

# PERMEATION AND SEPARATION CHARACTERISTICS OF MFI TYPE ZEOLITE MEMBRANES ON ZIRCONIA INTERMEDIATE LAYER BY TEMPLATE-FREE SECONDARY GROWTH METHOD

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## Abstract

MFI type zeolite membranes were synthesized on two types of supporting materials, alumina ( $\alpha$ -alumina) and yttria-stabilized zirconia (YSZ) coated alumina. Membranes were prepared by template-free secondary growth method with multiple growth steps in order to minimize intercrystalline gaps. Gas permeation characteristics, thermal and hydrothermal stability for MFI type zeolite membranes were examined.

It was found that MFI type zeolite membranes without YSZ intermediate layer showed relatively large  $H_2$  and He permeance above  $10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  with selectivity of around 95 ( $H_2/SF_6$ ) at  $25^\circ\text{C}$ . After repeated secondary growth ( $180^\circ\text{C}$ , 8 h), the temperature dependency of  $H_2$ , He and CO showed little change (Knudsen type diffusion) but the behavior of  $CO_2$  was dramatically different.

XRD results for MFI type zeolite membranes before and after heat treatment indicated that YSZ intermediate layer was quite effective in preventing the aluminum diffusion from alumina support to zeolite layer at high temperatures ( $500^\circ\text{C}$ ). A MFI type zeolite membrane with YSZ intermediate layer showed high stability in steam at high temperature ( $500^\circ\text{C}$ , partial pressure of steam: 100 kPa).

## Introduction

In the last two decades, much attention has been focused on inorganic zeolite membranes because they can be utilized under harsh conditions where organic polymer membranes are insufficient. The MFI structure type zeolite membranes have been studied extensively due to its pore size and ease of preparation [1-3]. In general, MFI-type zeolite membranes are synthesized on porous substrates such as stainless steel or  $\alpha$ -alumina to improve the mechanical stability. It is well known that substrate materials can affect the zeolite membrane quality. Vroon et al. [4] reported that ultra-thin silicalite films could not be grown on the mesoporous  $\gamma$ -alumina support due to its poor chemical stability. Sano et al. [5] and Dong et al. [6] investigated the use of two different materials as substrate to prepare MFI type zeolite membranes. Zeolite membranes formed on stainless steel or zirconia supports contain much lower aluminum content than those formed on a porous  $\alpha$ -alumina support. Pan and Lin [7] determined that the aluminum transport mechanism from the alumina support into the silicalite layer consisted of penetration silicalite layer by solid-state diffusion in calcination step and also by dissolution into the silicalite synthesis sol.

In many cases, intermediate layer was coated on porous substrate as a buffer layer, which could be improved the stability of membrane structure [6, 8-14]. Nam and Lee [8] introduced an intermediate layer of silica as a diffusion barrier between the palladium alloy layer and the stainless steel substrate. Yepes et al. [9] prepared Pd-Ag alloy membranes on two different intermediate layers

of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to improve the stability. These improved membranes were structurally stable and much more efficient for hydrogen permeances than those without diffusion barriers. Braunbarth et al. [10] reported that ETS-4 membranes on titania support showed high reproducibility of membrane properties compare to those on alumina support due to the dissolution of alumina under high alkaline conditions.

For the preparation of MFI type zeolite membranes on zirconia intermediate layer, some of research groups reported that MFI type zeolite crystals were formed in discontinuous form [6,11,12]. Geus et al. [11] tried to prepare MFI type zeolite membrane on several types of porous materials (clay,  $\alpha$ -alumina, zirconia and metakaolin). They found that only continuous MFI type zeolite membrane was formed on clay support. Lovallo and Tsapatsis [12] prepared well-intergrown silicalite films on silicalite-alumina composite supports, while silicalite particles were grown on the zirconia support with low coverage. Dong et al. [6] could grow continuous MFI zeolite films on YSZ support with oxygen vacancy defects. These membranes showed high H<sub>2</sub> permeance above 10<sup>-6</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>. However, H<sub>2</sub>/CH<sub>4</sub> permselectivity is not as good as those obtained with alumina supported silicalite membranes.

