Evaluation of the Effective Diffusivities of HD and HDO in a Pt/SDBC Catalyst Pellet

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Abstract: The effective diffusivities of HD (Deuterated Hydrogen) and HDO (Deuterated Water) in a Pt/SDBC (Styrene Divinylbenzene Copolymer) catalyst under the conditions of a hydrogen-water isotopic exchange reaction were evaluated. The dynamic-pulse response technique for a helium-nitrogen system was used to determine the tortuosity factor of the SDBC pellet, and the effective diffusivities of HD and HDO were calculated from it under the water vapor conditions. The SDBC single pellet was prepared using the bulk polymerization method; the experimental apparatus consisted of a diffusion cell, a pulse injection valve, a thermal conductivity detector, and the flow control valves. The tortuosity factor of the SDBC single pellet was 2.94. The effective diffusivities for HD were calculated to be 0.0096, 0.010, and 0.0101 cm²/s at 40, 60, and 80 °C, respectively; they were 0.0040, 0.0041, and 0.0042 cm²/s, respectively for HDO. These values can be used to calculate the Thiele modulus and the effectiveness factors that represent the mass transfer effect in a catalyst pore.

Keywords: effective diffusivity, tortuosity factor, SDBC single pellet, dynamic pulse-response technique

Introduction

The Pt/SDBC catalyst has been developed for the hydrogen isotope exchange reaction during the process of the removal of tritium or the production of heavy water. The method of preparation and the characteristics of the catalyst are well established [1-3], however, information on the effective diffusivity for defining the properties of mass transfer in a catalyst for the design of a reactor is not available.

In heterogeneous catalysis, internal diffusion is a significant, and often controlling, process, because the catalytic processes operate in the intra-pellet diffusion controlled regime as a result of the high reaction rates needed for commercial applications. Consequently, the efficiency of porous catalysts can be expressed by the effectiveness factor, which is often limited by the diffusive properties. The theoretical prediction of effective diffusivity of gases in a porous catalyst has still not been resolved, and in many cases it is not sufficiently accurate. Part of the reason for this phenomenon is that the diffusion flux may include a contribution from several mechanisms, including bulk, Knudsen, and surface diffusion; in addition, satisfactory geometric models for the pore structure are not yet available. Thus, data for the effective diffusivity of gases in porous catalysts still cannot be derived accurately from diffusion measurements.

Several experimental methods have been used to determine the effective diffusivities of gases in porous media. They can be broadly divided into the steady state and dynamic methods. The steady state technique using a diffusion cell, which is known as a Wicke-Kallenbach diffusion cell [4], was the first to be applied to determine the effective diffusivity. This steady-state technique is rather time consuming and suffers from several disadvantages: (1) dead-end pores are inaccessible, (2) misleading values of diffusivity may be obtained for anisotropic solids, and (3) misleading values may also be obtained for bidispersed catalysts in which micropores, contained over most of the surface area, would contribute little to the steady-state diffusion flux when compared to the contribution from large interconnected macropores. Since the transient version of the Wicke-Kallenbach diffusion cell, which was devised to answer these draw-
backs of the steady-state mode, was introduced in the 1970s [5-7], much effort has been directed toward new transient techniques.

The object of this study was to evaluate the effective diffusivities of HD and HDO in a Pt/SDBC catalyst under the conditions of a hydrogen-water isotopic exchange reaction. The effective diffusivities of a reacting gas cannot be measured directly because water vapor exists in the reacting gas stream. However, the tortuosity factor of a catalyst, which is determined from experiments using the dynamic pulse-response technique, is independent of the properties of the gas; it depends only on the catalyst pore structure. Therefore, in this study, to measure the tortuosity factor of the SDBC pellet, diffusion data were obtained with respect to the temperature. Measurements were made using the dynamic technique for a helium-nitrogen system incorporating a SDBC single pellet. Finally, the effective diffusivities of HD and HDO were calculated from the tortuosity factor of the SDBC pellet under water vapor conditions.

