Evaluating the effective diffusion coefficient within the automobile catalysts

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Abstract: Automobile catalysts have been changing to complicated structures in their form and component. For example, nitrogen oxide storage component and oxygen storage component are combined with precious metal catalysts supported on monolith structure. These catalysts are usually applied on a wall of monolith structure by wash-coat technology. So that the reactant gas diffusion in the coated catalyst layer gives significant effect to the overall activity of automobile catalysts. In this research, the diffusion within the automobile catalysts layer was focused. The apparatus that can measure the diffusion coefficient of the reactant gas within the coated layer was proposed. The diffusion coefficient based on Fick's equation was derived from the experimental data. Three kinds of diffusion coefficients ($\text{N}_2$-$\text{Ar}$, $\text{CO}_2$-$\text{Ar}$, $\text{C}_3\text{H}_8$-$\text{Ar}$) were evaluated. The diffusion state within the coated layer could be the transitional state where both bulk-diffusion and Knudsen diffusion are possible.

Keywords: diffusion, automobile catalyst, porous material, pore size distribution

1. INTRODUCTION

The catalytic monolith reactor is generally utilized in catalytic combustion systems, many of which are related to pollution reduction. One of combustion applications is the automotive catalytic converter, where carbon monoxide and hydrocarbons are oxidized and oxides of nitrogen are reduced at the same time. The catalyst components are wash coated onto the surface of a monolith.

As metal catalyst is distributed within a porous support, the reactants have to diffuse through the pores of the support material and the products of the reaction also have to diffuse in the porous material. If the reaction rate is fast enough and the diffusion rate of the reactant is slower than that, then the reaction is limited by the diffusion, and effectiveness factor becomes smaller than one. It is necessary to obtain accurate values of the effective diffusion coefficient of the species of interest.

In recent study, diffusivity in the wash coat of a honeycomb monolith was evaluated \cite{1}. Heyes et al\cite{1} reported that the effective diffusivity of methane in nitrogen through two porous monoliths, monolith #1 which consisted of cordierite substrate only and monolith #2 which had a washcoat of $\gamma$-alumina applied to the channels, was evaluated experimentally using a technique adapted to that described by Beeckman \cite{2}. The effective diffusion coefficient of a washcoat layer alone was calculated indirectly with the obtained effective diffusion coefficients of monolith #1 and monolith #2.

It is the aim of this study to evaluate directly the effective diffusion coefficient of binary gases in the porous material of the washcoat used in an automotive catalyst component. The effective diffusion coefficient obtained by this experiment could estimate the diffusion state within the porous material. The mean diffusive radius $r$ derived by the effective diffusion coefficient was compared with pore-size distribution.

2. THEORETICAL

The binary gas diffusion system can be described by Fick's law when molar diffusion flux density is not so high.

$$N_\alpha = -D_{\text{eff}} \frac{dC_\alpha}{dz}$$  \hspace{1cm} (1)

Where $N_\alpha$ is the molar diffusion flux density of component $\alpha$, $D_{\text{eff}}$ is the effective diffusion coefficient, $C_\alpha$ is the molar gas concentration of component $\alpha$ and $z$ is the length for the diffusion direction, which is the thickness of the automotive catalysts layer in this research. The parameters used in this study are defined in Fig. 1. Figure 1 shows a model apparatus that has two compartments divided by automobile catalytic coated layer and carbon dioxide and argon are, for example, flowed in each compartment. Supposed three conditions. a) The apparatus system is under steady state. b) Each compartment is mixed completely. c) The concentration in a compartment is the same as that in outlet flow. Under these conditions, by using the parameters shown in Fig. 1, the molar diffusion flux density of component $\alpha$ can be described by the equation:

$$N_\alpha = C_2 \times \nu / A$$  \hspace{1cm} (2)
where \( C_2 \) is the molar gas concentration of component \( \mathcal{F}_2 \) in the cell compartment 2, in which component \( \mathcal{F}_2 \) has diffused from the cell compartment 1, \( v \) is the rate of outlet flow from compartment 2, \( A \) is the cross sectional area of the automobile catalytic coated layer. The concentration gradient can be also expressed by using the parameters in Fig. 1 to the equation 3.

\[
\frac{dC_0}{dz} = \frac{C_1 - C_2}{z} \quad (3)
\]

where \( C_1 \) and \( C_2 \) are the molar concentration of component \( \mathcal{F}_2 \) in compartment 1 and 2, and \( z \) is the thickness of automobile catalytic coated layer. The effective diffusion coefficient, \( D_{eff} \), can be derived from equation 2 and 3.

