Apparent Kinetics and Catalyst Poisoning in Strong Pore Diffusion Regimes for *nth* Order Reactions

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The falsification of kinetics for nth order catalytic reactions due to the poisoning of the catalyst can be derived by simple relations in connection with strong pore diffusion regimes. Under this hypothesis, the reactant concentration drops to a very small value, approximatively zero, at the pore ends. Let us consider single-pore and macro–micro-pore catalyst models and pore-mouth poisoning.

NOTATION

C_0	Concentration of reactant at the pore mouth
D	Diffusivity
E_0	Reaction activation energy
$E_{apparent}$	Apparent reaction activation energy
$f_{1,2}$	Diffusivity of reactant in the macropore/Diffusivity of reactant in the micropore
l	Pore length
l_1	Macropore length
l_2	Micropore length
n	Reaction order
$n_{apparent}$	Apparent reaction order
r	Pore radius
r_1	Macropore radius
r_2	Micropore radius
J	$\theta_2^{2/3}\Omega^{1/3}$
R_g	Gas constant
T	Absolute temperature

Greek Letters

α	Fraction of catalyst poisoning
β	Concentration of reactant at the interface poisoned–unpoisoned zone/Concentration of reactant at the pore mouth
θ_2	$l_1/r_1^{1/2}l_2^{1/2}f_{1,2}^{1/2}$
φ_1	Rate of transport of reactant into the poisoned section
φ_2	Rate of reaction in the unpoisoned zone
Ω	Generalized Thiele modulus

SINGLE-PORE MODEL

Previous authors (*1–9*) have discussed the catalyst poisoning which results from either very rapid adsorption of poison molecules or contamination by carbon deposition initiating at the external surface of a porous catalyst and moving progressively inwards. Therefore, the pore is divided into two zones, the first, inactive, starting at the pore mouth and extending αl distance into the pore and a second, active, extending from αl to l. The rate of transport of reactant into the poisoned section is

$$\varphi_1 = \frac{\pi r^2 D C_0}{\alpha l}(1 - \beta) \qquad (1)$$

The rate of reaction in the unpoisoned zone of the pore, in the strong pore diffusion regime, results by applying Petersen's asymptotic method (*4, 10*) to the differential equation of material balance

$$\varphi_2 = \frac{2\pi r^2 D C_0 \Omega}{(n + 1)l}\beta^{(n+1)/2} \qquad (2)$$

with Ω the generalized Thiele modulus for nth order reactions (*4, 11*). Equating φ_1 and φ_2:

$$1 - \beta = \frac{2}{n + 1}\Omega\alpha\beta^{(n+1)/2} \qquad (3)$$

The apparent reaction activation energy $E_{apparent}$, defined as

$$-R_g \frac{\partial \ln \varphi}{\partial(1/T)},$$

can be written

$$E_{\text{apparent}} = -R_g \frac{\partial \ln(1 - \beta)}{\partial (1/T)} \qquad (4)$$

Clearly from Eq. (3), supposing no influence of temperature on diffusivity, we have

$$\frac{E_{\text{apparent}}}{E_0} = \frac{1}{2 + (n + 1)(1/\beta - 1)} \qquad (5)$$

The apparent reaction order n_{apparent}, defined as $\partial \ln \varphi / \partial \ln C_0$, from the quite general relation

$$n_{\text{apparent}} = 1 + (n - 1)E_{\text{apparent}}/E_0 \qquad (6)$$

previously derived (12) for isothermal systems, becomes

$$n_{\text{apparent}} = 1 + \frac{n - 1}{2 + (n + 1)(1/\beta - 1)} \qquad (7)$$

The results from Eq. (4) and Eq. (7), through the Eq. (3), are shown on Figs. 1 and 2 as E_{apparent}/E_0 and n_{apparent} against α for $n = 0, 1, 2$ and $\Omega = 10, 20$.