**Experimental**

Figure 1 shows the experimental apparatus used to measure the gas flow rates to each face of the single pellet. The main components of the apparatus were the diffusion cell enclosed in a constant temperature oven, a pulse injection valve, a thermal conductivity detector, and flow controlling equipment. Figure 2 shows the diffusion cell in detail. The upper stream was brought to the top of the pellet and the lower stream was passed directly across the lower face of the volume \( V_3 \). A manometer was connected to the chambers on either side of the pellet. The dead volumes between the pulse injection and the catalyst holder and between the lower face of the pellet and the detector were minimized to reduce the corrections to the observed first moment. The pressure was maintained constant in both chambers of the diffusion cell by adjusting the upper flow control valve in the outlet line. After establishing equal pressures on both sides of the pellet, the valves connected to the manometer were closed prior to a pulse injection to reduce an additional contribution to the dead volume. Nitrogen was used as the carrier gas and pulses of pure helium (1 cc) were injected to the upper stream. Diffusion measurements were made at 40, 60, and 80 °C. The upper flow rate was maintained at 200 cc/min while the response peaks were measured for lower flow rates ranging from 30 to 300 cc/min.

The thermal conductivity detector of a Gas Chromatograph recorded the response peaks of the pulse injection. The analysis conditions of the detector were a temperature of 80 °C and a filament current of 80 mA. The response peak was integrated using the slice mode of the software (dsCHROM).

**Results and Discussion**

**Properties of Single Pellet**

The cylindrical catalyst pellet was prepared through bulk polymerization. The procedures for preparing the single pellet were similar to the established method [3]. A 1/2-inch Teflon tube was used to increase the pellet diameter. The prepared single pellet had a diameter of...
Figure 3. Pore size distribution of the SDBC single pellet.

Figure 4. Mesopore cumulative volume distribution of the SDBC single pellet.

Figure 5. First absolute moment of the SDBC single pellet at $F_u=210$ cc/min.}

Figure 4 shows the cumulative pore size distribution. The mean pore radius was calculated to be 186 Å, based on Equation (1) and Figure 4.

\[ r_c = \frac{\int_{V_1}^{V_2} r \cdot dV}{V_2 - V_1} \]  

Equation (1)

**Measurement of First Absolute Moment**

The observed and corrected first absolute moments are shown in Figure 5 under the conditions of 60 °C and $F_u=210$ cc/min. Helium was used as a diffusing gas and nitrogen was used as a carrier gas. The experimental first moment values can be determined from the measured response peaks by using equation (2).

\[ (\mu_1)_{obs} = \frac{\int_0^\infty C_A dt}{\int_0^\infty C_A dt} \]  

Equation (2)

The moments evaluated from equation (2) should be corrected because of the injection pulse volume and the dead volumes between the pulse injection and the upper face of the pellet and between the lower face and the detector. With these volumes, the corrected first moment was calculated using equation (3).

\[ (\mu_1)_{corr} = (\mu_1)_{obs} - (\mu_1)_{dev} - \frac{t_0}{2} \]  

Equation (3)
The values of \((\mu_1)_{\text{corr}}\) determined from equation (3) may then be used to determine the effective diffusivity.

The values of the first absolute moment decreased upon increasing the lower flow rate. Figure 6 represents the variation of the corrected first absolute moment with three upper flow rates of 60, 90, and 150 cc/min. The limiting values of the first moments at \(F_u = 150\) cc/min and 210 cc/min were almost identical, but a significant difference appeared at \(F_u = 90\) cc/min. The upper flow rate was maintained at 210 cc/min to reduce the influence of the dead volume. Figure 7 presents the corrected first absolute moments obtained at cell temperatures of 40, 60, and 80 °C. The upper flow rate was 210 cc/min and the lower flow rates ranged from 30 to 300 cc/min. The first absolute moments decreased upon increasing the cell temperature.

