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NOTES

Laboratory Catalytic Studies: The Role of Transport Phenomena

INTRODUCTION

In the conduct of laboratory investigations of solid catalyzed reactions, the simple fixed bed, i.e., a tube usually packed with small grains of a catalyst, is frequently employed. Whether the goal of the study be that of screening or the procurement of data from which kinetic models might emerge, it is imperative that the chemical behavior of the catalytic system is shown to be free of physical transport distortions.

Diffusional or transport effects may be manifested as long and short range gradients of species concentrations and fluid–solid temperatures. For a fixed bed, reactor gradients in the axial and radial directions are long range while those around and within the catalyst particle are appropriately termed short range. Should either long or short range gradients exist *undetected*, conclusions about intrinsic catalyst activity and selectivity can easily be erroneous.

The need to eliminate long range gradients has inspired the development of the gradientless catalytic reactor (*1, 2*), one form of which is the open-loop recycle reactor (*3*). In essence the recycle unit consists of a fixed bed reactor, the effluent from which is recycled back (via an appropriate pump) to the reactor inlet; a fraction (4% or less) of the recycled volume is fed and withdrawn from the system. When the ratio of recycle rate is fresh feed in 25/1 or greater, long range gradientless conditions prevail (*3*). The recycle unit is thus essentially a differential fixed bed reactor for which the overall conversion is that amplified by the recycle ratio and so, in the limit of recycle to fresh feed ratio of 25/1, we have a long range gradientless reactor (a CSTR). Short range, local interphase, and intraphase gradients are *not* always eliminated, however. Thus there is a need for criteria whereby these usually unmeasurable local gradients may be detected.

In Table 1 there are presented relationships for the detection of local (interphase–intraphase) gradients of concentration and temperature in terms of gradientless reactor conversion, x; contact time, θ; measurable concentrations C_f and C_0; thermal parameters, $\bar{\beta}$, λ; intraphase diffusivity, $\mathcal{D}$; particle/pellet dimension $L = 1/a$; *and* the interphase (external) fluid-particle/pellet mass transport coefficient, k_g. These criteria, all expressed in terms of observable, measurable, and/or predictable parameters, permit an a priori assessment of local diffusion disguise in any laboratory experiment conducted in any gradientless reactor (*4*) which hosts a fluid–solid-catalyzed reaction network.

Having said this, one is obliged to ask: What of the reliability of the measured/predictable parameters?

Of those cited in Table 1, surely λ, the effective thermal conductivity of the catalyst pellet, escapes precise measurement or a priori prediction. Happily, internal temperature gradients (ΔT_i) can be considered quite negligible for gas–solid catalyst systems, it having been predicted and verified (*5*) that of the potential overall ΔT_0, between catalyst centerline and bulk fluid, the major seat of temperature gradient is external, i.e.,

$$\frac{\Delta T_x}{\Delta T_0} = \frac{\text{external } \Delta T}{\text{overall } \Delta T} = \frac{r\left[\left(\frac{x}{1-x}\right)\frac{1}{k_g a \theta}\right]}{1 + \left(\frac{x}{1-x}\right)\left(\frac{r-1}{k_g a \theta}\right)}, \tag{1}$$

TABLE 1

Criteria for the Detection of Local (Interphase–Intraphase) Gradients in Any Gradientless Reactor

Conversion, $x = \frac{C_f - C_0}{C_f}$ y_0 = feed mol fraction

C_f = feed concentration: C_o = effluent concentration

θ = average holding time, $V\text{cat}/Q$

C_s = concentration at catalyst external surface

T_o = effluent (bulk) temperature

T_s = catalyst surface temperature

$\bar{\beta} = (-\Delta H)y_o/C_p\text{Le}^{2/3}$

External (interphase)

$\Delta C_x = C_o - C_s$	$\Delta T_x = T_s - T_o$
$\Delta C_x = \frac{C_f x}{k_g a\theta}$	$\Delta T_x = \frac{\bar{\beta} x}{k_g a\theta}$

Internal (intraphase)

$\Delta C_i = C_s - C_{\text{int}}$	$\Delta T_i = T_s - T_{\text{int}}$
$\Delta C_i = 0 \quad \text{if} \left(\frac{x}{1-x}\right) \frac{L^2}{\mathcal{D}\theta} < 1.0$	$\Delta T_i = \left(\frac{-\Delta H \cdot \mathcal{D}}{\lambda}\right) C_f \cdot \left(\frac{(k_g a\theta - x(1 + k_g a\theta)}{k_g a\theta}\right)$

where

$$r = \frac{\lambda}{\mathcal{D}\rho C_p \text{Le}^{2/3}}. \tag{2}$$

As it happens, for gas–solid catalyst systems,

$$r >\!>\!> 1.0$$

and so internal gradients in temperature, ΔT_i, are insignificant relative to an external temperature gradient, ΔT_x. So our ignorance of precise values of λ is of no practical consequence.

