On the Merits of Partially Impregnated Catalysts

SARDUL MINHAS* AND J. J. CARBERRY†

*Department of Chemical Engineering, University of Notre Dame,
Notre Dame, Indiana 46556*

A digital computer simulation of adiabatic SO_2 oxidation over supported platinum
was carried out in which performance of partially impregnated catalysts (Pt deposited
solely to within a fractional distance of total support radii) is compared to that of a
totally impregnated support. In this diffusion-affected reaction, definite advantages
in space-time-yield are shown for the partially impregnated support.

INTRODUCTION

Diffusion of heat and mass in series with (interphase) and simultaneous with (intraphase) catalytic reaction affects both conversion and yield in many systems, e.g., NH_3 oxidation over Pt, its synthesis over iron and SO_2 oxidation over Pt and V_2O_5. The expedient of reducing particle size to increase interphase transport and intraphase catalytic effectiveness is not always possible nor desirable. For with a reduction of pellet or particle size, interparticle radial gradients and pressure drop increase. In a laboratory inquiry the nonisothermality due to radial temperature gradients renders resulting data meaningless while a large pressure drop may prove economically undesirable in a plant reactor. Ideally, one would want a reactor characterized by a catalytic effectiveness factor of unity, of negligible pressure drop and a negligible radial temperature profile. Yet the latter two characteristics are associated with large pellet size and the former (effectiveness) by often quite small particle size.

THEORY

Catalytic effectiveness, η, is related to the Thiele modulus φ by

* Present address: Scientific Design Corp., New York City.
† To whom all enqueries should be directed.

$$\eta = \frac{\tanh \varphi}{\varphi},$$

where

$$\varphi = L \sqrt{\frac{kf(c)}{D}}.$$

L is the characteristic pellet size, if and only if the actual catalytic agent is deposited uniformly throughout the porous pellet. In fact, L represents the actual catalytic-diffusion path length. Its definition invites the possibility that for a given pellet diameter, the catalytic agent may be gainfully deposited only partially; i.e., a thin shell of catalytic ingredient may be deposited upon a large pellet. In practice, due to diffusion limitations in deposited catalyst preparation, such a partially impregnated formulation is often inadvertently created.

The consequences of partial impregnation, by *a priori* design, have been explored by digital computer simulation of SO_2 oxidation over supported Pt in a fixed bed adiabatic reactor. Specifically the model invoked contains the following features: (a) Plug flow of the gas stream, an assumption justified in view of the large reactor length to pellet diameter ratio. A pellet size of 1 cm is employed. Adiabaticity eliminates radical temperature and therefore, radial concentration gradients; (b) at any point a concentration gradient can exist between bulk gas and the pellet exterior (inter-

phase) and within the porous pellet (intraphase); (c) at any point a temperature difference can exist between bulk gas and pellet exterior, however, an interphase temperature gradient is assumed to be negligible relative to the interphase gradient. Justification of this latter assumption has been set forth earlier (1, 2); (d) the catalytic reaction rate, *per se*, is the rate model presented by Hougen and Watson (3), as follows:

$$\text{Rate} = \frac{k(SO_2)(O_2)^{1/2}}{[1 + \sqrt{K_1O_2} + K_2 \cdot SO_3]^2}$$

$$\times \left[1 - \frac{(SO_3)}{K_e(SO_2)(O_2)^{1/2}} \right],$$

where

$$k = \exp \left[\frac{-8000}{T} + 14.154 \right]$$

$$K_1 = \exp \left[\frac{20,360}{RT} - \frac{23}{R} \right]$$

$$K_2 = \exp \left[\frac{16,800}{RT} - \frac{17.51}{R} \right]$$

$$K_e = \exp \left[\frac{22,600}{RT} - 10.68 \right].$$

(Oxidation over V_2O_5 has also been simulated and comparative performances for fully impregnated supports are revealed elsewhere (4).)