### Table 1. First Moment Data for the Helium Pulses in Nitrogen (\(F_u = 300\) cc/min)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>(F_u) cc/min</th>
<th>First moment, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>210</td>
<td>5.38</td>
</tr>
<tr>
<td>60</td>
<td>210</td>
<td>5.42</td>
</tr>
<tr>
<td>150</td>
<td>210</td>
<td>5.81</td>
</tr>
<tr>
<td>90</td>
<td>210</td>
<td>6.74</td>
</tr>
<tr>
<td>80</td>
<td>210</td>
<td>5.06</td>
</tr>
</tbody>
</table>

The tortuosity factor of the SDBC pellet was calculated from \(D_{\text{eff},\text{He}}\), from the expression of the parallel pore model [8].

\[
\tau = \frac{L^2 c_p}{6 D_e} \tag{4}
\]

The tortuosity factor of the SDBC pellet was calculated from \(D_{\text{eff},\text{He}}\), from the expression of the parallel pore model [8].

\[
D_e = \frac{c_p D}{\tau} \tag{5}
\]

In general, for a constant pressure diffusion of a binary system in a capillary, the diffusive flux due to a combined Knudsen and bulk molecular process is [9] given by

\[
N_A = -D \frac{dC_A}{dx} \tag{6}
\]

where the composite diffusivity \(D\) is given by

\[
\frac{1}{D} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}} \tag{7}
\]

and

\[
\alpha = 1 + \frac{N_B}{N_A} = 1 - \left( \frac{M_B}{M_A} \right)^{1/2} \tag{8}
\]
Table 2. Diffusivity and Tortuosity Factor Data for the Helium-Nitrogen System in the SDBC Single Pellet

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle t \rangle_{\text{corr}}$ (sec)</td>
<td>4.67</td>
<td>4.45</td>
<td>4.24</td>
</tr>
<tr>
<td>$D_{\text{He},\text{N}_2}$ (cm$^2$/s)</td>
<td>0.160</td>
<td>0.165</td>
<td>0.169</td>
</tr>
<tr>
<td>$D$</td>
<td>0.763</td>
<td>0.851</td>
<td>0.942</td>
</tr>
<tr>
<td>$D_{\text{eff},\text{He}}$</td>
<td>0.0080</td>
<td>0.0084</td>
<td>0.0088</td>
</tr>
<tr>
<td>$\tau$</td>
<td>2.95</td>
<td>2.94</td>
<td>2.93</td>
</tr>
</tbody>
</table>

If the mole fraction $\alpha y_A$ approaches zero, the $\alpha y_A$ term in Equation (7) becomes negligible and $D_e$ is independent of the concentration. In the pulse-response technique, the concentration of a diffusing component decreases with respect to the distance in the direction of diffusion [10]. In addition, with a sensitive detector, the concentration in the input pulse can be very low. Hence, $y_A$ in Equation (7) can be very small so that $D$ for a capillary, and also the effective diffusivity $D_e$ in a catalyst pellet, are essentially independent of the composition. Therefore, the composite diffusivity ($D$) was evaluated from Equation (7) with $\alpha y_A \rightarrow 0$.

The molecular diffusivity was obtained from the experimental data of Fuller and coworkers [11].

$$D_{AB} = \frac{10^{-3} T^{1.75} (1/M_A + 1/M_B)^{1/2}}{P[(\sum v_A)^{1/3} + (\sum v_B)^{1/3})^2]^{1/2}}$$ (9)

where T is in Kelvin, P is in atmospheres, and $D_{AB}$ is in cm$^2$/s. $M_A$ and $M_B$ are respectively the molecular weights of A and B. The values for the atomic diffusion volumes, $\sum v_i$, of helium and nitrogen were 2.88 and 17.9, respectively. The Knudsen diffusivity was calculated using Equation (10) at a mean pore radius of 180 Å, evaluated using Equation (1)

$$D_K = 9700 r_e \sqrt{T/M}$$ (10)

Table 2 shows the various diffusivities obtained experimentally and the tortuosity factor of the SDBC pellet. The resultant tortuosity factor of 2.94 can be used to calculate the pore-volume diffusivities for HD and HDO using Equation (5).

