Analysis of the Gas Diffusivity in the Simulated Washcoat Layer Based on Mean Transport Pore Model and the Mean Molecular Speed

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The pore structure of a simulated washcoat layer was evaluated using the Mean Transport Pore Model (MTPM). The MTPM provides the mean diffusive pore radius (r_m) of a simulated washcoat layer from the experimentally measured effective diffusion coefficient (D_e). However, data previously published in the literature indicated that the value of r_m depended on the choice of diffusive gas for the measurement of D_e. Therefore, a new, more efficient method was developed to estimate r_m. To obtain base data, D_e was measured in a binary gas diffusion system using a modified Wicke-Kallenbach diffusion cell at room temperature, 473 K, and 673 K. The diffusive gases tested were H_2, He, CH_4, Ne, N_2, O_2, C_3H_6, CO_2, and C_3H_8, and a simulated washcoat layer was used. The results confirmed that the value of r_m depended on the type of diffusive gas used. However, many measurements of D_e are required to avoid problems. In the catalytic R&D process, the measurement of many D_e values for every experiment is impractical. To balance validity against efficiency for estimating r_m, a combination of experimentally measured D_e and predicted D_e was used. This method is effective for predicting D_e using the mean molecular speed instead of a porous structure, and is more efficient than the conventional method of using MTPM. This method also can contribute to investigations of automotive catalysts.

1. Introduction

A washcoated catalyst on a honeycomb substrate is used widely for automotive catalysts to improve fuel economy while reducing exhaust back pressure. Modeling the reaction and gas diffusion in the washcoat layer helps design an effective catalytic converter. Corbetta et al. (2013) proposed a reactive computational fluid dynamics based modeling approach, and reported the kinetics of the automotive catalyst converter. To evaluate gas diffusivity, the pore radius of the washcoat layer was an important factor. The mean diffusive pore radius (r_m) was estimated from a set of experimentally measured effective diffusion coefficient (D_e) values using the mean transport pore model (MTPM) (Pazdernik and Schneider, 1982). The r_m value is a parameter unique to the MTPM that represents the average pore size of the gas diffusion route. The r_m value for a simulated washcoat layer has been estimated (Kato et al., 2013a). But since evaluating r_m requires a pair of experimentally measured D_e values (Pazdernik and Schneider, 1982), data previously reported (Pazdernik and Schneider, 1982, Kato et al., 2013a, Schneider and Gelbin, 1985) indicated that the value of r_m depended on the choice of diffusive gas used to measure D_e. This issue is investigated in the present report along with an effective method for estimating r_m from a minimum number of D_e values.

2. Experimental

A simulated washcoat layer was made using a procedure reported previously (Kato et al., 2013a). The simulated washcoat layer was applied to a metal mesh by dip coating. The used slurry contained ZrO_2 powder and zirconium nitrate. After dip coating, the sample was dried at 393 K for 12 h and then calcined at 773 K for 1 h. Using a metal mesh as the substrate instead of a cordierite honeycomb substrate to measure the gas diffusivity in the washcoat layer was advantageous because the metal mesh had no diffusion resistance. The gas diffusivity was measured in a binary gas diffusion system using a modified Wicke-Kallenbach diffusion cell (Kato et al., 2015b) at room temperature, 473 K, and 673 K. The tested diffusive gases included H_2, He, CH_4, Ne, N_2, O_2, C_3H_6, CO_2, and C_3H_8. For a pair of tested diffusive gases, Ar was used. The concentration of the diffusive gases tested was 100 %.

