhler number, $= \mathcal{R}r_p^2/D_eC_5$
$\mathrm{Da}_{\mathrm{IV}}$	fourth Damköhler number, $= \Delta H\mathcal{R}r_p^2/\lambda T_s$
D_e	effective diffusivity of catalyst
E	activation energy
h	interphase heat transfer coefficient
G	mass velocity
H	modified thermal Biot number, $= hr_p/\lambda$
ΔH	heat of reaction
k	thermal conductivity of the gas
k_c	interphase mass transport coefficient
k_v	reaction rate constant
M	modified mass Biot number, $= k_cr_p/D_e$
Nu	Nusselt number, $= hd_p/k$
Pr	Prandtl number, $= C_p\mu/k$
r_p	radius of catalyst particle
R	gas constant
Re	Reynolds number, $= Gd_p/\mu$
$\mathcal{R}$	observed reaction rate per unit particle volume
Sc	Schmidt number, $= \mu/\rho D$
Sh	Sherwood number, $= k_cd_p/D$
T	absolute temperature
β_a	Prater number, $= (-\Delta H)D_eC_a/\lambda T_a$
γ	Arrhenius number, $= E/RT$
λ	thermal conductivity of catalyst particle
μ	viscosity
ρ	density of gas

INTRODUCTION

In a paper of similar title, Hudgins (*1*) recently determined the relative importance of intraparticle (internal) and interphase (external) heat transport effects through evaluation of diagnostic criteria for different types of catalytic reactors, and comparison of the results with actual experimental observations of significant temperature differences. Two different criteria were presented to compare the effects. One inferred from the work of Carberry (*2*) states that heat transfer effects occurring interphase will predominate over those occurring intraparticle providing:

$$\mathrm{Bi}_h < 1, \qquad (1)$$

where Bi_h is the thermal Biot number ($= hd_p/\lambda$) or modified Nusselt number, h is the interphase (gas–solid) heat transfer coefficient, d_p is the particle diameter, and λ is the effective thermal conductivity of the catalyst particle. This criterion is said to be based on the maximum temperature gradients possible in the particle, plus the intuitive notion that the relative sizes of the internal (ΔT_i) and external (ΔT_e) temperature differences should be approximately equal at the point of crossover from interphase to intraparticle predominance. In contrast, the criterion given by Mears (3) for the same situation:

$$\mathrm{Bi}_h < 10 \qquad (2)$$

was obtained by comparison of perturbation criteria (3, 4) for freedom from significant (5%) deviations in reaction rate due to temperature gradients occurring in each domain.

Strictly taken, the Mears criterion applies to determining if interphase heat transport effects become significant *before* the intraparticle effects, and not to determining their relative importance over the whole range of possible effects. The assumptions involved in the derivation of the original perturbation criteria hold only when the deviations from isothermal operation are just starting to become significant. However, if the heat transfer resistance in one region is significantly greater than the resistance in the other for small deviations from isothermality, it appears reasonable to assume it will also be greater when deviations are large.

Hudgins adopted Eq. (2) as the more fundamental and rearranged it for evaluation with correlations to the form:

$$\mathrm{Nu}\, k/\lambda < 10, \qquad (3)$$

where Nu is the Nusselt number ($= hd_p/k$) and k is the thermal conductivity of the gas. The ratio k/λ was shown to vary from about 0.02 to 0.2 for ordinary gases, and from 0.5 to 1.5 for hydrogen-rich gases. As an alternative method for estimating the group on the left from experimental temperature measurements, the relation:

$$\mathrm{Nu}\, k/\lambda = \Delta T_i/\Delta T_e \qquad (4)$$

was put forth as applying for small departures of the group from the value 10. The objectives of this paper are to determine why the criteria of Eqs. (1) and (2) differ by an order of magnitude, to examine the validity of Eq. (4), and to extend the comparison of the relative importance of the transport effects to include mass transport effects as well.

ANALYSIS

Eq. (4), also given by Carberry (2), is at best a rough approximation or proportionality derived from the boundary condition:

$$-\lambda \left.\frac{dT}{dr}\right|_{r_p} = h\Delta T_e, \qquad (5)$$

by making the assumption that the derivative is approximately equal to $\Delta T_i/d_p$. Examination of the schematic temperature profile on Fig. 1 shows a better estimate, although still an underestimate, would be $\Delta T_i/r_p$. This assumption gives:

$$\mathrm{Nu}\, k/\lambda \sim 2\Delta T_i/\Delta T_e. \qquad (6)$$

If the relative sizes of the internal and external temperature differences are to be approximately equal at the point of crossover from interphase to intraparticle predominance, the criterion of Eq. (1) would be obtained with a value of 2 on the right, a value which is clearly still on the low side.