### Nomenclature

- \( A \): cross sectional area of coated layer
- \( C_i \): molar gas concentration
- \( D \): binary bulk-diffusion coefficient
- \( D_b \): effective binary bulk-diffusion coefficient
- \( D_{eff} \): effective diffusion coefficient
- \( D_k \): effective Knudsen-diffusion coefficient
- \( N \): molar diffusion flux density
- \( K \): Knudsen coefficient
- \( V \): mean thermal velocity
- \( M \): molecular weight
- \( r \): mean diffusive pore radius
- \( R_g \): gas constant
- \( T \): temperature
- \( v \): the rate of outlet flow
- \( z \): thickness of coated layer
- \( \phi \): porosity of transport-pores
- \( \bar{\phi} \): tortuosity of transport-pores
- \( \mathcal{A} \): geometric parameter of a porous material

### 3. EXPERIMENTAL

#### 3-1 Porous material

The automobile catalytic coated layers used in the experiment were made from ZrO\(_2\). The substrate of the coated layer was metal mesh. Uncoated substrate and coated layer are shown in Fig. 2. The left side of Fig. 2 is an uncoated substrate of metal mesh and the right side is a coated layer after dip-coating of ZrO\(_2\) solution for metal mesh. Three identical coated layer samples (1, 2, 3) were prepared in the same coating method to tell the difference by each lot.

![Fig. 2 Substrate and coated layer](a: uncoated substrate, b: coated layer)
3-2 Cell description

The cell utilized for evaluating the diffusion coefficient is shown in Fig. 3. The upper and lower compartments of the cell are separated by a coated layer. The cell is made of glass. The coated layer was placed between two compartments of the cell and sealed by rubber O-ring. Different gases (carbon dioxide and argon for example in Fig. 3) flow steadily through the each compartment until the steady state is obtained in the cell.

3-3 Overall system

Fig. 4 shows the simplified scheme of the diffusion cell set-up. In this binary diffusion measurement, two pure gases charged into each cell compartment. Carbon dioxide and argon, for examples, charged from No.1 and No. 2 steadily by using both control valves 3 and 4 respectively. Both cell compartments were filled with pure gases, which transferred only through the coated layer by diffusion until the steady state. It is quite important that both cell compartments are kept at the same pressure. If there is small difference of pressure between two compartments, a gas in a compartment moves into the other compartment by pressure gradient. To avoid this, a manometer 6 (silicone oil 0.96g/cm$^3$) to measure the pressure difference of two compartments and two valves 10, 11 to control each compartments pressure were equipped as shown in Fig. 4. After steady state was obtained, each gas flowing out of each compartment was sampled at gas sampling valve 8, 9 and analyzed by TCD gas chromatograph (Shimadzu GC-8A with porapack Q and MS 5A). Flow meters 12, 13 are equipped to measure the rate of outlet gas streams. Three samples of coated layer were prepared to evaluate the
effective coefficient. The evaluating gases are nitrogen, carbon dioxide and propane. The sweeping gas was argon for all the evaluating gases. All measurements conditions were under laboratory room temperature and pressure.

4. RESULTS AND DISCUSSION

The effective diffusion coefficients observed in this study are shown in Fig. 5. Each value is average of about 5 samples or more sampling data. It can be seen from Fig. 5 that the effective diffusion coefficient of nitrogen is higher than that of any other gases in argon. It can be the reason that nitrogen is smaller than the other gases and bulk-diffusion coefficient of nitrogen is larger than the others so that the effective diffusion coefficient of nitrogen is higher than the others. The values obtained from different of three samples of coated layers the same value for each evaluating gas.

