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Contributed Paper

A New Analytical Expression of the Gas Conversion for TAP Experiments with Bimodal-Pore-Structure Catalyst

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ABSTRACT

The TAP transient pulse response experiment has been used for heterogeneous catalytic reaction studies. Interpretation of TAP response data by moment analysis requires analytical moment expression of the gas exit flow rate. The zeoth moment expression of the exit flow rate of a reactant gas from the TAP reactor packed with bimodal-pore-structure catalyst for irreversible reaction case is proposed. The obtained expression was found to be similar to that for non-porous catalyst except that the rate constant is multiplied by an overall effectiveness factor. The overall effectiveness factor is the product of the effectiveness factors in the two porous regions in the catalyst pellet. Both effectiveness factors as well as the overall effectiveness factor are defined similarly to those in steady-state conditions.

Keywords: Temporal analysis of products, TAP reactor, Bimodal-pore-structure catalyst, Zeroth moment.

1. INTRODUCTION

The information of the chemical reaction kinetics is essential for the design and optimization of chemical reactors. Two types of experiment including steady-state and transient experiments are applied for kinetic studies. Most industrial catalysts are tested under the steady-state conditions. The design of the reactor is accomplished using parameters from this type of experiment. On the other hand, the transient experiment is applied for unraveling complex catalytic reactions and detailed mechanisms.

The temporal analysis of products or TAP [1, 2] is a transient pulse response experiment for heterogeneous catalysis reaction studies. The TAP experiment is performed by injecting a narrow gas pulse into an evacuated microreactor containing catalyst particles. The gas molecule of each species that leaves the reactor is detected by a mass spectrometer providing a time-dependent response curve. The size and the shape of the response curve depend on transport and kinetic characteristics.

To interpret TAP response data, mathematic models are required. Estimation of either transport or kinetic parameters can be performed by curve fitting (regression analysis) between experimental and model responses or by moment analysis. When the moment analysis is applied, analytical expressions of the moment of the exit flow rate are required. The frequently-used moment expressions involve zeroth moment and first moment. Zeroth moment of the exit flow rate is the area of the exit flow rate curve which is equal to the amount of gas leaving the reactor. The ratio between the first moment and the zeroth moment is the mean residence time. Many moment expressions for non-porous and porous catalysts have been reported [3-6].

Many catalytic systems involve bimodal-pore-structure catalyst. A biporous system of Zeolite on silica-alumina support has been investigated using TAP technique [7]. Kinetic parameters were determined by regression analysis. Since moment analysis has also been used for parameter estimation, it will be useful to develop moment expressions for bimodal case. In our present work, we determine the zeroth moment expression of exit flow rate for the TAP reactor packed bimodal-pore-structure catalyst for a first order irreversible reaction.

2. MATHEMATICAL METHODS

In this study, we focus the case in which the catalyst pellet is composed of macropore and mesopore regions. Each region is in a spherical space. This corresponds to the case in which spherical particles with mesopores are compressed into spherical pellets. The void between the compressed particles is referred as macropore region. The gas transport in the reactor therefore takes place in three regions including bed interparticle, macropore, and mesopore regions. The micropore domain was excluded in our study in order to focus only the case in which Knudsen diffusion is applied. The reaction is assumed to take place only in the mesopores. The mass balance equations for the reactant gas can be written in different regions as follows:

Interparticle region:

$$\varepsilon_b \frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} - \frac{3}{R_p}(1-\varepsilon_b) D_p \left.\frac{\partial C_p}{\partial r_p}\right|_{r_p=R_p} \tag{1}$$

Macropore region:

$$\varepsilon_p \frac{\partial C_p}{\partial t} = D_p \left[\frac{\partial^2 C_p}{\partial r_p^2} + \frac{2}{r_p}\frac{\partial C_p}{\partial r_p}\right] - \frac{3}{R_m}(1-\varepsilon_p) D_m \left.\frac{\partial C_m}{\partial r_m}\right|_{r_m=R_m} \tag{2}$$

Mesopore region:

$$\varepsilon_m \frac{\partial C_m}{\partial t} = D_m \left[\frac{\partial^2 C_m}{\partial r_m^2} + \frac{2}{r_m}\frac{\partial C_m}{\partial r_m}\right] - k_a \rho_s C_m \tag{3}$$

The definition of the variables and parameters is given in the nomenclature.