The problem can be handled without re-

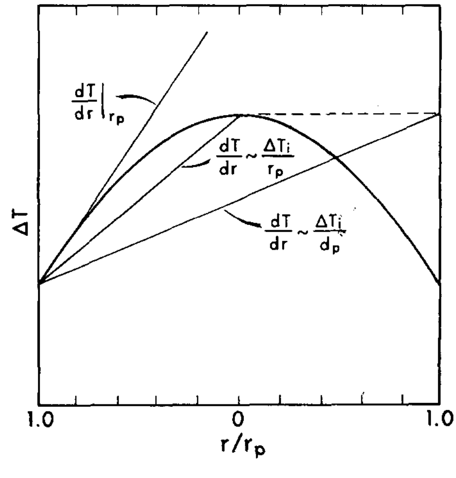

FIG. 1. Schematic intraparticle temperature profile and comparison of assumptions on temperature gradient.

course to assumptions about the gradient by following the approach of Lee and Luss (*5*). The Damköhler–Prater equation (*6*), relating temperature T and concentration C at any point in a catalyst particle, is written here in dimensionless form:

$$\frac{T - T_s}{T_a} = \frac{(-\Delta H) D_e C_a}{\lambda T_a} \frac{(C_s - C)}{C_a} = \beta_a \frac{C_s - C}{C_a}, \quad (7)$$

where ΔH is the heat of reaction, D_e the effective diffusivity of the catalyst, and subscripts s and a refer, respectively, to exterior surface and ambient (bulk fluid) conditions. This equation was combined with heat and material balances across the gas–solid boundary:

$$(T_s - T_a)/T_a = \Phi_a \beta_a / 3H, \quad (8)$$

$$(C_a - C_s)/C_a = \Phi_a / 3M, \quad (9)$$

where the dimensionless rate modulus* Φ_a and the groups M and H defined:

$$\Phi_a = \frac{r_p^2}{D_e C_a}\left(-\frac{1}{V_p}\frac{dn}{dt}\right), \qquad H = h r_p/\lambda,$$

$$M = k_c r_p / D_e,$$

and k_c is the interphase mass transfer coefficient.

By assuming $C = 0$ at the center of the particle, an upper bound on the maximum temperature T_m in the particle was obtained:

$$(T_m - T_a)/T_a = \beta_a(1 - \Phi_a/3M). \quad (10)$$

Comparison with exact solutions (*5*) shows that Eq. (10) provides a good estimate when $\Phi_a > 10$, which is required for C to approach zero at the center. Now taking the ratio of Eqs. (8) and (10) and rearranging to the form of Eq. (4) there results:

$$\mathrm{Nu}\frac{k}{\lambda} = \frac{0.67\Phi_a}{(1 - \Phi_a/3M)} \frac{\Delta T_i}{\Delta T_e}$$

$$\Phi_a > 10. \quad (11)$$

Setting $\Delta T_i/\Delta T_e$ equal to 1 gives a criterion with right side of order-of-magnitude 10, in general agreement with Eq. (2). Thus, two completely different approaches, one applying when transport effects are just starting to become significant and the other when such effects are large, give approximately the same prediction.

Examples in which intraparticle heat transport effects predominate over interphase effects are rare, and, as Hudgins (*1*) points out, seem to have occurred primarily in hydrogen-rich cases (*7*, *8*) which have high values of k/λ and also high heats of reaction. Another characteristic of these cases seems to have been the use of unusually large particle sizes. In short, it is necessary to choose experimental arrangements far from typical to encounter the predominance of heat transfer resistance within a catalyst particle.

In contrast, the intraparticle *mass* transfer resistance is normally greater than the corresponding interphase resistance. Hudgins (*9*) recently derived a criterion analogous to Eq. (2) which shows that interphase mass transport effects become significant before the intraparticle ones only if:

$$\mathrm{Bi}_m = k_c d_p / D_e = \mathrm{Sh}\, D/D_e < 10, \quad (12)$$

where Sh is the Sherwood number $(= k_c d_p / D)$ and D is the bulk diffusivity. Examination of typical values shows that this condition is normally exceeded in fixed-bed reactors when Reynolds numbers $(= G d_p / \mu)$ are greater than about 1–5.

