estimated from one-shot measurement than from step response. For one-shot measurement a short adsorption bed is usually preferable. It is interesting that a solid-gas adsorption bed as short as five particle layers may successfully be used in estimating the adsorption equilibrium constant provided that inert beds are installed between test bed and concentration detecting filament. A short adsorption bed can be effectively employed, particularly when the system has a large adsorption equilibrium constant and a long time is required to obtain response signal in a conventional long bed.

Nomenclature

a	= surface area per unit volume of packed bed, $a=3(1-\epsilon_b)/R$ for spheres	$[\text{m}^{-1}]$
C, C', C_D	= bulk gas concentrations in adsorption bed, inert bed and empty section, respectively	
C^I, C^{II}	= input and response signals	$[\text{mol} \cdot \text{m}^{-3}]$
c	= intraparticle gas concentration	$[\text{mol} \cdot \text{m}^{-3}]$
c_{ad}	= amount adsorbed	$[\text{mol} \cdot \text{kg}^{-1}]$
D_{ax}, D_{ax}', D_D	= axial gas dispersion coefficients in adsorption bed, inert bed and empty section, respectively	$[\text{m}^2 \cdot \text{s}^{-1}]$
D_e	= intraparticle effective diffusivity	$[\text{m}^2 \cdot \text{s}^{-1}]$
D_p	= particle diameter	$[\text{m}]$
D_0	= molecular diffusivity	$[\text{m}^2 \cdot \text{s}^{-1}]$
$F(s)$	= transfer function	$[-]$
K_A	= adsorption equilibrium constant	$[\text{m}^3 \cdot \text{kg}^{-1}]$
k_a	= rate constant of first-order adsorption	$[\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}]$

k_f	= particle-to-gas mass transfer coefficient	$[\text{m} \cdot \text{s}^{-1}]$
L	= adsorption bed length	$[\text{m}]$
L', L'', L_D	= lengths, refer to Fig. 2	$[\text{m}]$
R	= particle radius	$[\text{m}]$
Re	= $D_p U \epsilon_b \rho_F / \mu$, Reynolds number	$[-]$
Sc	= $\mu / (\rho_F D_0)$, Schmidt number	$[-]$
Sh	= $k_f D_p / D_0$, Sherwood number	$[-]$
U, U'	= interstitial gas velocities in adsorption bed and inert bed, respectively	$[\text{m} \cdot \text{s}^{-1}]$
u	= gas velocity in empty column	$[\text{m} \cdot \text{s}^{-1}]$
ϵ	= root-mean-square-error, defined by Eq. (13)	$[-]$
ϵ_b, ϵ_b'	= void fractions in adsorption bed and inert bed, respectively	$[-]$
ϵ_p	= intraparticle void fraction	$[-]$
μ	= gas viscosity	$[\text{Pa} \cdot \text{s}]$
ρ_F	= gas density	$[\text{kg} \cdot \text{m}^{-3}]$
ρ_p	= particle density	$[\text{kg} \cdot \text{m}^{-3}]$

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THE REACTION ORDER OF SOLID CONCENTRATION FOR VOLUME REACTION MODEL

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A fluid-solid reaction such as

has often been analyzed kinetically by the volume reaction model^{1,3-5)}. In this model, the disappearance rate of component A per unit volume of bulk solid ($-r_A$), is assumed to be a function of the fluid and solid concentrations,

$$(-r_A) = kf(C_A, C_S) \quad (2)$$

The function $f(C_A, C_S)$, however, could not be represented theoretically. Thus the rate has been described approximately by the following form:

$$(-r_A) = kC_A C_S^m \quad (3)$$

Chida and Tadaki²⁾ reported recently that the solid concentration dependence of the rate can be expressed in the form of Eq. (3), on the basis of a structural model in which a solid pellet is composed of a large number of fine spherical particles. However, the case where m is less than $2/3$ could not be explained

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Fig. 1 Relations between Y and $(R)_p$ (cylindrical particle)

Fig. 2 Relations between Y and $(R)_p$ (slab-like particle)

Fig. 3 Relations between Y and $(R)_p$ (pore model)

by this consideration.

This paper shows that m can take a value less than $2/3$, and even a negative value under extreme conditions, on the basis of other structural models different from that mentioned above.

1. Assembly Models of Non-Spherical Particles

1.1 Cylindrical particle

Consider that a porous spherical pellet is composed of a large number of fine, dense cylindrical particles whose radii are sufficiently small compared to their length, and that reaction (1) takes place in the particles. It is assumed that the unreacted core shrinking model is applied to the kinetic analysis of the particles and that the disappearance rate of fluid component A per unit reaction area is given as

$$(-r_A)' = k' C_A \quad (4)$$

Then the overall reaction rate of a particle, $(-r_A)_p$, is given in the following form based on the analysis in the previous paper²⁾:

$$(-r_A)_p = 2\pi r_0 l (-r_A)'_{r=r_c} \quad (5)$$

And the dimensionless overall reaction rate, $(R)_p = (-r_A)_p / 2\pi r_0 k' C_{Ab}$, is represented as follows.

$$(R)_p = \frac{\sqrt{Y}}{1 - N_k \sqrt{Y} \ln \sqrt{Y}} \quad (6)$$

where $N_k = k' r_0 / De$, $Y = C_s / C_{s0}$ and De is the effective diffusivity in the product layer of the particle.

On the other hand, the volume reaction model with Eq. (3) gives the following equation²⁾.

$$(R)_p = Y^m \quad (7)$$

Therefore, if Eq. (6) is approximated by Eq. (7), the value of m can be estimated.

