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LETTERS TO THE EDITORS

Comment on "Theoretical and Experimental Aspects of Surface Diffusion in Porous Catalysts"

In a recent paper Tsotsis, Sane, Webster, and Goddard (*1*), discussed the problem of surface diffusion in a porous catalyst and the possible mechanisms for enhancing the "normal" diffusion by surface transport. In this communication we show that their treatment is in fact incorrect and based on contradictory assumptions. In addition we present some new (elementary) results on this diffusion problem.

The model used by Tsotsis *et al.* is basically a cylindrical pore of radius r and length L that separates two reservoirs with constant concentrations C_0 and C_L, respectively. Adsorption on the inner pore surface is allowed with distance dependent surface concentration $n(x)$. The bulk concentration is denoted $C(x)$ and a simple diffusion mechanism (Fick's law) is assumed throughout. This leads immediately to their equations

$$D_b \frac{d^2C(x)}{dx^2} - g(C(x), n(x)) = 0 \quad (1)$$

$$D_s \frac{d^2n(x)}{dx^2} + \frac{r}{2} g(C(x), n(x)) = 0, \quad (2)$$

where D_b and D_s are the bulk and surface diffusion coefficients and $g(C(x), n(x))$ is the net rate of adsorption on the surface. As boundary conditions Tsotsis *et al.* consider

$$C(0) = C_0 \quad \frac{dn(x)}{dx} = 0 \quad \text{at } x = 0 \quad (3)$$

$$C(L) = C_L \quad \frac{dn(x)}{dx} = 0 \quad \text{at } x = L. \quad (4)$$

Given an expression for the net rate of adsorption g, the problem is one of (possibly involved) mathematics.

Assuming at first for simplicity that adsorption equilibrium is attained throughout the pore, Tsotsis *et al.* correctly put g equal to zero. However, in this case Eqs. (1) to (4) are solved immediately by

$$C(x) = \frac{C_L - C_0}{L} x + C_0 \quad (5)$$

$$n(x) = \text{constant}. \quad (6)$$

Thus the surface diffusional flux

$$J_s = -D_s \frac{dn(x)}{dx} \quad (7)$$

equals zero and it is not erroneous to conclude that "adsorption equilibrium, assumed in most published studies, implies zero surface transport" (*1*). There is, however, one important conclusion to be drawn from Eqs. (5) and (6). If the surface coverage is independent of the (local) bulk concentration and adsorption equilibrium exists, the adsorption isotherm must be such that the amount adsorbed is independent of the bulk concentration. Physics then dictates that no adsorption can take place and the "constant" in Eq. (6) is in fact zero.

One might guess that this behavior arises from the boundary conditions on $n(x)$. Relaxing these leads to the solution (still assuming no net adsorption on the surface)

$$C(x) = \frac{C_L - C_0}{L} x + C_0 \quad (8)$$

$$n(x) = \frac{n_L - n_0}{L} x + n_0, \quad (9)$$

which implies a surface diffusional flux that is non-zero in general.

$$J_s = -D_s \frac{n_L - n_0}{L}$$

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The boundary values n_L and n_0 still need to be specified, but we first note that, upon eliminating x between Eqs. (8) and (9), the adsorption isotherm is found as

$$n(x) = \frac{n_L - n_0}{C_L - C_0}(C(x) - C_0) + n_0. \quad (10)$$

Again physics dictates that $n(x) = 0$ when $C(x) = 0$, so that the adsorption isotherm is necessarily of the Henry type

$$n(x) = \text{const } C(x) \quad (11)$$

The foregoing discussion clearly shows that, irrespective of the boundary conditions imposed on $n(x)$, the assumption of adsorption equilibrium throughout the pore determines the adsorption isotherm. The "equilibrium limit" taken by Tsotsis *et al.* using a Langmuir adsorption isotherm is thus inconsistent with Eqs. (1) to (4) and violates the condition of adsorption equilibrium throughout the pore. As given by them it assumes equilibrium only at $x = 0$ and $x = L$.

REFERENCE

1. Tsotsis, T. T., Sane, R. C., Webster, I. A., and Goddard, J. D., *J. Catal.* **101,** 416 (1986).

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