THE EFFECT OF THE ADSORPTION UPON THE SELECTIVITY AND THE EFFECTIVENESS FACTOR*

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The effectiveness factor and the selectivity are calculated for a consecutive reaction where the kinetics follow the Langmuir-Hinshelwood types of rate equations. The computational results are extended to cases where the first order specific catalytic activity varies inside a catalyst pellet and it is shown that the selectivity is greatly changeable by the difference in the distribution of the rate constant inside the catalyst even in the case where the overall reaction rate of the reactant has the same value.

In the previous work²⁾ on the hydrogenation of acetylene on nickel catalyst, the authors found that the selectivity to ethylene was reduced with increase in catalyst size, and the degree of the reduction in selectivity was larger than that predicted for a first order consecutive reactions system as derived by Wheeler³⁾. In that paper²⁾, the discrepancy was proved to be due to the difference in kinetics which followed the Langmuir-Hinshelwood types of rate equations in our experiments.

In this paper, the effects of the types of kinetics upon the selectivity of the intermediate product and upon the effectiveness factor for the rate of conversion of the reactant are discussed.

The systems assumed in the analysis are as follows: the catalyst is a porous spherical particle, the reaction is consecutive and is

and the effective diffusion coefficients of the components A, B and C are identical.

Basic equations and boundary conditions are expressed by Eqs. (1) and (2).

$$D\left(\frac{d^2 p_A}{dr^2} + \frac{2}{r} \frac{dp_A}{dr}\right) = R_1; \quad D\left(\frac{d^2 p_B}{dr^2} + \frac{2}{r} \frac{dp_B}{dr}\right) = -R_1 + R_2 \quad (1)$$

$$\text{At } r = R, \quad p_A = p_{As} \text{ and } p_B = p_{Bs}; \\ \text{at } r = 0, \quad \frac{dp_A}{dr} = \frac{dp_B}{dr} = 0. \quad (2)$$

For the system, four types of reaction kinetics are analyzed which are shown in Table 1. For comparison with the previous experiments, where $K_A p_{As} = 23$ and $s = 7$, the conditions for computations are taken for all

systems as

$$p_{Bs} = 0, \quad K_A p_{As} = 0, 10, 30, \\ M_1 = 0.5 \sim 50 \text{ and } s = 7.$$

The condition of $p_{Bs} = 0$ is realized in a flow reactor with short contacting time. The selectivity under the condition of $p_{Bs} = 0$ can be attained by extrapolation of the data obtained with various contacting times as described in the previous paper²⁾.

Computational Results

1) Effectiveness factor (E_1)

The computational results for some of the conditions are shown in Fig. 1. Here, the moduli for the catalyst are expressed by the use of the rate at the outer surface of the catalyst, as shown in Table 1. The values of E_1 for the values of M_1 larger than about 20 can be derived theoretically in Case 1 and Case 2.

$$\text{Case 1} \quad E_1 = 3/M_1 \quad (3)$$

$$\text{Case 2}^{**} \quad E_1 = \frac{3/M_1 \sqrt{2(1 + K_A p_{As})(K_A p_{As} - \ln[1 + K_A p_{As}])}}{K_A p_{As}} \quad (4)$$

These relations are shown by the dotted lines A, B₁ and B₂ in Fig. 1 and, as expected, coincide well with the computational results.

2) Selectivity (S)

In the simple consecutive reaction, the selectivity to

Table 1

Adsorbed component		Rate expression		Modulus: M_1
Case 1		$R_1 = k_1 p_A$	$R_2 = k_2 p_B$	$R \sqrt{\frac{k_1}{D}}$
Case 2	A	$R_1 = \frac{k_1 p_A}{1 + K_A p_A}$	$R_2 = \frac{k_2 p_B}{1 + K_A p_A}$	$R \sqrt{\frac{k_1}{D(1 + K_A p_{As})}}$
Case 3	B	$R_1 = \frac{k_1 p_A}{1 + K_B p_B}$	$R_2 = \frac{k_2 p_B}{1 + K_B p_B}$	$R \sqrt{\frac{k_1}{D}}$
Case 4	C	$R_1 = \frac{k_1 p_A}{1 + K_C p_C}$	$R_2 = \frac{k_2 p_B}{1 + K_C p_C}$	$R \sqrt{\frac{k_1}{D}}$

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Fig. 1 The relations between effectiveness factor (E_1) and M_1 ($s=7$)

the intermediate product becomes to unity as M_1 becomes smaller than unity and decreases with increase of M_1 . The detailed relations of the selectivity with the modulus for four cases are shown in Fig. 2. As shown in the figure, the selectivity is lowest in Case 2. Case 3 and 4 give a larger selectivity than Case 1. In the region where M_1 is not so large, Case 3 gives a larger selectivity than Case 4.

The limiting selectivity at large M_1 and $K_A p_{As}$ in Case 2 can be derived theoretically and the result is**:

$$S = \frac{s}{s-1} \cdot \frac{(3 - \sqrt{1+8/s})}{4} \quad (5)$$

Along with these computations, the concentration and the reaction rate profiles inside the particle are also evaluated. These results are applicable to the systems where the apparent rate constant is distributed inside the catalyst. For example, these systems are equivalent to the cases where the first order catalytic rate constant ($k_{app.}$) changes as $k_{1(or 2)app.} = \frac{k_{1(or 2)}}{1 + K_i p_i(r)}$. Here $p_i(r)$ is the partial pressure distribution of i component inside the particle, which is obtained in the above computation.

That is:

- Case 1 $k_{app.}$ is constant.
- Case 2 $k_{app.}$ increases towards the center of the catalyst.
- Case 3 $k_{app.}$ decreases towards the center of the catalyst at small M_1 and has the minimum on an intermediate position at large M_1 .
- Case 4 $k_{app.}$ decreases towards the center of the catalyst.

From this analysis, it is clear that the selectivity is greatly changeable by the difference of the distributions of $k_{1(or 2)app.}$, even if the average reaction rates of a single catalyst pellet ($k_{1app.}$ (at surface) $E_1 p_{As}$) are the same. This paper is the first one which shows the large effect of the distribution of the apparent rate

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Fig. 2 The relations between the selectivity (S) and M_1 ($s=7$)

constant inside a catalyst particle upon the selectivity, with the exception that J. B. Butt¹⁾ calculated the selectivity for the nonisothermal first order reaction system.

This treatment may be applied to the analysis of the gradual deactivation of a single catalyst particle. The observed behaviour of the selectivity and the effectiveness factor during the reaction will give insight into the mechanism of the deactivation of the catalyst. Details of the studies of catalyst deactivation will be presented in the near future.

Nomenclature

- A = reactant
- B = intermediate product
- C = final product
- D = effective diffusion coefficient inside the catalyst particle
- E_1 = effectiveness factor for the rate of conversion of the reactant
- $k_{1(or 2)}$ = rate constant defined in Table 1
- $k_{1(or 2)app.}$ = apparent rate constant
- K_i = equilibrium constant of adsorption of i component; $i=A, B, C$
- M_1 = modulus defined in Table 1
- p_i = partial pressure of i component
- p_{is} = partial pressure of i component at the outer surface of a catalyst particle; $i=A, B, C$
- r = radial distance in a catalyst particle
- R = radius of the catalyst particle
- $R_{1(or 2)}$ = rate of the first (or second) step of the consecutive reactions system
- s = k_1/k_2
- S = selectivity defined as the ratio of B produced to A consumed

Literature Cited

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