The governing reactor equations are, for mass and heat, respectively:

$$\frac{dx}{dz} = \frac{\eta(\text{rate})\rho_B M}{G y_0}$$

and $\quad k_g(c_g - c_s) = -D \left(\dfrac{dc}{dr} \right)_{r=R}$

$$\frac{dT}{dz} = \frac{\eta(\text{rate})(-\Delta H)\rho_B}{G C_p}$$

and $\quad h(T_g - T_s) = \lambda \left(\dfrac{dT}{dr} \right)_{r=R}.$

To simulate partial impregnation, two factors are required: F_1 = fraction of pellet radius actually occupied by the deposited Pt; thus, a value of $(F_1 = 0.1)$ represents a pellet (1 cm in this study) whose outer shell contains a 1-mm thickness of catalyst.

Thus,

$$\phi = F_1 L \sqrt{\frac{F^2 k f(c)}{D}}.$$

F_2 = fraction of original weight percent of Pt which is deposited. So surface rate is F_2 (rate).

The base case (total impregnation) is then F_1 and F_2 equal to unity. If half the amount of Pt is assumed to be deposited within the outer shell of the porous support to the extent of 10% penetration, then $F_1 = 0.1$ and $F_2 = 0.5$.

Solution of the governing equations was achieved on the University of Notre Dame, Univac 1107, using a fourth-order Runge-Kutta technique. Resulting profiles (conversion, gas and solids temperature and catalytic effectiveness) were displayed digitally and graphically as a function of reactor length. The criterion for single stage conversion is 98% of equilibrium at the exit temperature.

RESULTS

The following table summarizes the finding for three broad cases involving: (a) The base weight of Pt catalyst ($F_2 = 1$) deposited to the extent of 100, 50, and 10% depth of penetration; (b) half the amount of Pt ($F_2 = 0.5$) at 50 and 10% of penetration; and (c) 10% of base amount of Pt ($F_2 = 0.1$) impregnated to the extent of 50 and 10% of total pellet depth. For these cases conversion, x, bed length Ξ, effectiveness at bed entrance η_0 and exit η_f are tabulated below:

TABLE 1

% of impregnation		$\begin{array}{c}x\\(\%)\end{array}$	Ξ	η_0	η_f
$F_2 = 1$	1 (base Case)	81	2 ft	0.28	0.04
	0.5	81	1.55	0.52	0.26
	0.1	81	1.05	0.96	0.84
$F_2 = 0.5$	0.5	81	3.3	0.54	0.25
	0.1	81	2.35	0.96	0.84
$F_2 = 0.1$	0.5	77	15.5	0.55	0.23
	0.1	77	11.	0.96	0.8

DISCUSSION

Clearly significant advantages are realized by partial impregnation. Further, interpolating between the base case ($F_2 = 1$) and that in which half the catalytic agent is deposited ($F_2 = 0.5$) suggests that economies in catalyst investment for a desired space-time-yield (moles of product per unit time per unit of reactor volume) can be realized by partial impregnation with less Pt than is employed in the totally impregnated base case. Experimental support of these contentions was realized in a study of CO oxidation over various supported transition metal catalysts (5). A shell of metal was deposited upon 3/16 in. tablets, ($F_1 \cong 0.2$). In consequence, effectiveness factors of unity prevailed in the study cited. Certainly partial impregnation is indicated in automotive exhaust catalysts.

While in the case of SO_2 and CO oxidation, only activity is involved, it is evident that in systems where yield is of import any step undertaken to eliminate mass inter-intraphase diffusional limitations will prove beneficial to yield of product (6) in consecutive reaction networks, such as ethylene or naphthalene oxidation.

REFERENCES

1. HUTCHINGS, J., AND CARBERRY, J. J., *A.I.Ch.E.* **12**, 20 (1966).
2. CARBERRY, J. J., *Ind. Eng. Chem.* **58**, 40 (1966).
3. HOUGEN, O., AND WATSON, K. M., "Chem. Process Principles" Vol. 3, Wiley, New York.
4. MINHAS, S., AND CARBERRY, J. J., *British Chem. Eng.* (in press) **1969.**
5. TAJBL, D., SIMONS, JOSEPH L., AND CARBERRY, J. J., *Ind. Eng. Chem. Fundamentals* **5**, 171 (1966).
6. CARBERRY, J. J., *Chem. Eng. Science* **17**, 675 (1962).