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Nonuniform Distribution of Catalysts on Supports

I. Bimolecular Langmuir Reactions

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An "egg-yolk" catalyst where the active ingredients are deposited towards the interior of a support can have greater activity than the more traditional uniform distribution, or the "egg-shell" distribution towards the exterior of a support. For the bimolecular Lagmuir kinetics under isothermal conditions, such as the oxidation of carbon monoxide over platinum, the effectiveness factors are computed and compared for four catalysts: active ingredient deposited in an interior layer, in a middle layer, in an exterior layer, and uniformly in the entire support. The interior layer catalyst is more advantageous at lower temperatures.

NOMENCLATURE

c	CO concentration (mole%)
D_e	Effective diffusivity (cm^2/sec)
k	Second order rate constant (1/sec mole% O_2)
K_a	Adsorption rate constant (1/mole% CO)
K_{av}	$(z_2 - z_1)K_r/l$, volume averaged rate constant (1/sec)
K_r	Pseudo-first order rate constant $k(O_2)$ (1/sec)
l	Catalyst layer thickness (cm)
L	Length of monolith reactor (cm)
x	z/l, dimensionless distance
y	c/c_s, dimensionless concentration
y_L	fraction of remaining reactant
z	distance (cm)
γ	$K_a c_s$, adsorption parameter
η	effectiveness factor
ψ	$l(k_r/D_e)^{\frac{1}{2}}$ dimensionless
ϕ	Thiele modulus defined by Eq. (11)
ϵ_c	Fraction of volume occupied by catalyst
ϵ_g	Fraction of volume occupied by void
τ	Contact time (sec)

Subscripts

av	average
int	intrinsic
obs	observed
s	surface

INTRODUCTION

For positive order chemical reactions, diffusional resistance produces a reduction of reaction rate. Incomplete utilization of the catalytic surface results, with a concomitant drop of the effectiveness factor to values below unity. However, in reactions of negative order kinetics, a diffusion resistance can enhance the rate of chemical reaction. A drop in reactant concentration towards the catalyst particle interior increases the reaction rate.

In bimolecular Langmuir kinetics, negative order is exhibited when one reactant is strongly adsorbed on the catalyst surface.

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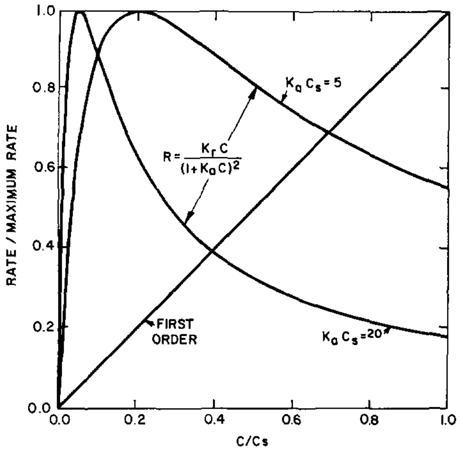

FIG. 1. Reaction rate vs concentration for bimolecular Langmuir kinetics and first-order kinetics.

An important example of such a reaction is the carbon monoxide oxidation over noble metal catalysts. The oxidation rate of CO over platinum at 400–700°F is inversely proportional to CO concentration when the latter is larger than about 2 Torr. The rate expression for this reaction was determined by Voltz and co-workers (*1*) for automotive catalysts and is given by:

$$\text{rate} = \frac{k[\mathrm{O_2}][\mathrm{CO}]}{(1 + K_a[\mathrm{CO}])^2}. \tag{1}$$

The reaction rate curves for CO oxidation in excess oxygen are plotted in reduced form in Fig. 1. Here $K_r = k(\mathrm{O_2})$, C refers to CO concentration, and C_s is a reference concentration

Under isothermal conditions, the effectiveness factor for this bimolecular Langmuir kinetics exceeds the value of one in the diffusion influenced reaction rate zone (*2*, *3*). Wei and Becker (*2*) also showed the existence of multiple values of the effectiveness factors in the diffusion influenced zone.