3. Result and Discussion

3-1. Experimentally measured D_e

The experimentally measured D_e values are shown in Figure 1. The driving force for the gas diffusion phenomena was the random motion of the gas molecules. The mean molecular speed is given by Eq(1), in which R, T, and M are the gas constant, temperature, and molecular weight, respectively. An increase in D_e with increasing temperature or decreasing molecular weight is due to an increase in the mean molecular speed.
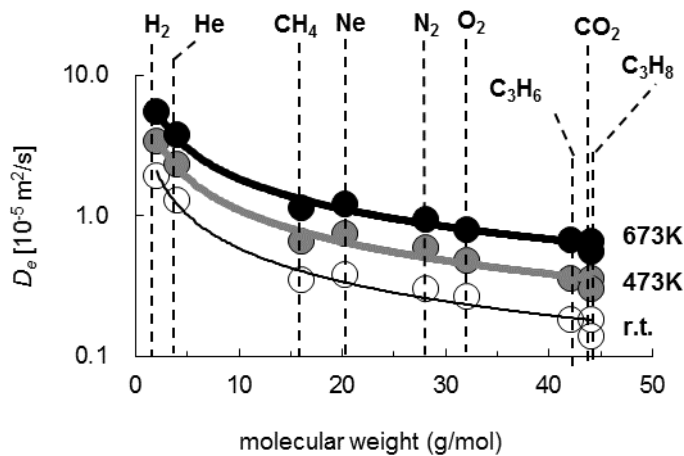
$$v_m = \left(\frac{8RT}{\pi M} \right)^{1/2} \tag{1}$$

Figure 1. experimentally measured D_e.

3-2. Problem involved in conventional usage of MTPM

The MTPM describes gas diffusivity in a porous material according to Eq(2). Here, $D_{e,ij}^{b}$, Ψ, D_{ij}^{b}, $D_{e,i}^{k}$, r_m, and K_i are the effective bulk diffusion coefficient, a geometric factor, the bulk diffusion coefficient, the effective Knudsen diffusion coefficient, the mean diffusive pore radius, and the Knudsen constant, respectively.

$$D_{e,ij}^{b} = \psi D_{ij}^{b} \tag{2a}$$

$$D_{e,i}^{k} = r_m \psi K_i \tag{2b}$$

Eq(3) can be obtained by substituting Eq(2) into the modified Stefan-Maxwell equation (e.g., Schneider and Gelbin, 1985), because bulk and Knudsen diffusion occur simultaneously in the simulated washcoat layer (Kato et al., 2013a and 2015b). In Eq(3), y_i represents the molar fraction in the diffusion cell:

$$(1/D_{e,i}) = 1 / r_{mi} \psi K_i + (1 - \alpha_i y_i) / \psi D_{ij}^{b} \tag{3}$$

$$\alpha_i = 1 - (M_i / M_j)^{1/2} \tag{3a}$$

For the MTPM, r_m and Ψ are estimated by substituting experimental values of D_e into Eq(3). The r_m value is the main focus of this research. To obtain r_m, Eq(3) is converted to Eq(4), and then D_e, y_i, D^b and K are substituted into Eq(4):

$$\left(K_i/D_{eff,ij}\right)=\left(1/r\psi\right)+\left(1/\psi\right)\{(1-\alpha_i y_i)K_i/D_{ij}^{\ b}\}$$ **(4)**

Results obtained at room temperature, which produced mostly linear relations, are shown in Figure 2. The slope and intercept provided an r_m value of 267 nm.
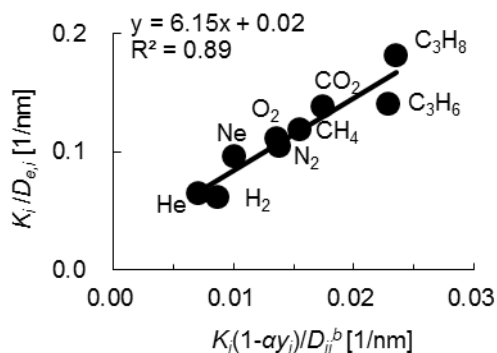