A very large drop in the ratio E_{apparent}/E_0 is caused by a small amount of poison when the reaction in the unpoisoned pore is in the diffusion-influenced region. Correspondingly, the apparent reaction order tends to 1.0 with poisoning. Of course, there is no falsifi-
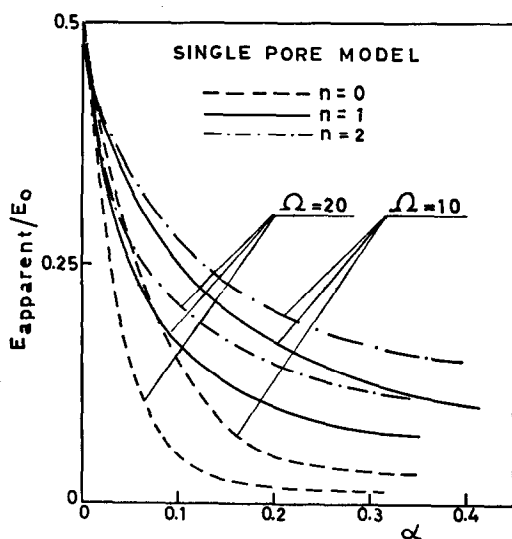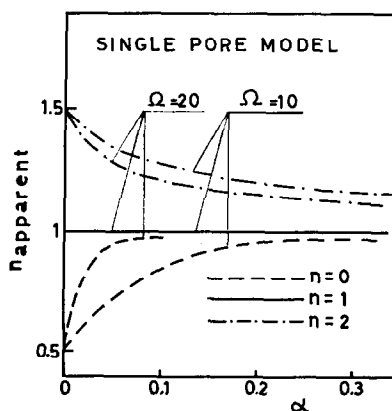

FIG. 2. Plot of n_{apparent} against the fraction of catalyst poisoning α for different reaction orders n and Thiele moduli Ω.

cation of reaction order for first order reactions.

It must be considered, nevertheless, that the results are valid in the strong pore diffusion regime; in effect, as α approaches unity, the reaction must be become kinetics-controlled. In this last case we obtain

$$1 - \beta \cong \frac{2}{n + 1} \alpha(1 - \alpha)\Omega^2\beta^n \qquad (8)$$

and Eq. (4) and Eq. (7) become

$$\frac{E_{\text{apparent}}}{E_0} = \frac{1}{1 + n(1/\beta - 1)} \qquad (9)$$

and

$$n_{\text{apparent}} = 1 + \frac{n - 1}{1 + n(1/\beta - 1)} \qquad (10)$$

Because the overall rate of reaction for the pore approaches zero, $1/\beta$ is approximatively 1.0 and $E_{\text{apparent}} = E_0$ and $n_{\text{apparent}} = n$.

MACRO–MICRO-PORE MODEL

This catalyst model, discussed by Mingle and Smith (13), Carberry (14, 15), and Tartarelli et al. (12, 16–20), can be visualized by considering a cylindrical pore of radius r_1 (macropore) from which micropores of radius $r_2 < r_1$ branch along the length and at right angles to the macropore. Carbonaceous deposits can obstruct the micropore mouth, so that the micropores αl_1 distant from the macropore mouth are ruled out from the reactant; the other ones, on the contrary, are completely active.
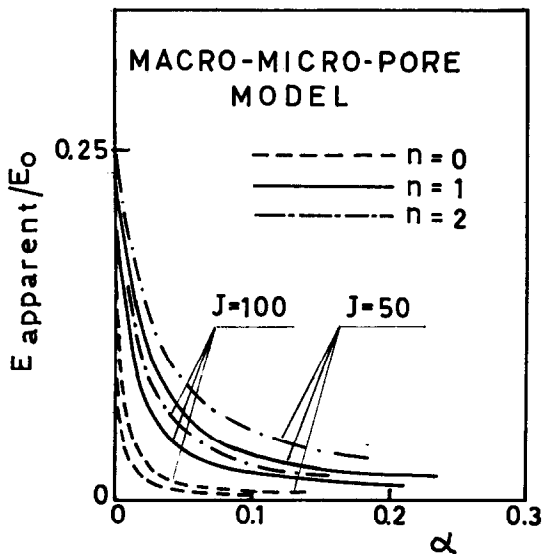

FIG. 1. E_{apparent}/E_0 against the fraction of catalyst poisoning α for different reaction orders n and Thiele moduli Ω.

FIG. 3. $E_{apparent}/E_0$ against the fraction of catalyst poisoning α for different reaction orders n and $J = \theta_2^{2/3} \Omega^{1/3}$.

