R & D NOTES

Importance of Finite Adsorption Rate in the Evaluation of Adsorption and Diffusion Parameters in Porous Catalysts

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Introduction

The effectiveness of porous catalysts is often limited by diffusional resistances that result from the high reaction rates required in commercial operations (Katzer, 1980). Many supported catalysts have a bidisperse pore structure that is the result of the agglomeration of porous microparticles to form catalyst pellets. Pores within these particles are usually called micropores (< 100Å or 10 nm) and pores between the agglomerated particle are called macropores (> 100Å). The effectiveness of such bidisperse catalysts depends on the rate of diffusion and, therefore, on the tortuosities in the macro- and micropores (Dogu and Dogu, 1980).

A common method for predicting diffusivity values at high reaction temperatures is to extrapolate from values obtained at low temperatures (Park and Kim, 1984). A number of methods are available to determine diffusion coefficients for bidisperse catalysts:

- Chromatography (Hashimoto and Smith, 1974)
- Diffusion Cell (Dogu and Smith, 1975)
- Batch reservoir (Ma and Lee, 1976)
- Flow-through reservoir (Frost, 1981)
- Infinite reservoir (Ruthven and Derrah, 1973)

The methods usually involve applying a step or pulse of adsorbing tracer to the catalyst pellet and evaluating the diffusion and adsorption parameters from the transient and steady state responses.

Figure 1 compares for many cases the important parameters in the diffusion and adsorption process at low and high temperatures. Since many diffusion parameters are measured at low temperatures (~25–100°C) for extrapolation to much higher values, it is extremely important that the pore diffusivity (the tortuosity is extracted only from the pore diffusivity) be evaluated without a contribution from the surface diffusion and adsorption. The discussion here is applicable to sorbents such as alumina or silica gel, which can accommodate adsorption and diffusion occurring in parallel. For zeolite crystals, adsorption on the crystal surface is usually a prerequisite for intracrystalline diffusion.

The majority of bidisperse models used in the literature (e.g., Dogu and Ercan, 1983; Haynes and Sarma, 1973) assume that the rate of adsorption is much faster than the diffusion rate. For large catalyst pellets (~3 mm) or for macropores where the surface area is small (~2 m^2/g) and where the temperatures of the gases are quite far from their boiling point, the resistance due to surface diffusion and finite adsorption should be sufficiently small not to affect the overall rate of gas uptake by the particle. On the other hand, in microspheres (sphere radius ~40 μm and surface area ~200–400 m^2/g) both phenomena may be significant (Schneider and Smith, 1968a, 1968b).

The aim of this note is to show the importance of modeling the finite surface adsorption rate in extremely small monoporous sorbents or in microspheres in bidisperse sorbents to obtain

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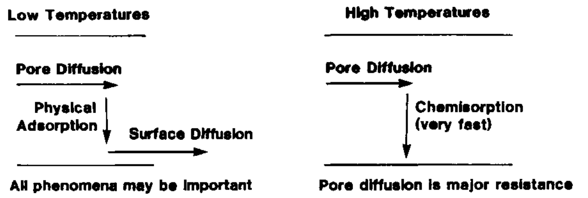

Figure 1. Adsorption/diffusion mechanisms at low and high temperatures.

accurate estimates of the diffusivity in the catalyst. Effects of surface diffusion have not been considered in this paper.

Theory

Consider a batch of monoporous microspheres in an infinite reservoir subjected to a step change in tracer concentration at time $t = 0^+$. Table 1 shows two mathematical models which may be used to describe the uptake behavior of the catalyst. In both models an effective pore diffusivity is used together with the assumption of negligible external mass transfer. Model I assumes a finite adsorption rate at the surface while model II assumes that adsorption is instantaneous. The generalized integral transform technique of Ramkrishna and Amundson (1974) was used. One parameter, ψ, which compares the relative capacities of the pores and the surface for the diffusing species, is common to both models. Model I is also written in terms of the Thiele modulus for adsorption, ϕ^2, which is the ratio of the rate of adsorption to the rate of diffusion.