In terms of catalyst design, the beneficial influence of diffusion implies that a thick catalyst layer (high Thiele modulus) may be preferred over a thin catalyst layer (low Thiele modulus) for optimum reaction rate. The implications of the thickness of automotive catalyst on the efficiency of CO oxidation were discussed by Wei and Becker (*2*).

A reaction where the rate increases by lowering reactant concentration suggests a catalyst design with increased diffusion resistance. A thick support layer can provide the necessary resistance. An alternate approach is to bury the catalytically active ingredient in the interior of a support, leaving an inert diffusion layer at the surface.

Nonuniform distribution of catalysts on supports has long been taken advantage of in the so called "egg shell" catalysts to minimize diffusion resistance. For a positive order reaction, in the absence of selectivity or poisoning considerations, an "egg shell" catalyst is optimum. For a negative order reaction this no longer holds. The effect of poisoning on catalyst performance will be dealt with separately in part II (*11*) of this study.

Nonuniform distribution of catalytic ingredient has been analyzed to determine selectivity of consecutive reactions and regeneration of fouled catalysts by a num-

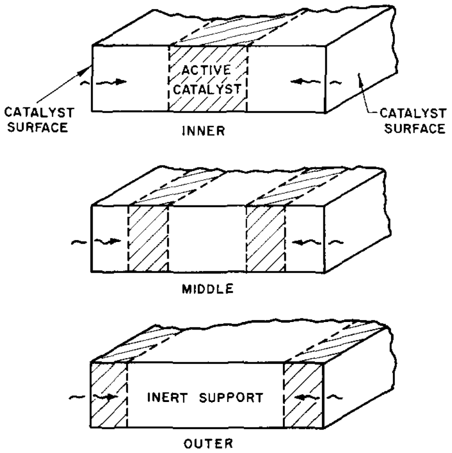

FIG. 2. Nonuniform distribution of active ingredient in a flat plate catalyst support: inner, middle and outer.

ber of authors (4–6). Roth and Gambell (7) measured the behavior of "egg shell" and uniformly distributed platinum catalyst in automotive use. Michalko (8) has demonstrated the preparation and superior performance of an interior layer or "egg-yolk" catalyst in the oxidation of combustible waste gases.

CATALYST DISTRIBUTION

The three catalyst distributions shown in Fig. 2 were chosen for the effectiveness factor calculations. The outer or "egg shell" distribution occupies one-third of the volume in a flat plate support, and corresponds to present day monolith design for automotive catalysts. For the inner ("egg yolk") distribution, the active ingredient is concentrated in one-third of the volume at the center of the support slab, leaving a substantial inert portion of the porous structure adjacent to the surface. The intermediate case, here referred to as middle distribution, lies between the two extremes.

The efficiencies for each of the distribution modes are compared to a uniformly distributed catalyst with the same total metals loading, consequently with a lower local metal concentration that is one-third of the other three cases.

One may consider an optimization procedure with respect only to depth and width of the active layer. However, other factors, such as dispersion limitations, sintering behavior, poisoning and preparation process economics would all play a part in finding an optimum distribution.

ANALYSIS

Using the notations of Fig. 3, the steady-state material balance equations for the bimolecular Langmuir reaction, in a flat plate support with nonuniform distribution of active ingredient, are:

$$\text{Zone 1: } D_e \frac{d^2c_1}{dz^2} = 0, \qquad \frac{dc_1}{dz} = 0 \quad \text{at} \quad z = 0. \tag{2}$$

$$\text{Zone 2: } D_e \frac{d^2c_2}{dz^2} = \frac{K_r c_2}{(1 + K_a c_2)^2}, \qquad \left.\begin{aligned} \frac{dc_2}{dz} &= \frac{dc_1}{dz} \\ c_2 &= c_1 \end{aligned}\right\} \quad \text{at} \quad z = z_1. \tag{3}$$

$$\text{Zone 3: } D_e \frac{d^2c_3}{dz^2} = 0, \qquad \left.\begin{aligned} \frac{dc_3}{dz} &= \frac{dc_2}{dz} \\ c_3 &= c_2 \end{aligned}\right\} \quad \text{at} \quad z = z_2, \qquad c_3 = c_s \quad \text{at} \quad z = l. \tag{4}$$