Figure 2. Plot of $K_i (1-\alpha y_i) /D_{ij}^b$ vs $K_i /D_{e,i}$

In Figure 2, the correlation coefficient for the linear equation was 0.89, indicating that r_m was dependent on the diffusive gas selected. In principle, evaluating r_m requires at least a pair of experimentally measured D_e values (Pazdernik and Schneider, 1982). But if the diffusivity of only CH_4 and C_3H_8 was measured, the r_m value would be approximately -31354 nm. This value is unrealistic and far from the value of 267 nm, estimated from multiple D_e values. This situation is problematic for the use of the MTPM to evaluate r_m for the simulated washcoat layer. Figure 3(a) demonstrates the dependence of r_m on the selected number of D_e value at room temperature. When the number of D_e values was 2, 3, 4, 5, 6, 7, or 8, the estimated r_m value was 36, 84, 126, 126, 84, 36, or 9, respectively.
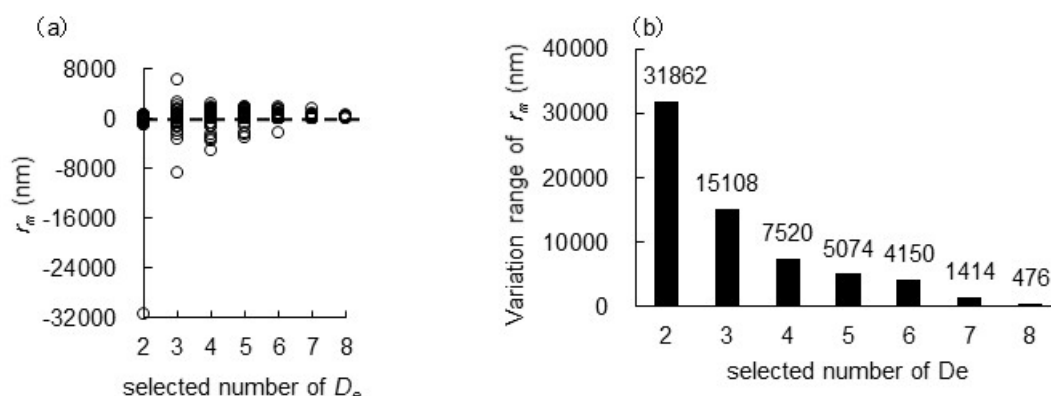

Figure 3. Dependence of number of D_e values on (a) value of r_m, (b) variation range of r_m

As shown in Figure 3(a), a negative value of r_m often occurred when the number of D_e values was less than 6. When the number of D_e values was greater than 7, r_m was never negative. When 8 values of D_e were used, the minimum and maximum values of r_m were 646 and 170 nm, respectively. These values are both close to 267 nm. Figure 3(b) shows that the range of variation in r_m decreases as the number of D_e values increases. This was also found to be the case for D_e measured at 473 and 673 K.

Thus, the value of r_m depended on the number of experimentally measured D_e values. This was related to the inherent conventional use of the MTPM. Although Figure 3(b) implies that more than 8 D_e values may be required to obtain reasonable value of r_m, in catalytic R&D processes measuring many D_e values is impractical. Thus, a new method is proposed to estimate reasonable r_m values with minimal experimental effort.

3-3. Estimating reasonable r_m values with minimal experimental effort

If D_e can be predicted accurately, combining experimentally measured D_e and predicted D_e values to provide a reasonable r_m value. Although many models are available for predicting D_e for a porous structure, the D_e

values obtained using these models often have large errors due to the difficulty in factoring in the porous structure. For example, Hayes et al. (2000), measured the diffusivity of CH_4 in a washcoat layer and compared the experimentally measured D_e value with the predicted D_e value. The D_e value was predicted using the pore size distribution of the washcoat layer based on the random pore model (Wakao and Smith, 1962). The pore size distribution was measured using mercury porosimetry. The results indicated that the predicted D_e was approximately seven times greater than the experimentally determined D_e value. This difference was too large to use for estimating a valid r_m value.