Discussion

Figure 2 shows the ratio of the predicted uptakes (F_{II}/F_I) from Models I and II as a function of time for ethanol on a silica gel sorbent. Figure 3 contains a similar plot for ethane on the same adsorbent. The characterization data is from Masamune and Smith (1965) and Schneider and Smith (1968a). For a species which does not adsorb significantly, such as ethyl alcohol ($\psi = 4.3$), the assumption of instantaneous adsorption does not cause serious error because of the high equilibrium capacity in the pore space compared to the surface ($\psi = 4.3$). Therefore, the pore diffusivity will usually be the limiting factor. However, it can be seen from Figure 2 that this is not valid for very small particles or for an extremely slow adsorption rate ($\phi^2 \sim 0.01$). Furthermore, Figure 3 shows that the finite adsorption rate also becomes important when a significantly adsorbed adsorbate, such as ethane ($\psi = 0.03$), is the diffusing species.

Table 2 shows the typical diffusivities evaluated from model II that give best fits of the experimental data (time domain fitting) derived from parameters given in Schneider and Smith (1968a). It can be seen from this table that for particle sizes of silica gel typical of microspheres in bidisperse catalysts (~40 μm), the calculated effective micropore diffusivity can be an order of magnitude smaller than the true value. This will cause a corresponding error in the calculated effectiveness factor if the diffusivity data is extrapolated to high temperatures, or if microsphere tortuosity factors are calculated from the data. A microsphere size of 400 μm is required before the calculated diffusivity by model II becomes equivalent to that assuming a finite rate of adsorption.

For compounds exhibiting stronger adsorption behavior (e.g., *n*-butane), we might expect a greater effect on overall uptake behavior of a finite rate of adsorption. Figure 4 shows that this is not necessarily true. The higher adsorption rate constant and lower diffusivity of butane, due to the larger size molecule, give higher values of ϕ^2, hence increasing the importance of the diffusion resistance compared to adsorption resistance.

In summary, it has been shown that the assumption of instantaneous adsorption in microspheres of bimodal catalysts can lead to large errors in the calculated value of the diffusivity. This is due to the importance of the adsorption resistance. Under these conditions, the effect is more significant at low temperatures, with small adsorbing molecules and small microspheres.

Although the effect of surface diffusion has not been quantified, Schneider and Smith (1968b) showed that at low tempera-

Table 1. Models Used to Describe Rate of Uptake of a Diffusing Species by a Monoporous Sorbent in an Infinite Reservoir

Model I	Model II
Differential Equations	
$\frac{\partial A_i}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial A_i}{\partial x}\right) - \phi^2 (A_i - A_{si}),$ $A_i(x,0) = 0$ $\partial A_i(0,t)/\partial x = 0$ $A_i(1,t) = 1$ $\frac{\partial A_{si}}{\partial \tau} = \psi\phi^2 (A_i - A_{si}),$ $A_{si}(x,0) = 0$	$\left(1 + \frac{1}{\psi}\right)\frac{\partial A_i}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2 \frac{\partial A_i}{\partial x}\right)$ $A_i(x,0) = 0$ $\partial A_i(0,t)/\partial x = 0$ $A_i(1,t) = 1$
Nondimensional Groups	
$A_i = C_i/C_o \quad A_{si} = C_{si}/C_o K_i \quad x = r_i/R_i$ $\tau = \mathcal{D}_{ei} t/\epsilon_i R_i^2 \quad \psi = \epsilon_i/\rho_i K_i$ $\phi^2 = \rho_i k_{ads} R_i^2/\mathcal{D}_{ei}$	$A_i = C_i/C_o \quad x = r_i/R_i$ $\tau = \mathcal{D}_{ei} t/\epsilon_i R_i^2 \quad \psi = \epsilon_i/\rho_i K_i$
Solution	
$F_I = \frac{m_t}{m_\infty} = \frac{\sum_{n=1}^{\infty} \frac{\alpha_1}{\alpha_2 \xi_n^2}\left(1 - e^{-\xi_n^2 \tau}\right)}{\sum_{n=1}^{\infty} \alpha_1/\alpha_2 \xi_n^2}$ where $\xi_n^2 = \frac{1}{2}\{[\phi^2(1+\psi) + n^2\pi^2] \pm \sqrt{[\phi^2(1+\psi) + n^2\pi^2]^2 - 4\psi\phi^2 n^2\pi^2}\}$ $\alpha_1 = 1 + \phi^2/(\psi\phi^2 - \xi_n^2)$ $\alpha_2 = 1 + \psi\phi^4/(\psi\phi^2 - \xi_n^2)^2$	$F_{II} = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2\tau}{1 + \frac{1}{\psi}}\right)$