In terms of the dimensionless variables: $y = c/c_s$, $x = z/l$, $\psi = l(K_r/D_e)^{\frac{1}{2}}$, and $\gamma = K_a c_s$ Eqs. (2) to (4) reduce to:

$$\text{Zone 1: } y_1'' = 0, \quad y_1'(0) = 0. \tag{5}$$

$$\text{Zone 2: } y_2'' = \psi^2 y_2/(1 + \gamma y_2)^2, \quad y_2'(x_1) = y_1'(x_1), \quad y_2(x_1) = y_1(x_1). \tag{6}$$

$$\text{Zone 3: } y_3'' = 0, \quad y_3'(x_2) = y_2'(x_2), \quad y_3(x_2) = y_2(x_2), \quad y_3(1) = 1. \tag{7}$$

The effectiveness factors are derived by first finding the concentration profiles. Equations (5) to (7) are integrated and the solutions are matched at the boundaries x_1 and x_2. The values of γ and $y(0)$ are fixed, leaving the parameter ψ (which is related to the Thiele modulus) as an un-

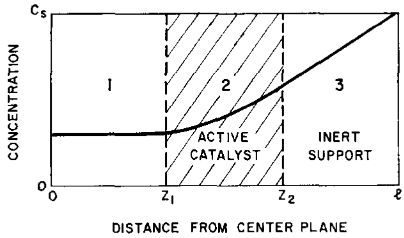

FIG. 3. Schematic of CO concentration profile in a support with nonuniform distribution of active ingredient.

known. In this way an iterative procedure can be avoided and the unstable points can be calculated. Details of the solution procedure are given elsewhere (*9*).

The steady-state flux of reactants into the catalyst is derived from the surface concentration gradient and is related to the effectiveness factor.

In terms of dimensional quantities:

$$\eta = \frac{(1 + K_a c_s)^2 D_e dc/dz\,|_{z=l}}{(z_2 - z_1) K_r c_s}. \qquad (8)$$

In terms of the reduced variables:

$$\eta = \frac{(1 + \gamma)^2 dy/dx\,|_{x=1}}{\psi_{\mathrm{av}}^2}. \qquad (9)$$

The average, ψ_{av}, resembling Thiele's modulus for a first order reaction, is a function of the local rate constant K_r and the thickness of the active region $(z_2 - z_1)$.

$$\psi_{\mathrm{av}} = l[(z_2 - z_1)K_r/D_e l]^{\frac{1}{2}} = l(K_{\mathrm{av}}/D_e)^{\frac{1}{2}}, \qquad (10)$$

where $K_{\mathrm{av}} = K_r(z_2 - z_1)/l$ is the volume-averaged rate constant.

The Thiele modulus represents the ratio of reaction rate to diffusion rate:

$$\phi = \frac{l(K_{\mathrm{av}}/D_e)^{\frac{1}{2}}}{(1 + K_a c_s)}. \qquad (11)$$

EFFECTIVENESS FACTOR

The effectiveness factors calculated in the above outlined manner are plotted in Fig. 4 for the case when $K_a c_s = 20$. In automotive catalysis this corresponds to roughly 4 mole% CO. A region of enhanced efficiency appears for all four modes of distribution when the Thiele modulus lies between 0.4 and 4. Effectiveness factor for the inner layer rises above unity at the lowest values of ϕ, reaches a maximum of 5 and drops below one when $\phi > 1.2$. In contrast, η for the outer distribution rises above unity at higher values of ϕ,