Calculation of Effective Diffusivities of HD and HDO

Because there is a considerable amount of water vapor in the gas stream at high temperatures, a bulk diffusion of HD and HDO will be affected by the composition of the gas mixture. The following simple relations were used to calculate the bulk diffusion coefficients of HD and HDO in the reaction mixture [12]:

$$D_{\text{HD},\text{mix}} = \frac{y_{\text{HD}}}{D_{\text{HD}}/D_{\text{HD},\text{H}_2}} + \frac{y_{\text{H}_2}}{D_{\text{H}_2}/D_{\text{HD},\text{H}_2}}$$ (11)

$$D_{\text{HDO},\text{mix}} = \frac{y_{\text{HDO}}}{D_{\text{HDO}}/D_{\text{HDO},\text{H}_2}} + \frac{y_{\text{H}_2}}{D_{\text{H}_2}/D_{\text{HDO},\text{H}_2}}$$ (12)

The values of the bulk diffusion coefficients ($D$) were calculated using the Fuller, Schettler, and Giddings relation [11]. Because the values for the atomic diffusion volumes of HD and HDO are not useful from Fuller’s table, the values of HD and HDO were used for HD and HDO. The value for HD is 7.07 and that for HDO is 12.7. The error involved will be very marginal due to this assumption, when considering the large number of assumptions and approximations used in these calculations. Table 3 shows the various diffusivities calculated using the above-mentioned method. The calculated effective diffusivities for HD and HDO will be used for a calculation of the Thiele modulus and the effectiveness factor.

Table 3. Calculated Diffusivities for HD and HDO

<table>
<thead>
<tr>
<th>Diffusivities (cm$^2$/s)</th>
<th>40 °C</th>
<th>60 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{HDO},\text{H}_2}$</td>
<td>0.77</td>
<td>0.91</td>
<td>1.01</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{HDO}}$</td>
<td>0.28</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{H}_2}$</td>
<td>1.17</td>
<td>1.38</td>
<td>1.52</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{HDO}}$</td>
<td>0.65</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{mix}}$</td>
<td>1.10</td>
<td>1.19</td>
<td>1.11</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{H}_2}$</td>
<td>0.69</td>
<td>0.68</td>
<td>0.56</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{HDO}}$</td>
<td>0.18</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td>$D_{\text{HDO},\text{H}_2}$</td>
<td>0.73</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td>$D_{\text{eff},\text{HD}}$</td>
<td>0.0096</td>
<td>0.0100</td>
<td>0.0101</td>
</tr>
<tr>
<td>$D_{\text{eff},\text{HDO}}$</td>
<td>0.0040</td>
<td>0.0041</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Conclusions

The dynamic pulse-response technique was used to measure the effective diffusivities of helium in a nitrogen flow. An SDBC single pellet was prepared for the experiment. The diameter of the single pellet was 0.94 cm and its height was 1.12 cm. The evaluated mean pore radius was 186 Å. The first absolute moments were measured by fixing the upper flow rate at 210 cc/min and varying the lower flow rate from 30 to 300 cc/min. The experimental results show that the tortuosity factor of SDBC, which was used to calculate the effective diffusivities of HD and HDO in water vapor, was 2.94, based on the effective diffusivities of helium. The effective diffusivities for HD were calculated to be 0.0096, 0.010, and 0.0101 cm$^2$/s, and for HDO to be 0.0040,
0.0041, and 0.0042 cm²/s, at 40, 60, and 80 °C, respectively. These values can be used to calculate the Thiele modulus and the effectiveness factors that represent the mass transfer effect in a catalyst pore.

**Acknowledgment**

This project has been performed under the Nuclear R & D program of MOST.

**Nomenclature**

- $C_A$: concentration of tracer gas A (moles/cm³)
- $D$: composite diffusivity in a capillary (cm²/s)
- $D_{AB}$: molecular diffusivity (cm²/s)
- $D_e$: effective diffusivity in binary system of A and B (cm²/s)
- $D_{eff,i}$: effective diffusivity of species i (cm²/s)
- $D_K$: Knudsen diffusivity (cm²/s)
- $L$: pellet length (cm)
- $M_A, M_B$: molecular weights of A and B
- $N_A, N_B$: diffusion fluxes of A and B (moles/cm² s)
- $r_e$: mean pore radius (cm)
- $V_1, V_3$: volumes of upper and lower chambers (cm³)
- $X$: distance in pellet (cm)
- $y_i$: mole fraction of species i
- $\alpha$: ratio of diffusion fluxes
- $\varepsilon_p$: porosity of pellet
- $(\mu_1)_{obs}$: observed first moment (sec)
- $(\mu_1)_{corr}$: first absolute moment for the pellet (sec)
- $\tau$: tortuosity factor

**References**