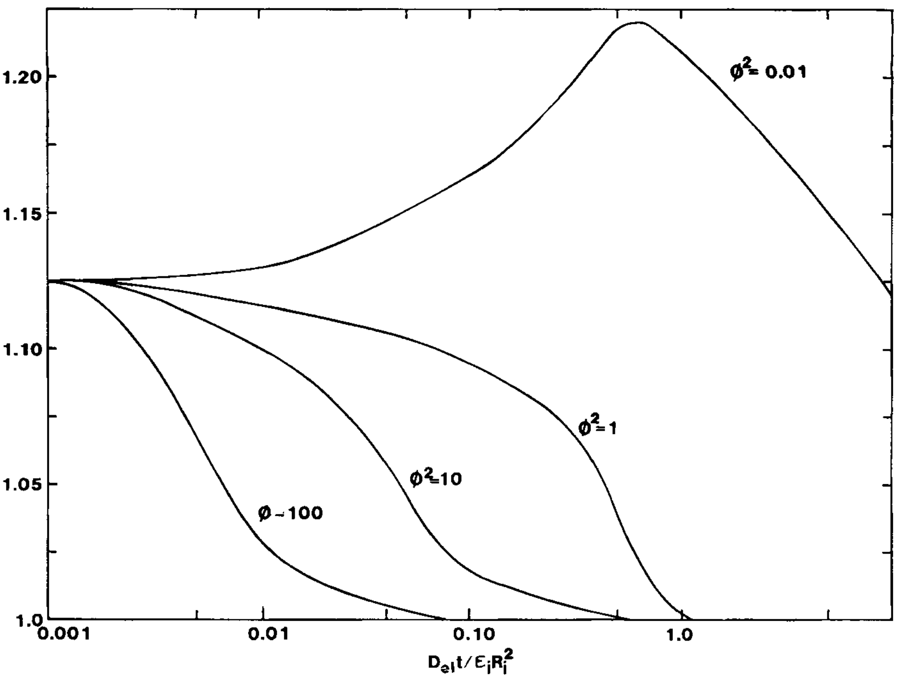

Figure 2. Comparison of models I and II for ethanol adsorption on silica gel; $K_i = 0.1$ cm^3/g, $\psi = 4.3$.

tures surface diffusion may be a major contributor to the effective diffusivity of a catalyst. The important resistance in high temperature applications is pore diffusion, and chemisorption, rather than physical adsorption. Therefore, it is recommended that bimodal tortuosity factors be evaluated at temperatures where it can be shown that both surface diffusion and adsorption rates are not significant.

It should be noted that only gases have been considered in this analysis. For liquid adsorbates, multilayer adsorption and associated surface diffusion in macropores complicate the above phenomena (Peel et al., 1981; Weber and Liang, 1983).

Notation

A_i = nondimensional microsphere pore concentrations
A_{si} = nondimensional microsphere surface concentration
C_o = infinite reservoir concentration
C_i = microsphere pore concentration
C_{si} = microsphere surface concentration