Clearly, however, the remaining criteria cited in Table 1, rely, for their effective application, upon precise values of k_g, the interphase (external) mass transport coefficient. Qualitatively this coefficient (a velocity of convection transport between bulk and catalyst external surface) is equivalent, *not equal*, to

$$k_g \equiv \frac{D}{\delta} \tag{3}$$

where D is bulk molecular diffusivity of the key species and δ is the thickness of the Nernst "diffusion layer" surrounding the catalyst particle/pellet. That diffusion layer thickness, δ, is reduced as increases in fluid flow rate about the catalyst particle/pellet are imposed. A measure of the corresponding level of convective turbulence (and thickness of δ) is the Reynolds number

$$\text{Re} = \frac{d_p u}{\nu} = \frac{\text{convective}}{\text{molecular}}\ \text{transport} \tag{4}$$

so $\delta \equiv 1/\text{Re}$.

Formally (4)

$$\frac{k_g}{u}(\text{Sc})^{2/3} = \frac{\text{constant}}{\text{Re}^{\alpha}}, \tag{5}$$

where $\text{Sc} = \nu/D$ = (momentum/mass) · molecular diffusivity.

Of the criteria cited in Table 1, the value of k_g proves to be quite important. For the Notre Dame Spinning Basket gradientless reactor (rpm = 1400; 90 × 90-mm vessel), $k_g = 7$ cm/s.

For the commonly employed fixed bed recycle reactor and the internal recycle reactor (2), a fixed bed k_g correlation is needed. For values of $\text{Re} > 1$, conventional k_g correlations (*6, 7*) can be relied upon.

For example, Re = 1 to 1000 (*6*)

$$\frac{k_g}{u}(\text{Sc})^{2/3} = \frac{2}{\sqrt{\text{Re}}}. \tag{6}$$

However, in many if not most laboratory solid catalyst studies conducted in the fixed bed mode, quite small values of Re prevail since it is quite common practice to utilize catalyst candidates of quite small d_p; i.e., $\text{Re} = d_p u/\nu$ may then be less than 0.1. To date no correlation is at hand for fixed bed values of k_g at Re between 0.1 and 0.01—a flow regime often encountered in small scale laboratory studies.

Interphase mass transfer at low Re

To remedy the paucity of data and correlation at $\text{Re} \leq 0.1$, a fixed bed external recycle (gradientless) system was utilized (*8*) to study the adsorption of methyl iodide (in an inert carrier) upon activated charcoal. The adsorption events patently include interphase–intraphase diffusional steps. The appropriate continuity equations were solved to yield k_g as a function of the low Reynolds numbers encountered.

TABLE 2

Experimental Data for Mass Transfer Controlled Adsorption of Methyl Iodide upon a Fixed Bed of Charcoal (B)

$\mathrm{Re} = \frac{d_p u}{\nu}$	$k_g(\mathrm{Sc})^{2/3}/u$
0.013	8.8
0.026	6.2
0.034	6.5
0.034	5.8
0.033	5.3
0.04	5.3
0.073	4.4
0.073	5.1

The resulting data for k_g are adaquately correlated by

$$\frac{k_g}{u}(\mathrm{Sc})^{2/3} = \frac{1.26}{\mathrm{Re}^{0.45}} \tag{7}$$

for Re = 0.1 to 0.01.

Data are set forth in Table 2 (*8*).

DISCUSSION AND CONCLUSIONS

To be sure, the extraction of a single transport coefficient (k_g) from data reflecting complex adsorption phenomena coupled with interphase–intraphase transport presents a challenge. However, with quite rapid adsorption of the methyl iodide upon and within the porous charcoal, the overall adsorption event is governed by external (interphase) mass transfer, so permitting a determination of k_g (*8*). In effect intraphase effectiveness is, in this system, quite small so that the overall rate process is governed by rate of supply of the methyl iodide from the bulk fluid to the external surface of the charcoal.

Our results and their correlation (Eq. (7)) compare rather favorably with the correlation of Hsing and Thodos (*7*) for Re = 0.1:

$$\frac{k_g}{u}(\mathrm{Sc})^{2/3} = \frac{1.33}{\mathrm{Re}^{0.4}}. \tag{8}$$

Thus the criteria of Table 1, so critically dependent upon sound values of k_g, may now be safely applied in the interpretation of those *gradientless* laboratory catalytic reactor studies which quite frequently are marked, by reason of small d_p and low fluid velocities, by rather small values of the Reynolds number.

APPENDIX: NOMENCLATURE

a = external surface to volume of catalyst, cm^{-1}, 1/liter
C = concentration of species, $\mathrm{mol/cm}^3$
C_p = molar heat capacity of fluid, Cal/mol°K
d_p = particle/pellet diameter
D = bulk molecular diffusivity, cm^2/s
$\mathcal{D}$ = intraphase diffusivity, cm^2/s
$-\Delta H$ = reaction enthalphy change
k_g = external (interphase) mass transfer coefficient cm/s
Le = Lewis No: molecular thermal/mass diffusivities
L = $1/a$
r = defined by Eq. (2)
T = temperature, °K
u = fluid velocity, cm/s
x = key reactant conversion
y_0 = feed mole fraction
ρ = fluid molar density, $\mathrm{mol/cm}^3$
λ = catalyst thermal conductivity, cal/cm · s °K
δ = Nernest diffusion layer thickness
$\bar{\beta}$ = $(-\Delta H \cdot y_0/C_p\mathrm{Le}^{2/3})$
θ = contact time: Vol. catalyst/vol. feed rate
ν = kinematic viscosity of fluid, cm^2/s
Re = Reynolds number, $d_p u/\nu$
Sc = Schmidt number, ν/D

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