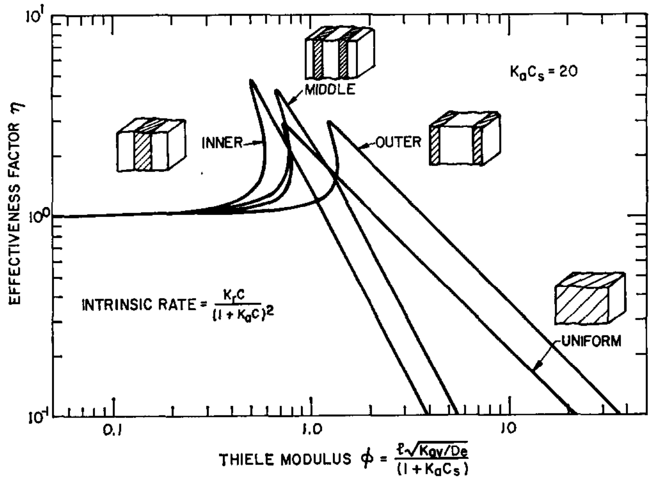

FIG. 4. Isothermal effectiveness factors for bimolecular Langmuir kinetics in nonuniformly distributed flat plate catalysts, for $K_a c_s = 20$.

reaches a maximum of 3 when $\phi = 1.2$ and drops below unity only when $\phi > 4$. A region of multiple steady-states exists for each distribution. The inner and middle distributions with inert support layers at the surface are characterized by a sharp drop of η in the high ϕ region. This asymptote is proportional to ϕ^{-2} and implies a severe penalty in performance when diffusion rates dominate. The η asymptote for the uniform and outer distributions are proportional to ϕ^{-1} as is the case with positive order reactions.

At values of ϕ between 0.4 and 1.0, the inner and middle distributions hold an advantage in η over the uniform and outer distributions. This advantage is reversed when ϕ is greater than 1.2.

The complete results for eight values of $K_a c_s$ ranging from zero (first order) to 100 may be found elsewhere (*9*).

CONVERSION

An illustrative conversion calculation is appropriate to demonstrate the effect of distribution of active ingredient in a catalyst on reactor performance. The monolith reactor in automobile converters lends itself to this calculation. The efficiency of CO removal depends on a number of variables: inlet temperature and CO concentration, space velocity, and quantity of catalyst. The rate of external heat and mass transport, the heat generated by the CO conversion, the decline in self-poisoning of CO oxidation as conversion proceeds, the deposition of poisons on exterior layers all play roles. An initial analysis is presented which ignores the four above-mentioned factors to simplify the complexities. The aim is to identify an

TABLE 1

Constants for CO-Oxidation Kinetics and Conversion Calculations

$k(\text{av}) = 1.14 \times 10^{12}$
$\times \exp(-22{,}600/°R)$ (1/sec mole% O_2)
$[O_2] = 4.0$ mole%
$K_a = 0.655 \exp(1730/°R)$
Flowrate = 20 standard ft^3/min
Reactor vol = 0.03 ft^3
Inlet CO concn = 6 mole%
$D_e = 0.06$ cm^2/sec
$\epsilon_c = 0.3$
$\epsilon_g = 0.7$