Recently, Dong et al. [13] reported that annealing the MFI type zeolite membrane prepared by in-situ method prior to template removal facilitated the formation of bonds linking the YSZ intermediate layer and MFI zeolite layer (crystallites), resulting in improvement of membrane quality on YSZ coated alumina support. Seike et al. [14] also reported that MFI thin films with b-axis orientation were successfully prepared on YSZ plates by the in situ hydrothermal method through dissolution of the silicalite glasses used as a source material. However, no work has been published before on structural stability improvement and gas permeation characteristics of MFI type zeolite membrane on alumina support with a zirconia buffer layer.

In our previous work [15], MFI type zeolite membranes were prepared by template-free secondary growth method in order to minimize the chance for defects ( $d_p$ : >2 nm) and/or intercrystalline gaps ( $d_p$ : 0.6~2 nm) that tend to form during the template removal step [13,16]. Membranes were synthesized on two types of supporting materials; alumina and YSZ coated alumina. The membrane preparation conditions (dip coating times, hydrothermal synthesis time) were optimized in order to obtain high quality membrane. The objectives of this work are to (1) investigate the gas permeation characteristics for MFI type zeolite membranes which are prepared with optimized conditions and (2) examine the thermal and hydrothermal stability of MFI type zeolite membranes on  $\alpha$ -alumina and/or YSZ coated supports at high temperatures (500°C).

## Experimental

### *Preparation and characterization of MFI type zeolite membrane*

Yttrium stabilized zirconia suspension was prepared as reported previously [17]. Silicalite suspension was prepared by hydrothermal treatment (at 120°C for 12 h) from fumed silica (99.98%, Aldrich) and NaOH-TPAOH (1g-SiO<sub>2</sub>, 5ml (1M)-TPAOH, 0.07g-NaOH). The detail was described in previous publication [7,15].

MFI type zeolite membranes were fabricated on homemade porous  $\alpha$ -alumina disks (average pore diameter: 0.2  $\mu$ m, porosity: 45%). YSZ intermediate layers were coated on porous  $\alpha$ -alumina disks by dip coating with the YSZ suspension, followed by drying and calcination at 750°C for 3 h (heating/cooling rate: 100°C·h<sup>-1</sup>).

Alumina supports or YSZ coated alumina were dip-coated with silicalite suspensions and dried for two days at 40°C, three times each to ensure adequate coverage with seed layer [15]. Seeded

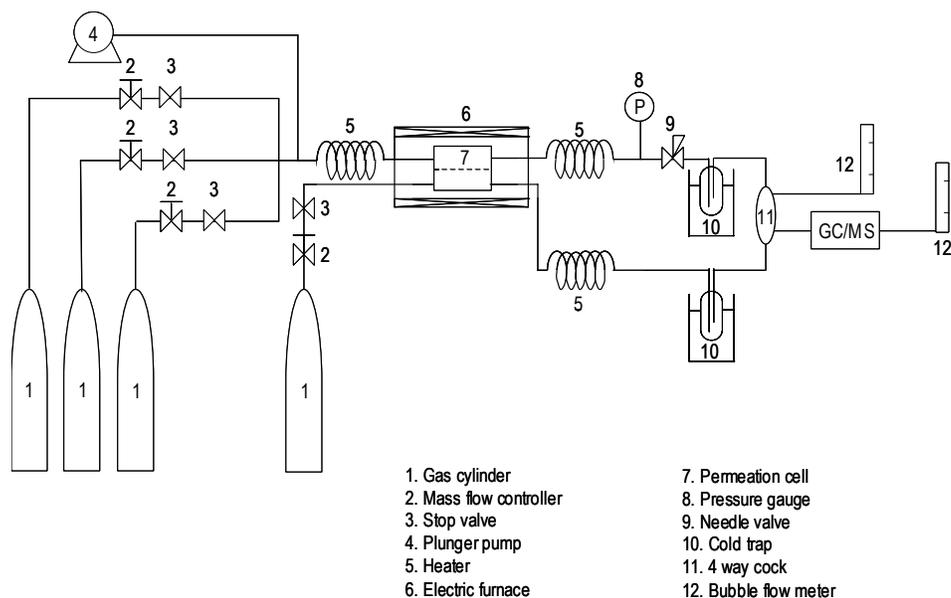
supports were calcinated after each dip coating for template removal. Annealing method was applied for calcination of silicalite seed layer on YSZ intermediate layer [15]. The alumina-zirconia-silicalite or alumina-silicalite supports were placed in the silicalite synthesis solution (0.15g-NaOH, 1g-SiO<sub>2</sub>, 10.5g-H<sub>2</sub>O) with silicalite seed layer face up in a teflon-line autoclave [7,15]. The autoclave was placed in an oven at 180°C for 8 h to allow silicalite crystals in the silicalite seed layer to grow into a continuous film. After cooling to the room temperature, the membranes were removed from the autoclave and washed with distilled water.