With the obtained effective diffusion coefficient, the state of diffusion within the coated layer could be estimated. If only bulk-diffusion exists through the coated layer, the effective diffusion coefficient can be written in equation (4)

$$D_b = \psi D$$  \hspace{1cm} (4)

where \(D_b\) is effective bulk-diffusion coefficient, \(\psi\) is the geometric parameter of a porous solid and \(D\) is bulk-diffusion coefficient.

$$\psi = \frac{\varepsilon}{\tau}$$  \hspace{1cm} (5)

the ratio of porosity \(\varepsilon\) and tortuosity \(\tau\) of transport pores. For this experiment, however, the values of \(\psi\) calculated with the obtained effective diffusion coefficient and bulk-diffusion coefficient were different from the value of each gas. This indicates that the state of diffusion within the coated layer can hardly be only bulk-diffusion condition. Therefore, it was assumed that both bulk-diffusion and Knudsen diffusion take place within the coated layer. In this case, the effective diffusion coefficient is described by

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_b} + \frac{1}{D_k}$$  \hspace{1cm} (6)

where \(D_k\) is the effective Knudsen coefficient defined as

$$D_k = r\psi K$$  \hspace{1cm} (7)

where \(r\) is the mean diffusive pore radius, \(K\) is the Knudsen coefficient

$$K = \frac{2}{3} v$$  \hspace{1cm} (8)

\(v\) is the mean thermal velocity of molecules

$$v = \sqrt{\frac{8RT}{\pi M}}$$  \hspace{1cm} (9)

By substituting the obtained effective diffusion coefficient, bulk-diffusion coefficient and Knudsen-diffusion coefficient for equation 11, the assumption of the transitional state where both bulk-diffusion and Knudsen-diffusion take place was verified shown in Fig. 6.

In Fig. 6, all the data from all coated layer sample 1, 2 and 3 are plotted for \(X\)-axis as \(K/D\) for \(Y\)-axis as \(K/D_{\text{eff}}\). Almost all data is plotted on a straight line, which means

$$\frac{1}{D_{\text{eff}}} = \frac{1}{\psi D} + \frac{1}{r\psi}$$  \hspace{1cm} (10)

multiply equation 10 by \(K\)

$$\frac{K}{D_{\text{eff}}} = \left(\frac{1}{\psi D} + \frac{1}{r\psi}\right)$$  \hspace{1cm} (11)

$$(\text{Fig. 5})$$

$$(\text{Fig. 6})$$
that equation 6 and 11 can be satisfied with the obtained effective diffusion coefficient so that the state of diffusion through the coated layer was revealed to be the transition state of diffusion. In addition, the mean diffusive radius of transport-pores can be estimated with y-intercept and the slope of the straight line. The mean diffusive radius based on this data is 0.49 \( \mu \text{m} \). Figure 7 compares the evaluated mean diffusive radius with pore size distribution measured by mercury porosimetry. The coated layer used in the experiment has two peaks of pore size distribution. The peak of wider pores is expected to control the bulk-diffusion and the other peak to Knudsen-diffusion. The mean diffusive radius is positioned between peaks of pore size distribution closer to the peak for wider pores. This result may also indicates that the state of diffusion through the coated layer is the transition state of diffusion, that is, gas transferring through the coated layer could be effected by both bulk-diffusion and Knudsen-diffusion. Figure 7 suggests that bulk-diffusion gives more contribution than Knudsen-diffusion.

5. CONCLUSIONS

The diffusion cell to measure the effective diffusion coefficient was designed. The effective diffusion coefficients of three kinds of gases (nitrogen, carbon dioxide and propane) in argon through the coated catalytic layer for automobile catalyst were evaluated experimentally. The average effective diffusion coefficients through the coated catalytic layer were \( D_{\text{eff}} = 0.11 \text{ cm}^2/\text{s} \) for nitrogen in argon, \( D_{\text{eff}} = 0.060 \text{ cm}^2/\text{s} \) for carbon dioxide in argon and \( D_{\text{eff}} = 0.054 \text{ cm}^2/\text{s} \) for propane in argon. Using the obtained effective diffusion coefficient, the state of diffusion through the coated layer was estimated to be the transition state where both bulk-diffusion and Knudsen-diffusion take place. The mean diffusive radius was derived from the transition state equation with all the obtained effective diffusion coefficient. The mean diffusive radius \( r \) was 0.49 \( \mu \text{m} \). The pore size distribution of the coated catalytic layer obtained from mercury porosimetry was compared with the mean diffusive radius. The mean diffusive radius was positioned between two peaks of pore size distribution. This well agreed that the transition state take place through the coated catalytic layer.

REFERENCES