The initial and boundary conditions are written as follows:

Initial conditions:

$$0 \le z \le L,\ t = 0,\ C_b = 0 \tag{4}$$

$$0 \le r_p \le R_p,\ t = 0,\ C_p = 0 \tag{5}$$

$$0 \le r_m \le R_m,\ t = 0,\ C_m = 0 \tag{6}$$

Boundary conditions:

Interparticle region:

$$x = 0,\ t > 0,\ -D_b \frac{\partial C_b}{\partial x} = \delta\left(t - 0^+\right)\frac{N_p}{A} \tag{7}$$

$$x = L,\ t > 0,\ C_b = 0 \tag{8}$$

Macropore region:

$$r_p = R_p,\ t > 0,\ C_b = C_p \tag{9}$$

$$r_p = 0,\ t > 0,\ \frac{\partial C_p}{\partial r_p} = 0 \tag{10}$$

Mesopore region:

$$r_m = R_m,\ t > 0,\ C_p = C_m \tag{11}$$

$$r_m = 0,\ t > 0,\ \frac{\partial C_m}{\partial r_m} = 0 \tag{12}$$

Eq. (7) specifies that the flux at the reactor entrance is represented by delta function. Eq. (8) results from the fact that the outlet of the reactor is maintained at vacuum conditions, and the concentration of gas at the reactor exit is very close to zero. Eqs. (9) – (12) follow the conditions typically assumed for spherical catalyst pellets with bimodal-pore-structure [8]. In the TAP experiments, the measured variable is the gas exit flow rate, F, and is described by

$$F = -A \cdot D_b \left.\frac{\partial C_b}{\partial z}\right|_{z=L} \tag{13}$$

The zeroth moment of the exit flow rate is the amount of gas that leaves the reactor. If the exit flow rate of the reactant gas is normalized by the amount of the inlet reactant gas, the gas conversion is equal to unity minus the zeroth moment. The zeroth moment of the pulse-intensity (PI) normalized flow of reactant gas, $\frac{F}{N_p}$, is described by

$$m_o = \int_0^\infty \frac{F}{N_p} dt = 1 - X \tag{14}$$

To determine the zeroth moment expression of the pulse-intensity normalized exit flow rate, the set of differential equations was transformed into the Laplace domain. The solution for the pulse-intensity normalized exit flow rate in the Laplace domain, $\frac{F(s)}{N_p}$, was determined. The zeroth moment expression can be determined [9, 10] using

$$m_0 = \lim_{s \to 0} \frac{F(s)}{N_p} \tag{15}$$

3. RESULTS AND DISCUSSION

The zeroth moment of the pulse-intensity normalized exit flow rate was found to be described by

$$m_0 = \frac{1}{\cosh\left(\sqrt{\psi \eta_{overall}}\right)} = 1 - X \tag{16}$$

where ψ is the dimensionless kinetic parameter and $\eta_{overall}$ is an overall effectiveness factor.

This zero moment expression was found to be similar to zeroth moment expression for non-porous catalyst [2] except that the rate constant is multiplied by the overall effectiveness factor ($\eta_{overall}$) defined by

$$\eta_{overall} = \eta_{ma} \cdot \eta_{me} \tag{17}$$

where η_{ma} is the effectiveness factor in the macropore region and η_{me} is the effectiveness factor in the macropore region.

