

Zeolite Membrane for High Temperature Gas Separation

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ABSTRACT:

The present study reports the preparation of a compact ZSM-5 membrane showing high thermal stability and high separation factors, especially *n*/*i*-butane isomers at high temperatures. ZSM-5 membrane was prepared on a porous α -Al₂O₃ tube (an average pore diameter, ca. 100 nm) at 180°C by the seed-assisted crystallization method. The XRD and SEM results showed that a thin zeolite layer (ca. 1 μ m) was formed on the support surface. The single gas permeances of N₂, H₂, SF₆, *n*-butane, and *i*-butane were taken at 270°C. *i*-Butane permeance hardly changed after repeated thermal treatments up to 400°C, indicating the membrane is thermally stable. On the other hand, other single gas permeances increased when the membrane was further dried at 400°C, indicating thermal pretreatment at 270°C could not remove all the adsorbed species in the membrane. *i*-Butane and SF₆ permeances were significantly lower than the permeances of smaller molecules, indicating that the membrane has a low concentration of defects. The ideal selectivities at 270°C were 61 for H₂/*i*-butane and 47 for H₂/SF₆. The temperature dependency of *n*/*i*-butane ideal selectivities and separation factors for an equimolar *n*/*i*-butane mixture was studied. The ideal selectivity showed a maximum of 36 at 300°C. The separation factors increased with temperature and reached around 12 at 300-400°C, which were much higher than those reported in the literature.

INTRODUCTION

MFI-type zeolite membranes (i.e. silicalite-1 and ZSM-5) are attractive for gas, vapor and liquid separations in view of their selective adsorption and molecular sieving properties. Most of these membranes were prepared in the presence of organic structure-directing agents (SDAs) [1]. These SDAs are incorporated in the zeolite channels during synthesis and should be removed by calcination after synthesis to open up the zeolite channels. While MFI-type membranes showing high performance after calcination at high temperatures have been reported [2], several studies have shown that cracks tend to form in the zeolite membranes during calcination due to the thermal stress, which is caused by the difference in thermal expansion between zeolite layer and support and/or by changes in lattice parameters of zeolite crystals as a consequence of the removal of templates [3]. The presence of cracks in the membrane will significantly deteriorate the separation performance of the membrane, in particular at high temperatures where differences in adsorption and mobility become less significant for the gas to be separated.

To avoid the risk of crack formation during calcination, several attempts have been made on the preparation of ZSM-5 membranes without SDAs [4-8]. These membranes have been studied for liquid or gas separations at elevated temperatures, while the reports on high-temperature gas separations are quite few. In a previous study [8], we have confirmed that a thin ZSM-5 membrane could be prepared on the outer surface of a porous α -alumina tube using an SDA-free gel. We recently found that ZSM-5 zeolite

membranes could also be prepared with an SDA-free clear solution [9]. The pervaporation properties of these membranes have been reported in these studies. Here we report the gas permeation properties of these membranes with an emphasis on the potential for high-temperature gas separations.

EXPERIMENTAL

Porous asymmetric α -Al₂O₃ tubes (NGK Insulators Co., Japan, length = 30 mm, i.d. = 10 mm, o.d. = 8 mm, average pore diameter in the outer top layer = 100 nm) were used as supports for zeolite membrane preparation. All ZSM-5 membranes were prepared on the outer surface of the tubular support by the seed-assisted crystallization method. Prior to crystallization, the outer surface of the tube was seeded by means of dip coating in a colloidal ZSM-5 crystal suspension. The colloidal suspension was prepared from commercially available template-free ZSM-5 powder (SiO₂/Al₂O₃ = 23.8, Tosoh Co., Japan) according to the procedure previously reported [10]. In this study, a colloidal suspension with the solids content of 3.8 g l⁻¹ and pH 7.4 was used for seeding.

The seeded tube was immersed vertically in a Teflon-lined stainless steel autoclave and filled with a synthesis mixture. Either an SDA-free gel or clear solution was used for the crystal growth. The molar compositions were 26.75Na₂O:Al₂O₃:100SiO₂:4600H₂O for the gel and 10Na₂O:0.15Al₂O₃:36SiO₂:960H₂O for the clear solution. Both were prepared in a similar way by mixing distilled water, sodium hydroxide, sodium aluminate, and colloidal silica (Nissan Chemical Ind.). Prior to use, the synthesis mixture was stirred at 50°C for 4 h for each case. The crystallization was performed under hydrothermal conditions at 180°C for a given period of time. For the simplicity, hereafter the ZSM-5 membrane prepared with the gel is referred to as GL-ZSM-5 membrane, while the one prepared with the clear solution is referred to as CS-ZSM-5 membrane.