The phase structure, the morphology and thickness of the supported MFI type zeolite membranes were characterized by using XRD (Cu K $\alpha$  radiation) and SEM (Philips, XL 30). The XRD measurements were performed by step-wise scanning (2 $\theta$  step-size: 0.025°, 5°<2 $\theta$ <35°).

**Gas permeation measurements, thermal and hydrothermal stability test**

Figure 1 shows schematic diagram of experimental apparatus. The membrane was fixed in a stainless steel cell with the top layer facing the upstream, and was sealed by graphite O-rings. Single gas of high purity (He, H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, SF<sub>6</sub>) was fed on the outside (upstream) of a disk membrane at 200 kPa, keeping the down stream pressure constant at the atmospheric pressure. The temperature of the membrane cell was kept constant at a specified temperature between 25 and 500°C. The permeation rate was measured by a bubble flow meter.

Thermal and hydrothermal stability tests were examined by observing gas permeances (He, H<sub>2</sub>, N<sub>2</sub>, CO and CO<sub>2</sub>) before and after exposed to a N<sub>2</sub> dry stream and a stream of N<sub>2</sub>-H<sub>2</sub>O gas mixture at 500°C for specified time intervals. For the hydrothermal stability test, the partial pressure of H<sub>2</sub>O was kept at 100 kPa. The feed gas flow rate was controlled by mass controller before introducing water from a plunger pump. The feed stream was preheated at a constant temperature (200°C) before fed to the test section. After exposing the membrane to the steamed stream at 500°C for specified time intervals, the membrane was dried completely in N<sub>2</sub> stream at the same temperature before permeance measurements.