The two effectiveness factors are described as described as a function of the Thiele modulus and are written as follows:

Mesopore:

$$\eta_{me} = \frac{3}{3M_{T,me}} \left(\frac{1}{\tanh 3M_{T,me}} - \frac{1}{3M_{T,me}} \right) \tag{18}$$

Macropore:

$$\eta_{ma} = \frac{3}{3M_{T,ma}} \left(\frac{1}{\tanh 3M_{T,ma}} - \frac{1}{3M_{T,ma}} \right) \tag{19}$$

The Thiele moduli for the two regions are described as follows:

Mesopore Thiele modulus

$$M_{T,me} = \frac{R_m}{3}\sqrt{\frac{k_a \rho_s}{D_m}} \tag{20}$$

Macropore Thiele modulus

$$M_{T,ma} = \frac{R_p}{3}\sqrt{\frac{k_a \rho_s \left(1-\varepsilon_p\right)\eta_{me}}{D_p}} \tag{21}$$

The effectiveness factors and Thiele moduli defined by Eqs. (17) – (21) are the same as those in steady-state conditions [8]. In TAP transient pulse response experiments, the gas concentration distribution in the catalyst pellet changes with time. As a result, the effectiveness factor corresponding to instantaneous gas concentration distribution is not constant during the experiment. This situation is different from the steady-state operation. However, the appearance of the effectiveness factor in Eq. (16) suggests that it is the average effectiveness factor of the whole pulse experiment. It is also noted that the zeroth moment of the exit flow rate for the bimodal case is similar to that for the unimodal case in which only one effectiveness factor is involved [11].

The effectiveness factors defined by Eqs. (18) – (20) are the same as those in steady-state conditions [8]. In TAP transient pulse response experiments, the gas concentration distribution in the catalyst pellet changes with time. As a result, the effectiveness factor determined from the gas concentration distribution is not constant during the experiment. This situation is different from the steady-state operation. However, the appearance of the effectiveness factor in Eq. (17) suggests that it is the average effectiveness factor of the pulse experiment.

4. CONCLUSIONS

The zeroth moment expression of the reactant pulse-intensity exit flow rate for TAP experiments with an irreversible reaction has been proposed. The expression is similar to that for non-porous case except that the rate constant is multiplied by the effectiveness factor which is defined as that in steady-state conditions.

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Nomenclature

C_b	gas concentration in the interparticle region, mol/m^3
C_p	gas concentration in the macropore region, mol/m^3
C_m	gas concentration in the mesopore region, mol/m^3
D_b	effective Knudsen diffusivity of gas in the interparticle region, m^2/s
D_p	effective Knudsen diffusivity of gas in the macropore region, m^2/s
D_m	effective Knudsen diffusivity of gas in the mesopore region, m^2/s
F	exit flow rate, mol/s

$F(s)$	exit flow rate in Laplace domain
k_a	adsorption or reaction rate constant, m^3 of gas/mol s
L	length of the reactor, m
m_0	zeroth moment of the exit flow rate
$M_{T,ma}$	macropore Thiele modulus
$M_{T,me}$	mesopore Thiele modulus
r_p	radial coordinate of the catalyst pellet, m
r_m	radial coordinate of the particle with mesopores, m
R_p	radius of the catalyst pellet, m
R_m	radius of the particle with mesopores, m
s	Laplace variable, 1/s
t	time, s
X	conversion of the reactant
x	axial coordinate of the reactor, m

Greek letters

$\delta(t-0^+)$	Dirac delta function placed at $t = 0^+$
ε_b	interparticle void fraction in the bed, m^3 of void in the interparticle region/ m^3 of bed
ε_p	macropore void fraction, m^3 of void in macropore region/ m^3 of catalyst pellet
ε_m	mesopore void fraction, m^3 of void in mesopore region/ m^3 of particle
η_{ma}	macropore effectiveness factor
η_{me}	mesopore effectiveness factor
$\eta_{overall}$	overall effectiveness factor
ψ	dimensionless kinetic parameter, defined by

$$\psi = \frac{k\rho_s\left(1-\varepsilon_p\right)(1-\varepsilon_b)L^2}{D_b}$$

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