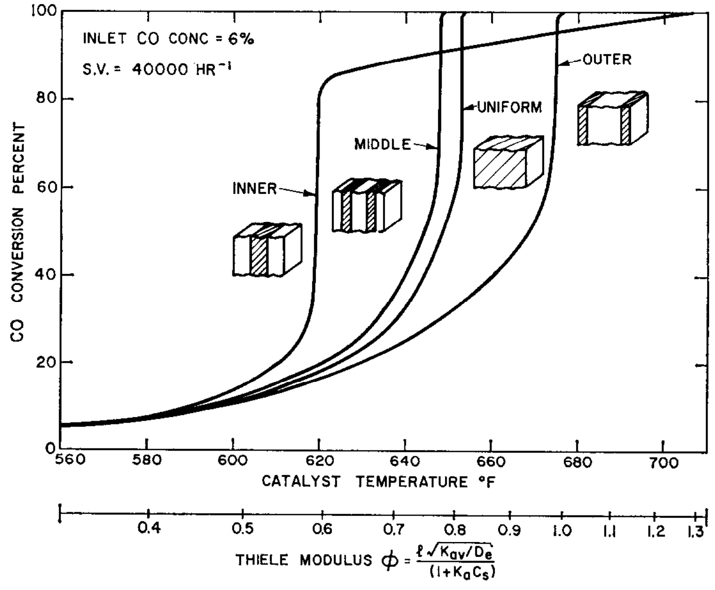

FIG. 5. Carbon monoxide conversion to CO_2 over a monolith reactor with platinum catalyst.

effect of catalyst distribution, if any, on conversion.

The conversion of CO on platinum supported on a monolith reactor is given by (*2*):

$$\gamma^2(1 - y_L^2)/2 + 2\gamma(1 - y_L) + \ln y_L = \frac{\epsilon_c}{\epsilon_g} K_r \eta \tau. \quad (12)$$

y_L is the fraction of unconverted CO in the outlet. Equation (12) is not explicit in y_L, and a trial-and-error procedure was employed to solve for conversion. The rate constants from Voltz and co-workers' work (*1*) and other constants used in the computation are listed in Table 1.

The conversion calculations were applied to a monolith 12 cm in diameter, 7.6 cm long with an inlet CO concentration of 6 mole%. The open area constitutes 70%, and the support layer is 0.05 cm thick.

It has been well established that the emissions from the catalytic converter are highest when the catalyst is cold, in fact 50% or more of the total pollutants are emitted during the first 2 min of the 23 min EPA-CVS test cycle (*10*). An early light-off of the reaction is therefore an important requirement of the converter.

Figure 5 shows the conversion versus temperature curves for the four distributions as indicated. The space velocity of 40,000 hr^{-1} is typical of idle and low speed conditions. The reaction in the flat plate catalyst with inner distribution ignites nearly 30°F before the uniform catalyst. The order of light-off follows the order of enhancement of effectiveness in Fig. 4. The conversion curve for the inner layer flattens off dramatically after light-off, indicating the severe drop in effectiveness which is manifested by the low temperature dependence of conversion. The observed rate here is the product of intrinsic rate and effectiveness factor:

$$r_{\text{obs}} = r_{\text{int}}\eta \rightarrow r_{\text{int}}/\phi^2, \quad \text{when} \quad \phi > 0.6.$$

The catalyst with middle distribution achieves complete conversion before encountering the steep decline in effectiveness. The "egg shell" or outer catalyst lights-off 50°F later than the inner layer. In the automotive converter, this may represent a substantial increase in emissions.

The beneficial effectiveness region is in the Thiele modulus range between 0.4 and 4, and is of advantage for low temperature light-off.

CONCLUSIONS

For a bimolecular Langmuir kinetics, concentrating the catalytic ingredient in a layer buried some distance from the surface results in higher effectiveness factors at low values of Thiele modulus. Maximum efficiency is predicted by leaving a substantial inert layer adjacent to the catalyst particle exterior.

High conversion of CO in a monolith reactor can be achieved at lower temperatures than those predicted for conventional uniform or "egg shell" catalyst when an interior layer catalyst is used. The conditions for which this phenomenon occurs fall into a narrow window. In automotive application, a nonuniform catalyst distribution herein referred to as inner or middle may be preferred.

At high values of ϕ, the effectiveness factors of uniform and outer catalyst distributions are superior to that of the interior layer catalysts. The presence of poison impurities in the feed can, however, change this preference. This aspect of catalyst performance will be discussed in Part II (*11*) of this work.

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