The present study focused on the mean molecular speed (v_m) to predict D_e because gas diffusivity depends on the v_m value, the v_m value is independent of the pore structure, and v_m can be estimated from gas kinetics. If D_e can be expressed as a function of v_m, other unmeasured D_e values could be predicted. The relation between experimentally measured D_e and v_m values is shown in Figure 4. D_e values measured at the same temperature can be described using a linear function of v_m. Although a rigorous theoretical explanation for this linear relationship is difficult to provide, the theoretical diffusion equation can explain part of the linear relation. Bulk diffusion is described by the Chapman-Enskog equation (Smith, 1981) as:

$$D_{ij}^b = 0.0018583 \frac{T v_{m,i} \left(1 + M_i / M_j\right)^{1/2}}{P \sigma_{ij}^2 \Omega_{ij} \sqrt{8R/\pi}} \tag{5}$$

where T and M_j are independent of $v_{m,l}$, indicating that the linear relation between v_m and D_e requires D_e to be measured at the same temperature and with the same gas. Figure 4 shows the relation between v_m and D_e and the temperature dependence of the slope. The relation between v_m and D_e can be verified with data previously reported by Pazdernik and Schneider (1982), Valuš and Schneider (1985). They determined D_e in porous material with the chromatographic method. Pazdernik and Schneider (1982) tested commercial porous pellet. Valuš and Schneider (1985) examined samples of bidisperse alumina with changing volume and size of pores. Figures 5(a) and 5(b) show the relation between D_e and v_m estimated from literature values. The relation between v_m and D_e is linear when measured with same gas pair.
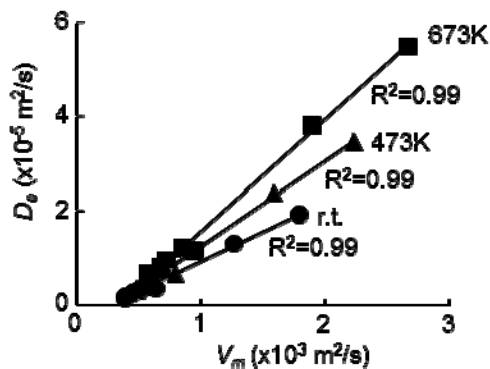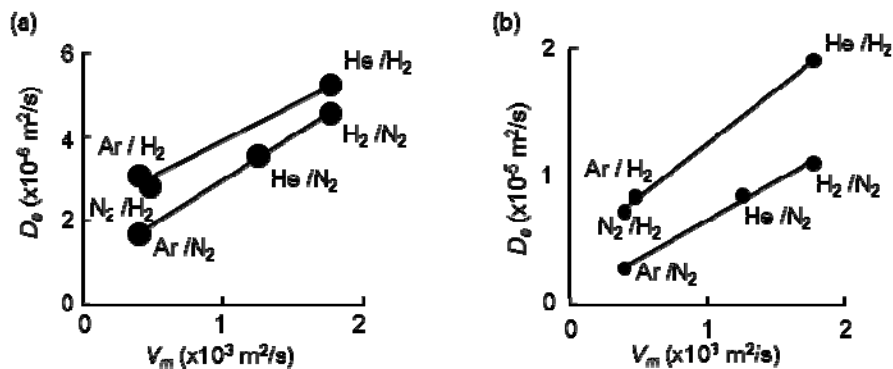

Figure 4. Relation between D_e and v_m

Figure 5. relation between De (diffusive gas / pair gas) and vm estimated from values reported by (a) Pazdernik and Schneider (1982) and (b) Valuš and Schneider (1985).

The linear relation between D_e and v_m is reasonable based on the data presented and allows the reliable prediction of any D_e value from one pair of experimentally measured D_e values. To estimate r_m from experimentally measured D_e values and predicted D_e values:

1. Measure two D_e values, such as for H_2 and C_3H_8. These two values can be used to create a line.
2. The new D_e value, not obtained from measurements, can be predicted from this line using the v_m of the specific molecule.
3. Thus, the r_m value can be estimated from the measured and predicted D_e values.

This method was verified using nine D_e values measured at room temperature. For example, the D_e values using H_2 and C_3H_8 were selected to provide a linear equation in Step 1. The linear relation between these values was used to predict D_e for He, CH_4, Ne, N_2, O_2, C_3H_6, and CO_2. Lastly, a combination of selected D_e values (H_2, C_3H_8) and predicted D_e values (He, CH_4, Ne, N_2, O_2, C_3H_6, and CO_2) were used to estimate r_m in Step 3. Because 36 pairs of D_e values were provided from nine sets of D_e values, 36 r_m values were estimated in Step 3. In comparison, conventional use of the MTPM results in 36 pair of D_e values for estimating r_m without the use of predicted D_e values. Figure 6 shows the relation between r_m and the ratio of the molecular weight of the two molecules. This new method is possible only when y_i in Eq(4) can be approximated by zero because the experimental conditions used cannot approximate y_i. Hence, measured y_i values were used for verification.

