Weber number. Carbon tetrachloride drops in 1.0wt%CMC aqueous, which is characterized as more non-Newtonian than 0.5wt%CMC aqueous, deform to prolate spheroidal drops. The spheroid can be either oblate or prolate depending on whether λ in Eq. (2) is, respectively, positive or negative. λ of carbon tetrachloride drops in 1.0wt%CMC aqueous is about 0.140 in this experimental region. Therefore, Eq. (2) predicts the appearance of oblate drops. Experimental data show a direction opposite to the calculated values of Eq. (2). The eccentricity of Newtonian drops in 1.0wt%CMC aqueous increases with increasing Weber number in this experimental region. The front of the prolate drop in 1.0wt%CMC aqueous becomes more flattened than the rear. The effect of non-Newtonian behavior of continuous phase on the shape of drops is remarkable.

The present paper contains an experimental study of the shape of drops in non-Newtonian fluid systems. A future paper will consider this problem in more detail.

Nomenclature

d_p = equivalent drop diameter [cm]

e_j^l	= component of the rate-of-deformation tensor	[sec ⁻¹]
K	= constant in the power law model	[g/cm·sec ²⁻ⁿ]
n	= constant in the power law model	[—]
U	= drop velocity	[cm/sec]
We	= Weber number	[—]
X	= viscosity ratio	[—]
ε	= eccentricity	[—]
λ	= defined by Eq. (3)	[—]
μ	= viscosity	[g/cm·sec]
ρ	= density	[g/cm ³]
τ_j^l	= component of the stress tensor	[g/cm·sec ²]
<Superscript>		
'	= dispersed phase	

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THE EFFECT OF INTRAPARTICLE DIFFUSION ON CATALYST FOULING — DEHYDROGENATION OF *n*-BUTANE OVER CHROMIA-ALUMINA CATALYST —

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In the previous study²⁾ on the dehydrogenation reaction of *n*-butane over chromia-alumina catalysts, the authors found that 1) coke formation occurred consecutively to the dehydrogenation of *n*-butane, or *n*-butane→*n*-butene→coke; 2) the dehydrogenation of *n*-butane mainly occurring on chromia and coke formation could be carried out γ -alumina as well as on chromia; and 3) the intraparticle diffusional resistance within micropores was considered negligible and the rate of each reaction was expressed by the following equations.

$$r_A = k_1^0 \left(1 - \frac{n_{C1}}{n_{C1}^\infty} \right) \frac{p_A}{1 + K_A p_A} \quad (1)$$

$$r_C = k_{C1}^0 \left(1 - \frac{n_{C1}}{n_{C1}^\infty} \right) \frac{p_B}{1 + K_A p_A} + k_{C2}^0 \left(1 - \frac{n_{C2}}{n_{C2}^\infty} \right) p_B \quad (2)$$

In this paper, the effect of intraparticle diffusion within macropores on catalyst fouling was analyzed computationally using these rate equations and the calculated and experimental results were compared.

Experimental

The dehydrogenation of *n*-butane was carried out using $5^\phi \times 5^H$ mm cylindrical pellets and crushed particles ($D_p = 0.21, 2.2$ mm) of a chromia-alumina catalyst (γ -Al₂O₃; 80 wt%, Cr₂O₃; 20 wt%) under almost the same conditions as those in the previous study²⁾.

The effective diffusivity of $5^\phi \times 5^H$ mm cylindrical pellet was measured in a N₂-C₂H₄ gas system at 28°C

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using a Wicke-Kallenbach type apparatus³⁾. Experimental results are shown in Fig. 1, where is seen that the value of effective diffusivity is constant regardless of coke content. This is probably due to the fact that coke deposits only in the micropores and that macropore size does not change, as is shown in Fig. 1.

Mathematical Descriptions

For simplicity of computations the following assumptions were postulated.

(1) A pseudo-steady state treatment can be applied to a change of catalyst activity, as the coke formation rate is much smaller than the main reaction.

(2) The catalyst bed is assumed to be completely of the mixing-flow type. This may approximate well the experimental condition as the conversion of reactant gas is small and the bed is very thin.

(3) The geometry of a catalyst is spherical and the equivalent radius of a $5^\phi \times 5^H$ mm cylindrical pellet is evaluated as $3V_p/A_p = 2.5$ mm.

(4) The temperature within a pellet is uniform.

