

## Gas Diffusion in Polycrystalline MFI-type Zeolite Membranes

*Hiromitsu Takaba<sup>1</sup>, Atsushi Yamamoto<sup>1</sup>, Kikuko Hayamizu<sup>2</sup> and Shin-ichi Nakao<sup>1</sup>*

<sup>1</sup>Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo Bunkyo-ku, Tokyo 113-8685, Japan, E-Mail: takaba@chemsys.t.u-tokyo.ac.jp, <sup>2</sup>National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Center 5, Tsukuba 305-8565, Japan

### 1. Introduction

Information on mass transport in polycrystalline zeolite membranes is necessary for a theoretical estimation of the membrane performances. Zeolite membranes are usually prepared as thin layer of an assembly of small zeolite crystals including many intercrystalline regions. Thus, the intercrystal region would influence their individual diffusion properties, which would differ from that in a single crystal. Characterization of the intercrystalline region by direct experimental methods is sometimes difficult because of their too small size to observe that is in the range of a few nanometers. Therefore, the investigation on the relationship between the structure of the intercrystalline region in the zeolite membranes and the diffusion properties are still limited [1], and it is not fully understood. In this study, we carried out <sup>1</sup>H pulse gradient-field spin-echo (PFG) NMR to obtain a diffusion coefficient of methane in MFI-type silicalite zeolite membranes, whose properties have been characterized to understand the feature of gas diffusion in polycrystalline zeolite.

### 2. Experiments

MFI type silicalite membranes were prepared by previously reported technique [2]. The membrane was broken into small pieces of membrane to be placed in 5 mm NMR glass tubes. The tube was degassed under vacuum at 673 K for at least 24 hours and then the methane gas ( $3 \times 10^4$  Pa) was loaded at 298 K. PFG NMR measurements were performed using a JEOL GSH-200 spectrometer with a 4.7 T wide-bore magnet controlled by a TecMag Apollo system. The stimulated echo pulse sequence was used. The measurements were made by holding  $g$  at 6.4 - 9.2  $T\ m^{-1}$  while varying  $\delta$  between 0.01 ms and 0.25 ms for different  $\Delta$  between 0.5 ms and 4 ms. Gas permeation test was also carried out using these membranes before NMR measurements.

### 3. Results and discussion

Fig. 1 shows the estimated diffusion coefficient of methane as a function of the root mean square

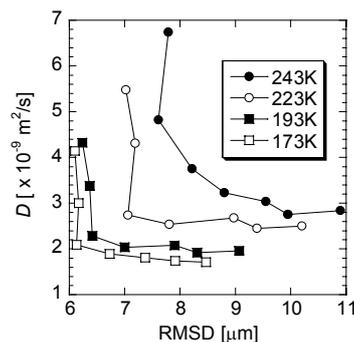


Fig. 1: The relationship of the estimated diffusion coefficients of methane and the RMSD.

displacement ( $\text{RMSD} = (6D\Delta)^{1/2}$ ) at various temperatures. The diffusion coefficients at all temperatures show strong decays and then become a constant. Observed drastic decreases in the diffusion coefficients suggest the existence of transport barriers in the membrane. The distance between the transport barriers was estimated to be much larger than 6  $\mu\text{m}$ . These estimated distances are larger than the smallest dimension of the crystals appearing in the membrane surface. Table 1 shows a comparison of the measured diffusivity with the short time diffusivity in the single crystal. By comparing the reported short-time diffusivities obtained by PFG NMR for single crystals, the long-time diffusivity in the membrane is reduced by a factor of three. This result implies that the difference in diffusivities for the membrane compared with single crystals is due to the  $\mu\text{m}$  order structural difference.

Table 1: Comparison of self-diffusivity of methane in the silicalite membrane with that in a single silicalite crystal. The long- and short-time  $D_s$  were calculated from the attenuation plots at  $\Delta = 7$  ms and  $\Delta = 1.5$  ms, respectively.

	method	$T$ [K]	$D_s$ (long-time / short-time) [ $\times 10^{-9}$ m <sup>2</sup> /s]
This work	PFG NMR	173	2.2 / 5.0
		193	2.4 / 5.4
		223	2.9 / 6.4
		243	3.1 / 7.6
		301	3.7 * / 8.8 *
Jobic [3]	QENS	250	4.8
Caro et al. [4]	PFG NMR	300	11–14

### 3. Conclusion

We carried out PFG-NMR to measure the diffusion coefficient in polycrystalline zeolite membranes. Measured diffusivities of methane decreased with increase in the diffusion distance and became constant at all investigated temperatures. The apparent diffusivity of methane in the silicalite membrane was smaller than that in a single crystal by a factor of three.

### References

- [1] Heink, W.; Karger, J.; Naylor, T.; Winkler, U. *Chem. Commun.* **1999**, *1*, 57–58.
- [2] Sano, T.; Yanagishita, H.; Kiyozumi, Y.; Mizukami, F.; Haraya, K. *J. Membr. Sci.* **1994**, *95*, 221–228.
- [3] Jobic, H.; Bee, M.; Kearley, G. J. *Zeolites* **1989**, *9*, 312–317.
- [4] Caro, J.; Bulow, M.; Schirmer, W.; Karger, J.; Heink, W.; Pfeifer, H.; Zdanov, S. P. *J. Chem. Soc. Faraday Trans.* **1985**, *81*, 2541–2550.