Figure 1 shows the relation between $(R)_p$ and Y of Eq. (6). If $N_k < 0.5$, $(R)_p$ is approximated by the function $Y^{1/2}$, and if N_k is in the range from 0.5 to 1, $(R)_p = Y^{2/3}$. When N_k is equal to zero Eq. (6) coincides with $Y^{1/2}$, and the value of m estimated is always larger than $1/2$ in this case.

1.2 Slab-like particle

Consider that a porous spherical pellet is composed of a large number of fine, dense slabs whose thickness is sufficiently thin. The other steps in the analysis are the same as those for the previous model.

Then $(R)_p = (-r_A)_p / 2A_s k' C_{Ab}$ is given as

$$(R)_p = \frac{1}{1 + N_k(1 - Y)} \quad (8)$$

Figure 2 shows the relation between $(R)_p$ and Y . If $N_k < 0.5$, $(R)_p$ may be approximated by a constant $Y^0 = 1$. However, if $N_k < 0.5$ it is difficult for $(R)_p$ to be approximated with a function in the form of Y^m .

2. Pore Model

Porous materials can be considered to be network systems composed of numerous cylindrical pores. This consideration means that fluid-solid reaction takes place on the pore wall at the beginning, and then proceeds into the solid centrifugally.

Now assume that all pores in the pellet are of uniform size, and that the solid phase is formed concentrically around the pore from r_0 to r_1 .

Then the outer radius of the space r_1 is given by the following equation.

$$r_1 = r_0 \sqrt{1/\epsilon} \quad (9)$$

The diffusion equation in the product layer ($r = r_0 \sim r_c$) is written as

$$d(R(dZ/dR))/dR = 0 \quad (10)$$

$$\text{B.C. } Z=1 \text{ at } R=1 \quad (11)$$

$$dZ/dR = N_k Z \text{ at } R=R_c \quad (12)$$

where $R=r/r_0$, $R_e=r_e/r_0$ and $Z=C_A/C_{A0}$

The solution of Eq. (10) with the boundary conditions (11) and (12) is

$$Z = \frac{1 + N_k R_e \ln(R_e/R)}{1 + N_k R_e \ln(R_e)} \quad (13)$$

In this equation R_e is given as follows.

$$R_e = \sqrt{(1 - (1 - \varepsilon)Y)/\varepsilon} \quad (14)$$

Then the dimensionless overall reaction rate, $(R)_p = (-r_A)_p / 2\pi l' r_0 k' C_{Ab}$, can be written as

$$(R)_p = R_e / (1 + N_k R_e \ln(R_e)) \quad (15)$$

Figure 3 shows the relation between $(R)_p$ and Y in the case of $\varepsilon=0.4$. If $0.5 < N_k < 1$, $(R)_p$ may be approximated by a constant $Y^0=1$, but it is difficult in the case of other values of N_k for $(R)_p$ to be approximated with a function in the form of Y^m . One should note that if $N_k < 0.8$, $(R)_p$ is larger than unity. This means that m is negative; that is, the reaction is accelerated with decrease of solid reactant. This phenomenon may be one of the explanations for sigmoidal conversion-time curves in fluid-solid reactions.

Conclusion

It is found on the basis of structural models and the pore model that the reaction order of solid concentration for the volume reaction model may take a positive value, say, 0, 1/2 or 2/3, and under extreme conditions a negative value.

Nomenclature

A_s = reaction surface area of solid [m²]

C_A, C_{A0}	= concentration of A in particle and bulk	[mol/m ³]
C_s, C_{s0}	= concentration and initial concentration of S	[mol/m ³]
D_e	= effective diffusivity	[m ² /s]
k	= rate constant defined by Eq. (3)	[(m ³ /mol) ^m /s]
k'	= rate constant defined by Eq. (4)	[m/s]
l	= length of a cylindrical particle	[m]
l'	= length of a cylindrical pore	[m]
m	= reaction order	[—]
N_k	= $k'r_0/D_e$	[—]
$(R)_p$	= dimensionless overall reaction rate	[—]
r	= radius coordinate	[m]
r_0	= radius of cylindrical particle or pore	[m]
r_1	= imaginary outer radius of solid defined by Eq. (9)	[m]
$(-r_A)$	= disappearance rate of A per unit volume of bulk solid	[mol/m ³ ·s]
$(-r_A)'$	= disappearance rate of A per unit reaction area	[mol/m ² ·s]
$(-r_A)_p$	= reaction rate of a particle	[mol/s]
r_e	= radius of reaction interface	[m]
Y	= dimensionless solid concentration	[—]
Z	= dimensionless fluid concentration	[—]
ε	= volume fraction of macropore	[—]

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CRITERION FOR SIMULTANEOUS INTERPHASE TEMPERATURE AND CONCENTRATION GRADIENTS

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A number of theoretical criteria for avoiding significant interphase temperature and concentration gradients have been developed for each gradient independently. Butt and Weekman⁽¹⁾ summarized criteria published before 1974. Since both thermal concentration gradients may occur simultaneously

near the surface of a catalyst pellet, a combined criterion would be more appropriate. The reason: the simultaneous existence of temperature and concentration gradients may have either a compensating or an amplifying effect on the global rate. For example, the effect of a temperature gradient in an exothermic reaction is to increase the global rate. Consequently, in an exothermic, positive-order reaction (e.g. CO oxidation on V₂O₅), the two gradients may

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