From these assumptions and the experimental findings, mass balance equations of *n*-butane (A), *n*-butene (B) and coke (C) in a spherical catalyst of radius R_s are written as

$$D_{eA} \left(\frac{d^2 p_A}{dx^2} + \frac{2}{x} \cdot \frac{dp_A}{dx} \right) = \frac{k_1^0 p_A \rho RT}{1 + K_A p_A} \phi_1 \quad (3)$$

$$D_{eB} \left(\frac{d^2 p_B}{dx^2} + \frac{2}{x} \cdot \frac{dp_B}{dx} \right) = - \frac{k_1^0 p_A \rho RT}{1 + K_A p_A} \phi_1 + \left(\frac{k_{C1}^0}{1 + K_A p_A} \phi_1 + k_{C2}^0 \phi_2 \right) p_B \frac{\rho RT}{\nu M_C} \quad (4)$$

$$\frac{\partial \phi_1}{\partial t} = - \frac{k_{C1}^0 p_B}{n_{C1}^\infty (1 + K_A p_A)} \phi_1 \quad (5)$$

$$\frac{\partial \phi_2}{\partial t} = - \frac{k_{C2}^0 p_B}{n_{C2}^\infty} \phi_2 \quad (6)$$

$$\frac{\partial n_C}{\partial t} = \left(\frac{k_{C1}^0}{1 + K_A p_A} \phi_1 + k_{C2}^0 \phi_2 \right) p_B \quad (7)$$

Initial and boundary conditions are as follows:

$$\text{I.C. } \phi_1 = \phi_2 = 1 \text{ at } t=0, R_s \geq x \geq 0$$

$$\text{B.C.1 } p_A = p_{As}, p_B = p_{Bs} \text{ at } x=R_s, t>0$$

$$\text{B.C.2 } \frac{dp_A}{dx} = \frac{dp_B}{dx} = 0 \text{ at } x=0, t>0$$

$$\text{B.C.3 } F(p_{Ai} - p_{As}) = \frac{3W_C}{\rho R_s} D_{eA} \frac{dp_A}{dx} \bigg|_{x=R_s} / RT \text{ at } x=R_s, t>0$$

$$\text{B.C.4 } -Fp_{Bs} = \frac{3W_C}{\rho R_s} D_{eB} \frac{dp_B}{dx} \bigg|_{x=R_s} / RT \text{ at } x=R_s, t>0 \quad (8)$$

where

$$\phi_1 = 1 - (n_{C1}/n_{C1}^\infty) \quad (9)$$

$$\phi_2 = 1 - (n_{C2}/n_{C2}^\infty) \quad (10)$$

The overall reaction rates are expressed by using

Fig. 1 Effect of coke on the pore distribution (Hg penetration method) and effective diffusivity

the effectiveness factors, which are defined as the ratios of the reaction rates for a pellet catalyst at any time after the start of a reaction, to those for a particle catalyst at the initial time.

$$E_{fA} = \frac{3R_s}{h_A^2 p_{As}} \frac{dp_A}{dx} \bigg|_{x=R_s} \quad (11)$$

$$E_{fB} = \frac{3R_s}{p_{As} \{ -h_B^2 + h_C^2 (1 + (1 + K_A p_{As}) k_{C2}^0 / k_{C1}^0) p_{Bs} / p_{As} \}} \times \frac{dp_B}{dx} \bigg|_{x=R_s} \quad (12)$$

where

$$h_A = R_s \sqrt{\frac{k_1^0 \rho RT}{D_{eA} (1 + K_A p_{As})}} \quad (13)$$

$$h_B = R_s \sqrt{\frac{k_1^0 \rho RT}{D_{eB} (1 + K_A p_{As})}} \quad (14)$$

$$h_C = R_s \sqrt{\frac{k_{C1}^0 \rho RT}{D_{eB} (1 + K_A p_{As}) \nu M_C}} \quad (15)$$

The amount of coke on a spherical catalyst is calculated by the following equation.

$$n_C = \int_0^{R_s} 4\pi x^2 \rho (n_{C1} + n_{C2}) dx \quad (16)$$

Computational Results

Eqs. (3)–(10) were solved numerically using a finite difference method combined with the simplex method proposed by Nelder and Mead¹⁾, which was employed to determine the real values of p_A and p_B at the center of a spherical catalyst. The value of effective diffusivity for a n -C₄H₁₀–(n -C₄H₈)–N₂ gas system was estimated by the single-pore model as

$$D_{ei} = \frac{D_i(\bar{r}_p)\varepsilon}{\kappa^2} = \frac{\varepsilon}{\kappa^2} \frac{1}{\frac{1}{D_{Ki}} + \sum_j \frac{\bar{y}_j - \bar{y}_i (N_j/N_i)}{D_{i-j}}} \quad (17)$$

$$= 0.0054 \text{ cm}^2/\text{sec} \quad (i=A, B)$$

Where the value of κ^2 was calculated from the result of a diffusion experiment for the N₂–C₂H₄ gas system.