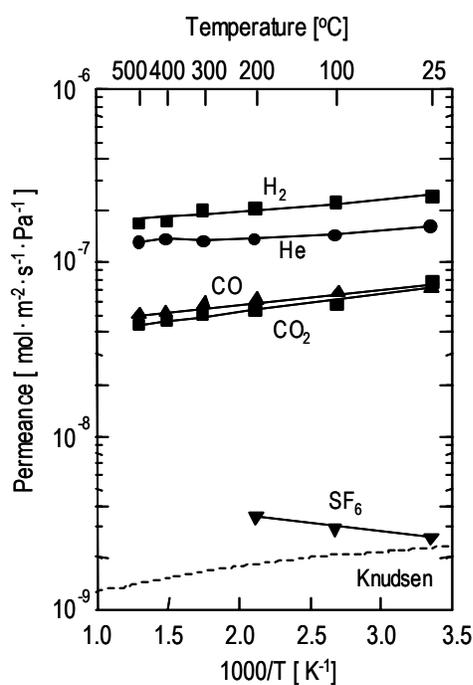


**Figure 1** Schematic diagram of experimental apparatus

## Results and Discussion

### *Gas permeation characteristic of MFI type zeolite membrane*

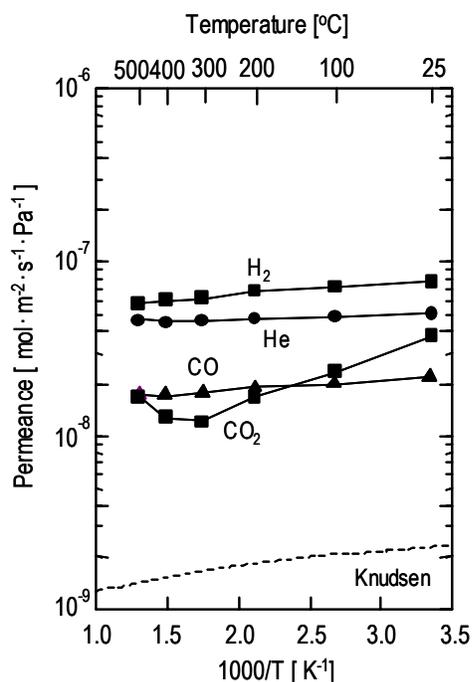
Figure 2 shows temperature dependency of gas permeances for MFI type zeolite membrane (M1) without YSZ intermediate layer. The broken line (no symbols) at the bottom of this figure shows a reference curve to compare the slope of the temperature dependency of the permeance with the Knudsen behavior. This membrane shows relatively large  $H_2$  and He permeance above  $10^{-7}$   $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  with selectivity of around 95 ( $H_2/SF_6$ ) at  $25^\circ\text{C}$ . This is approximately 12 times higher than Knudsen selectivity (8.54), indicating the number of defects and/or intercrystalline gaps is low. All gas permeances except for  $SF_6$  decrease with increasing temperature, which is similar to Knudsen diffusion. The permeance of  $SF_6$  slightly decreases with decreasing the temperature in a manner similar to activated permeation. There are previous studies that report  $H_2$  and He permeances for MFI type zeolite membrane increase with increasing temperature [18-20] but this was not found in this work. It is possibility that this discrepancy is due differences in membrane quality, i.e. the number of defects and/or intercrystalline gaps.



**Figure 2** Temperature dependency of gas permeances for MFI type zeolite membranes (M1) without YSZ intermediate layer

In order to examine the effect of membrane quality on gas permeation characteristics, hydrothermal treatment ( $180^\circ\text{C}$ , 8 h) was repeated for M1 membrane after gas permeation measurements to eliminate the intercrystalline gaps. Figure 3 shows temperature dependency for M1 membrane after repeated secondary growth ( $180^\circ\text{C}$ , 8 h). All gas permeances decreases about 70 % and  $SF_6$  permeance is less than  $10^{-9}$   $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ . After the repeated secondary growth, the temperature dependency of  $H_2$ , He and CO showed little change (Knudsen type diffusion) but the behavior of  $CO_2$  was dramatically different. The temperature dependency of  $CO_2$  permeance has a

minimum at 300°C. The temperature dependency (slope) between 25-300°C is much larger than that of Knudsen diffusion, while CO<sub>2</sub> permeance increases with increasing the temperature in a manner similar to activated permeation above 300°C. This can be explained by adsorption-diffusion model, since CO<sub>2</sub> is thought to strongly adsorb the MFI channels [21]. Therefore, with increasing temperature the mass-transport mechanism shifts from the surface diffusion regime to the activated gaseous diffusion regime. These results suggest that (1) some of intercrystalline gaps, through which CO<sub>2</sub> can permeate by Knudsen diffusion, could be covered after repeated secondary growth (2) the gas permeation characteristics of H<sub>2</sub> and He molecules are independent of these gaps.