Assuming reactant concentrations of zero at the micropore and macropore ends, and equating the reactant flux into the poisoned section and the rate of reaction in the unpoisoned zone, there is obtained

$$1 - \beta = \frac{4\theta_2^{2/3}\Omega^{1/3}\alpha}{(n+1)^{1/3}(n+3)^{2/3}} \beta^{(n+3)/4} \quad (11)$$
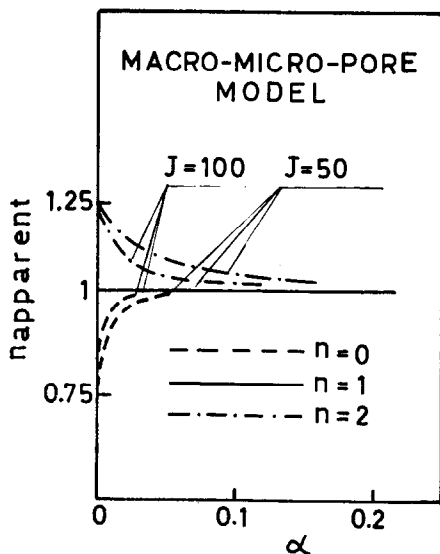

FIG. 4. Plot of $n_{apparent}$ against the fraction of catalyst poisoning α for different reaction orders n and $J = \theta_2^{2/3} \Omega^{1/3}$.

with

$$\theta_2 = l_1/r_1^{1/2}l_2^{1/2}f_{1,2}^{1/2}$$

Therefore

$$\frac{E_{apparent}}{E_0} = \frac{1}{4 + (n+3)/(1/\beta - 1)} \quad (12)$$

and

$$n_{apparent} = 1 + \frac{n-1}{4 + (n+3)/(1/\beta - 1)} \quad (13)$$

In Figs. 3 and 4 $E_{apparent}/E_0$ and $n_{apparent}$ are diagrammed against α for $n = 0$, 1, 2 and $J = \theta_2^{2/3} \Omega^{1/3} = 50$ and 100. In the macro–micro-pore model qualitative behavior, analogous to that shown in the single-pore model, is obtained.

REFERENCES

1. WHEELER, A., *Advan. Catalysis* **3**, 250 (1951).
2. WHEELER, A., *Catalysis* **2**, 105 (1955).
3. VAN ZOONEY, D., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam,* 1964.
4. PETERSEN, E. E., "Chemical Reaction Analysis." Prentice-Hall, Englewood Cliffs, New Jersey, 1965.
5. MASAMUNE, S., AND SMITH, J. M., *A. I. Ch. E. J.* **12**, 384 (1965).
6. SADA, E., AND WEN, C. Y., *Chem. Eng. Sci.* **20**, 783 (1965).
7. CAGIANELLI, S., MORELLI, F., AND TARTARELLI, R., *Ing. Chim. Ital.* **3**, 147 (1967).
8. FERRAIOLO, G., AND REVERBERI, A., *Ann. Chim.* **57**, 1151 (1967).
9. MORELLI, F., CAPOVANI, M., AND TARTARELLI, R., *Ann. Chim.* **58**, 223 (1968).
10. PETERSEN, E. E., *Chem. Eng. Sci.* **17**, 987 (1962).
11. TARTARELLI, R., *Chim. Ind. (Milan)* **49**, 1075 (1967).
12. TARTARELLI, R., *Chim. Ind.* (Milan) **50**, 556 (1968).
13. MINGLE, J. O., AND SMITH, J. M., *A. I. Ch. E. J.* **7**, 243 (1961).
14. CARBERRY, J. J., *A. I. Ch. E. J.* **8**, 557 (1962).
15. CARBERRY, J. J., *Chem. Eng. Sci.* **17**, 675 (1962).
16. TARTARELLI, R., *Chim. Ind. (Milan)* **48**, 723 (1966).
17. MORELLI, F., CAPOVANI, M., AND TARTARELLI, R., *Chim. Ind. (Milan)* **48**, 723 (1966).
18. TARTARELLI, R., *Chim. Ind. (Milan)* **49**, 620 (1967).
19. TARTARELLI, R., AND MORELLI, F., *Chim. Ind. (Milan)* **49**, 745 (1967).
20. TARTARELLI, R., AND MORELLI, F., *Ann. Chim.* **57**, 1316 (1967).