Fig. 2 Comparison of experimental and computational E_{fA}

Numbers are same as those in Fig. 2.

Fig. 3 Comparison of experimental and computational n_c

The values of h_A , h_B and h_C were evaluated as follows, using the experimental results in the previous paper²⁾ and the value of effective diffusivity:

$$\begin{aligned} \text{for a catalyst of 5 mm diameter} \quad h_A &= h_B = 4.68, \\ h_C &= 3.22 \\ \text{for a catalyst of 2.2 mm} \quad h_A &= h_B = 2.06, \\ h_C &= 1.42 \end{aligned}$$

The computational results for E_{fA} and coke content are plotted against $\theta (=k_{C1}^0 p_{Bi}/n_{C1}^0)$ in Figs. 2 and 3, respectively, and fairly good agreements between the theory and experiment is seen. The result of E_{fB} showed a quite similar tendency and gave a somewhat smaller value than that of E_{fA} .

The value of E_{fA} decreases as the reaction proceeds and its tendency depends on particle size. The result for the particle catalyst of 0.21 mm diameter is affected only by coke deposition, for which intraparticle diffusional effect can be ignored²⁾. However, in the case of catalysts of 2.2 and 5 mm diameter E_{fA} is affected by the intraparticle diffusional resistance as well as by coke accumulation. It is substantially impossible to separate them, because the coke content at any time depends on the particle size and also a coke distribution exists inside a pellet catalyst.

In the previous study²⁾, it was shown that the experimental results could be well explained by the dual active site model in the case of a reaction-limited

region. In this study it is found to be reasonable also for the case where the effect of intraparticle diffusion is not ignored.

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Nomenclature

A_p	= external surface area of pellet	[cm ²]
D_e	= effective diffusivity	[cm ² /sec]
$D_i(\bar{r}_p)$	= diffusivity of gas <i>i</i> and <i>j</i> in a pore of mean radius $\bar{r}_p$ under reaction conditions	[cm ² /sec]
D_{i-j}	= molecular diffusivity between gas <i>i</i> and <i>j</i>	[cm ² /sec]
D_K	= Knudsen diffusivity	[cm ² /sec]
E_f	= effectiveness factor	[-]
F	= flow rate	[mol/min]
K	= adsorption equilibrium constant	[1/atm]
k	= reaction rate constant	[mol/g-cat·sec·atm]
k_C	= rate constant for coke formation	[g-coke/g-cat·sec·atm]
M_C	= molecular weight of coke	[g/g-mole]
N	= flux of gas	[mol/cm ² ·sec]
n_C	= coke content	[g-coke/g-cat]
p	= partial pressure	[atm]
R	= gas constant	[cc·atm/g-mole·°K]
r	= reaction rate	[mol/g-cat·sec]
r_C	= rate of coke formation	[g-coke/g-cat·sec]
T	= temperature	[°K]
t	= time	[sec]
V_p	= volume of pellet	[cm ³]
W_C	= mass of catalyst	[g]
x	= radial distance in a sphere	[cm]
y	= mole fraction of gas	[-]
$\bar{y}$	= mean value of <i>y</i> within catalyst	[-]
ε	= porosity of catalyst pellet	[-]
θ	= $k_{C1}^0 p_{Bi}/n_{C1}^0$	[-]
κ^2	= tortuosity factor	[-]
ν	= stoichiometric ratio of <i>n</i> -butene conversion to coke formation	[-]
ρ	= bulk density	[g/cm ³]
ϕ	= defined by Eqs. (9) and (10)	[-]

<Subscripts>

<i>A</i>	= <i>n</i> -butane
<i>B</i>	= <i>n</i> -butene
<i>C</i>	= coke
<i>i</i>	= inlet of reactor
<i>j</i>	= gas component <i>j</i> (<i>n</i> -C ₄ H ₁₀ , <i>n</i> -C ₄ H ₈ , N ₂)
<i>s</i>	= value at a spherical surface
1	= active site 1(chromia)
2	= active site 2(γ -alumina)

<Superscripts>

⁰	= value at the start of reaction (at zero coke content)
∞	= maximum value

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