The conventional use of the MTPM estimated r_m within the range of -32000 to 600 nm, and approximately 42 % of the values were negative. In contrast, the new method did not produce a negative r_m value when the molecular-weight ratio was greater than 15. The range obtained was 121 to 400 nm, which contains the value of 267 nm estimated from 9 sets of experimentally measured D_e values.
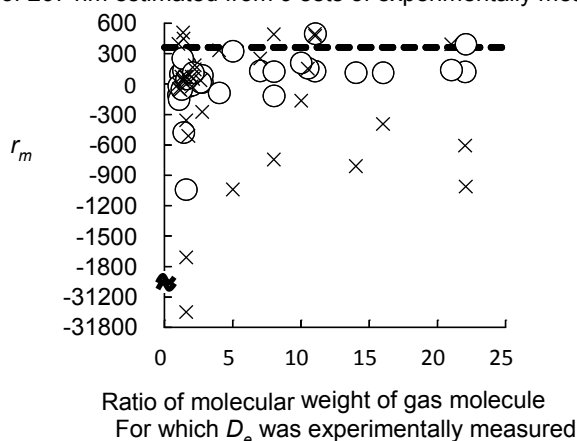

Figure 6. comparison of methods for estimating r_m values

$\times$ r_m estimated from pairs of experimentally measured D_e values
$\bigcirc$ r_m estimated from a combination of experimentally measured D_e and predicted D_e values
--- indicates the value estimated from 9 data points for experimentally measured D_e values

4. Conclusions

The validity of estimating r_m based on the MTPM was verified with experimentally measured D_e values. The diffusive gases tested were H_2, He, CH_4, Ne, N_2, O_2, C_3H_6, CO_2, and C_3H_8. Their diffusivity was measured in a binary gas diffusion system using a modified Wicke-Kallenbach diffusion cell at room temperature, 473 K, and 673 K. With the conventional MTPM, r_m depends on the number of D_e data sets, and many D_e values are required in order to obtain a reasonable r_m value. This is a problem with the conventional use of the MTPM. To obtain a reasonable r_m value with minimal experimental effort, a method combining measured D_e and predicted D_e values was proposed. Although many models exist to predict D_e for a porous structure, the D_e values predicted from these models often contain a large margin of error due to the difficulty in determining the pore structure. Hence, the relation between D_e and v_m was focused on to predict D_e because v_m is independent of the pore structure and can be estimated from kinetic gas theory. The results showed that D_e could be described as a linear expression of v_m, thus allowing the prediction of reliable D_e values from one pair of measured D_e values. The results also confirmed that combining measured D_e and predicted D_e values

provided a reasonable value for r_m when the ratio of the molecular weights was greater than 15. This new method combining measured D_e and predicted D_e values, estimated from v_m for the diffusive gases, is more efficient than the conventional use of the MTPM and can contribute to investigations involving automotive catalysts.

Nomenclature

$D_{e,i}$	effective diffusion coefficient for component i, m^2/s
$D_{e,i}^k$	effective Knudsen diffusion coefficients for component i, m/s
$D_{e,ij}^b$	effective binary bulk diffusion coefficient for pair i - j, m^2/s
D_{ij}^b	binary bulk diffusion coefficient for pair i - j, m^2/s
K_i	Knudsen diffusion constant of component i, m/s
M	molecular weight, kg
R	gas constant, J/(K mol)
T	temperature, K
r_m	mean diffusive pore radius, m
v_m	mean molecular speed, m/s
y_i	molar fraction of component i
Ψ	ratio of transport pore porosity and tortuosity
σ_{AB}	collision integral
Ω_{AB}	Lennard-Jones potential parameter

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