Comparison of Heat and Mass Transport Effects

The relative importance of the various possible heat and mass transport effects can now be put into perspective by further comparison of the relevant individual criteria. For reactions obeying simple power-law kinetics $(= k_v C^n)$, the following perturbation criterion (*10*) applies for freedom from significant (5%) intraparticle mass transport effect:

$$\mathrm{Da}_{\mathrm{II}} = \Phi_a < 1/|n|, \qquad n \neq 0, \quad (13)$$

where n is the order of reaction. This criterion is similar to, but more general than, the well-known Weisz–Prater (*11*) cri-

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* Correctly defined here in terms of reaction rate per unit particle volume rather than per particle as in (*6*).

terion. For freedom from significant interphase heat transfer effects, a criterion also developed by the author (*3*) requires:

$$\frac{|\Delta H|\mathcal{R}r_p}{hT_a} < \frac{0.15}{\gamma}, \qquad (14)$$

where $\mathcal{R}$ is observed reaction rate per unit particle volume ($= -(dn/dt)/V_p$) and γ is the dimensionless activation energy modulus ($=E/RT$). Comparison with Eq. (13) shows that intraparticle mass transfer becomes significant before interphase heat transfer if:

$$\frac{|\Delta H|D_eC}{hT_ad_p} = \frac{|\beta|}{\mathrm{Bi}_h} < \frac{|n|}{10\gamma} \quad n \neq 0. \qquad (15)$$

The new dimensionless group on the left expresses the ratio of heat release (or takeup in the case of endothermic reactions) from reactants supplied by intraparticle diffusion to heat supply by thermal convection.

Examination of values of the parameters in Eq. (15) has shown (*2, 12*) that γ typically varies between 5 and 40, Bi_h varies between 0.01 and 10, and β between 0.001 and 0.1. Consequently, the criterion is occasionally exceeded, particularly in the case of experimental reactors where the value of Bi_h is small due to low Reynolds numbers.

Similarly, comparison of Eq. (14) with the Mears (*10*) interphase mass transport criterion:

$$\frac{\mathcal{R}r_p}{k_cC_a} < \frac{0.15}{|n|} \qquad (16)$$

reveals that interphase heat transport effects become significant before interphase mass transport effects if:

$$\frac{|\Delta H|C_ak_c}{hT_a} = |\beta_2|\mathrm{Bi}_m/\mathrm{Bi}_h > |n|/\gamma \qquad (17)$$

The new dimensionless group on the left is a measure of the ratio of heat generation from reactants supplied by convection to heat removal (or supply) by thermal convection. The ratio $\mathrm{Bi}_m/\mathrm{Bi}_h$ typically (*2*) has values between 10 and 50,000. Consideration of the typical values for the other parameters shows interphase heat transport will usually be the more important except at very small values of β_a.

Continuing the comparisons to that between intraparticle heat transport predicted by the Anderson (*4*) criterion:

$$\mathrm{Da_{IV}} = \frac{|\Delta H|\mathcal{R}r_p^2}{\lambda T_a} < \frac{0.75}{\gamma}, \qquad (18)$$

and interphase mass transport given by Eq. (16), it is found that intraparticle heat transport becomes limiting first if:

$$\frac{|\Delta H|k_cC_ad_p}{\lambda T_a} = |\beta_a|\mathrm{Bi}_m > 10|n|/\gamma, \qquad (19)$$

where the new dimensionless group on the left expresses the ratio of heat generation from reactants supplied by convection to heat transfer by intraparticle conduction. The Bi_m number is found (*9, 12*) to vary between about 1 and 1000. At the low flow rates typical of many experimental reactors, the criterion is not met and interphase mass transfer is the more important.

Thus, the relative importance of the various transport effects in low-mass-velocity experimental reactors often falls in the order: interphase heat transport > intraparticle mass transport > interphase mass transfer > intraparticle heat transfer. Under these conditions, it is also necessary to consider the effects of intrareactor heat transfer and axial dispersion on the reaction rate or conversion. Criteria relating to these effects are reviewed elsewhere (*10*). At the high mass velocities and Reynolds numbers prevailing in commercial reactors, the interphase transport and axial dispersion effects normally become negligible, leaving only intraparticle effects to consider. Comparison of Eqs. (13) and (14) shows that intrareactor mass transfer becomes significant before intraparticle heat transfer if:

$$\gamma|\beta| < |n|. \qquad (20)$$

Evaluation shows this criterion is almost always met. The new criteria provided here are useful in assessing the relative importance of the effects in specific cases.

Overall Criterion

Finally, it should be remembered that the above comparisons are between the relative magnitudes of the effects, without regard to their sign. Exothermic heat transfer effects act in opposition to the mass transfer effects, so the *net* effect on the reaction rate will be less than the individual effects. The author (*10*) derived an overall criterion accounting for all the individual effects which can be put into the form:

$$\Phi < \frac{(1 + 0.33\gamma\beta_a\Phi_a/H)}{|n - \gamma\beta_a|(1 + 0.33\Phi_a/M)} \qquad |n - \gamma\beta| \neq 0. \qquad (21)$$

The terms in parentheses relate to interphase heat and transport effects, while those within the absolute value sign account for the corresponding intraparticle effects. This criterion does not guarantee freedom from significant individual transport effects, rather it provides that their net effect will distort the observed reaction rate by less than ±5% from the rate that would be obtained under isothermal, isoconcentration conditions. Note that the criterion, while complicated, is expressed in terms of observables and parameters which are readily estimated from reliable correlations.

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