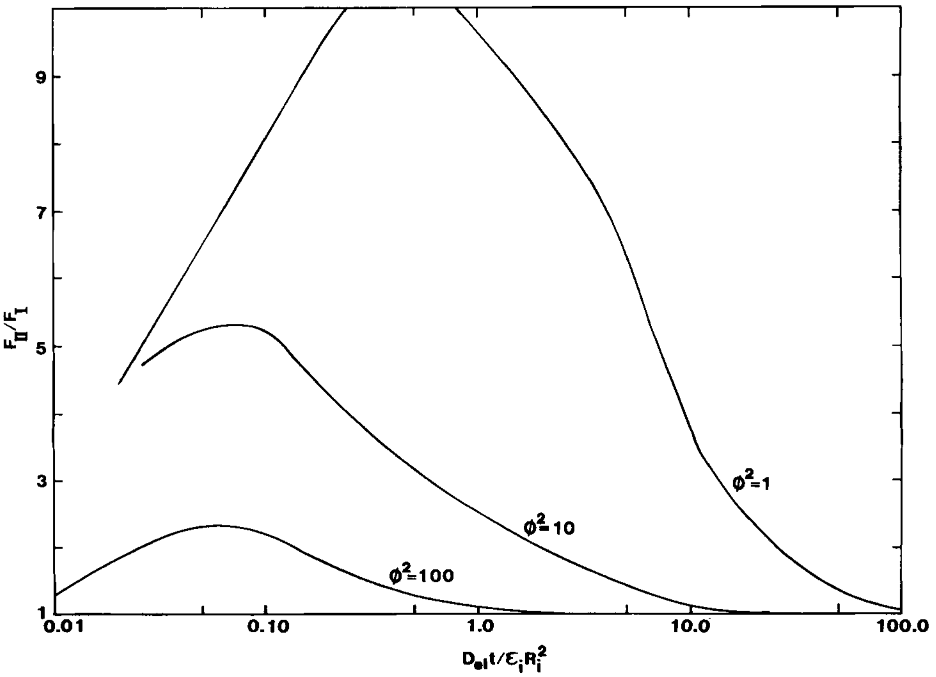

Figure 3. Comparison of models I and II for ethane adsorption on silica gel; $K_i = 14.6$ cm^3/g, $\psi = 0.029$.

Table 2. Values of Diffusivity of Ethane in Different Size Silica Gel Particles Calculated Using Model II

R μm	$\mathcal{D}_{ei}$ cm²/s
40	1.5×10^{-4}
100	5×10^{-4}
400	1.41×10^{-3}

Actual parameters evaluated using model I are $k_{ads} = 167$ cm³/g · s, $K_i = 14.6$ cm³/g, $\mathcal{D}_{ei} = 1.41 \times 10^{-3}$ cm²/s.

Data taken from Schneider and Smith (1968a).

$\mathcal{D}_{ei}$ = effective microsphere diffusivity
$F = m_t/m_\infty$
k_{ads} = rate constant for adsorption
K_i = equilibrium constant for adsorption
m_t = amount adsorbed at time t
m_∞ = maximum adsorption capacity of sorbent
R_i = microsphere radius
x = nondimensional radial coordinate in microsphere

Greek letters

ϵ_i = microsphere voidage
ϕ^2 = Thiele modulus for adsorption
ρ_i = microsphere density
ξ_n = eigenvalue
τ = nondimensional time
ψ = ratio of adsorption capacities of pore and surface

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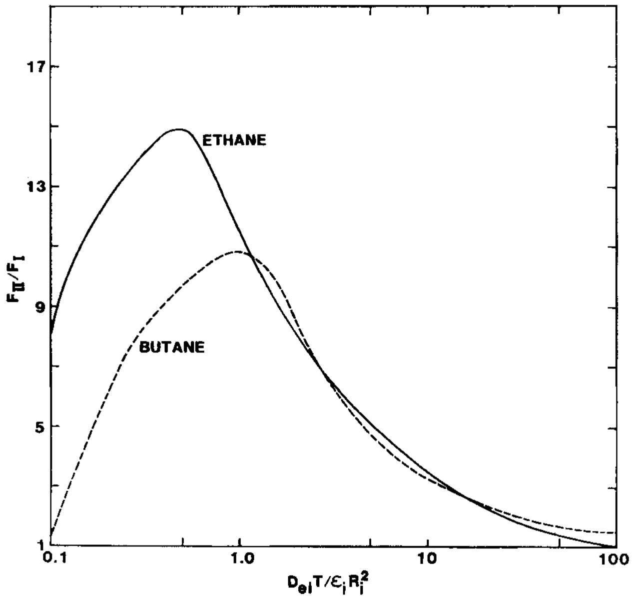

Figure 4. Comparison of ethane and *n*-butane adsorption on silica gel; $R_i = 40$ μm, $\rho_i = 1.13$ g/cm³, $\epsilon_i = 0.486$.

	Ethane	*n*-butane
K_i, cm³/g	14.6	311
$\mathcal{D}_{ei}$, cm²/s	1.47×10^{-3}	2.93×10^{-3}
k_{ads}, cm³/g · s	167	1,600

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