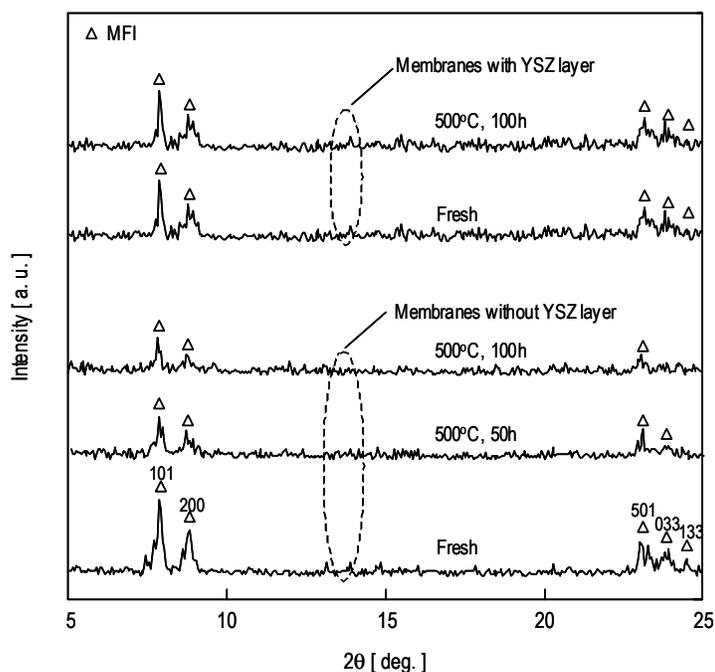
**Figure 3** Temperature dependency for M1 membrane after repeated secondary growth (180°C, 8 h)

### ***Thermal stability of MFI type zeolite membrane structure***

XRD results for MFI type zeolite membranes before and after heat treatment (500°C, 50, 100 h) are shown in Figure 4. The diffraction patterns for both membranes are independent of YSZ intermediate layer and show the non-oriented structure of the silicalite crystals. However, after heat treatment clear difference was observed in the diffraction patterns for MFI type zeolite membranes. For membrane without YSZ intermediate layer, the intensity of diffraction patterns (101, 200, 501) clearly decreases and those (033, 133) are gone after heat treatment. There is no significant difference between the intensity after 50 h and those after 100 h. For membrane with YSZ intermediate layer, the intensity of diffraction patterns show little change after heat treatment.

It is well known that silicious MFI type zeolite (silicalite-1) is one of the most thermally and chemically stable inorganic microporous materials due to the exclusion of Al from the crystalline framework. Deng and Lin [22] reported that there is no detectable change of crystalline structure of the silicalite powders caused by harsh thermal treatment (850°C, 168 h). In case of MFI type zeolite membrane on  $\alpha$ -alumina support (without YSZ intermediate layer), however, some of aluminum on alumina support diffuses into zeolite layer during the heat treatment, resulting in lower Si/Al ratio [15].

Since the high temperature structural stability of MFI zeolite membrane decreases with decreasing the Si/Al ratio, MFI microstructure was considered to break down after heat treatment. While membrane with YSZ intermediate layer, YSZ intermediate layer was effective to prevent the aluminum diffusion due to the elimination of interaction between alumina and silicalite coated on the surface of zirconia layer, resulting in higher thermal stability at 500°C. A MFI type zeolite membrane with YSZ intermediate layer also showed high stability in steam at high temperatures (500°C, partial pressure of steam: 100 kPa).



**Figure 4** XRD patterns of MFI type zeolite membranes before and after heat treatment (500°C, 50-100 h)

## Conclusion

MFI type zeolite membranes were synthesized on two types of supporting materials, alumina ( $\alpha$ -alumina) and yttria-stabilized zirconia (YSZ) coated alumina. Membranes were prepared by template-free secondary growth method with multiple growth steps in order to minimize intercrystalline gaps.

It was found that MFI type zeolite membranes without YSZ intermediate layer showed relatively large  $H_2$  and He permeance above  $10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$  with selectivity of around 95 ( $H_2/SF_6$ ) at 25°C. All gas permeances except for  $SF_6$  decreased with increasing temperature (Knudsen type diffusion). After repeated secondary growth (180°C, 8 h), the temperature dependency of  $H_2$ , He and CO showed little change (Knudsen type diffusion) but the behavior of  $CO_2$  was dramatically different. The temperature dependency (slope) between 25-300°C was much larger than that of Knudsen diffusion, while  $CO_2$  permeance increased with increasing the temperature in a manner similar to activated permeation above 300°C.

XRD results for MFI type zeolite membranes before and after heat treatment indicated that YSZ intermediate layer was quite effective in preventing the aluminum diffusion from alumina support

to zeolite layer at high temperatures (500°C). A MFI type zeolite membrane with YSZ intermediate layer showed high stability in steam at high temperature (500°C, partial pressure of steam: 100 kPa).

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