The quality of the prepared membranes was evaluated using single-gas permeation of H₂, *n*-C₄H₁₀, and *i*-C₄H₁₀ and an equimolar *n*/*i*-C₄H₁₀ mixture. In case of single gases, the permeances were measured using the pressure-drop method. The pressure difference across the membrane was kept at 100 kPa and the permeate side was kept at atmospheric pressure. The permeation of the gas mixture was conducted based on the Wicke-Kallenbach method. The mixture was fed to the outer side of the membrane tube at a flow rate of 20 ml min⁻¹. Helium was used as sweep gas that was introduced to the inside of the membrane tube at a flow rate of 20 ml min⁻¹.

RESULTS AND DISCUSSION

ZSM-5 membrane prepared with an SDA-free gel

Figure 1 shows the permeances of H₂ and *i*-C₄H₁₀ at 200°C as a function of permeation time for a GL-ZSM-5 membrane prepared at 180°C for 12 h. Prior to permeation measurements, the membrane was dried at 200°C for longer than 12 h. It can be seen that the H₂ permeance was much higher than the *i*-C₄H₁₀ permeance and the H₂/*i*-C₄H₁₀ ideal selectivity was 13.8. This result is in good agreement with the previously reported one (14.5) [8], indicating the acceptable reproducibility of the membrane quality.

Figure 2 presents the H₂ permeances as a function of temperature. It is shown that the H₂ permeances increase gradually with temperature below 280°C but increase sharply at the temperature close to 290°C. After the membrane was cooled down to 200°C, the permeances of H₂ and *i*-C₄H₁₀ were measured again. It was found that the H₂ permeance became much larger than the previously measured one (3.35×10⁻⁷ vs. 1.42×10⁻⁸ mol s⁻¹ m⁻² Pa⁻¹) as shown in Figure 2, and the H₂/*i*-C₄H₁₀ ideal selectivity was decreased to be 2.1. It is suggested that cracks might occur in the membrane near this temperature. Lassinantti

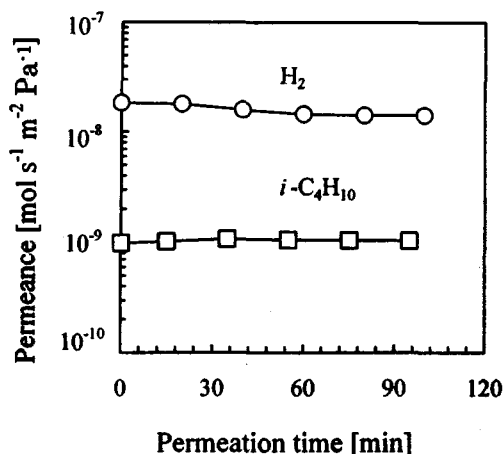


Figure 1. H₂ and *i*-C₄H₁₀ permeances at 200°C as a function of permeation time through GL-ZSM-5 membrane.

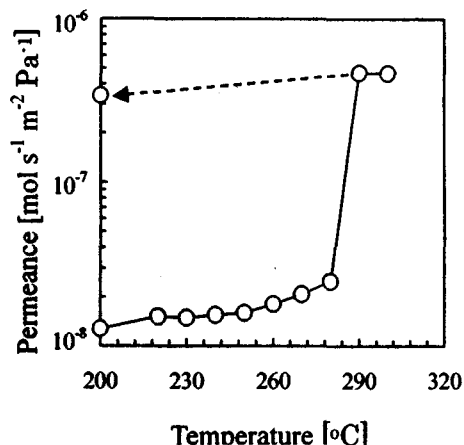


Figure 2. H₂ permeances as a function of temperature through GL-ZSM-5 membrane.

et al. have also observed that ZSM-5 membranes prepared with a similar SDA-free gel cracked around 270°C [7]. These results indicate that compact ZSM-5 membranes could be prepared with an SDA-free gel, but the thermal stability of this type of membrane should be improved for high-temperature gas separations.

ZSM-5 membrane prepared with an SDA-free clear solution

Table 1 shows the effect of thermal pretreatment on the permeances of H₂ and *i*-C₄H₁₀ and the H₂/*i*-C₄H₁₀ ideal selectivities at 270°C for a CS-ZSM-5 membrane prepared at 180°C for 6 h. It is shown that the *i*-C₄H₁₀ permeance measured after the pretreatment at 400°C is quite similar to that measured after the pretreatment at 270°C, indicating the membrane is quite stable against the temperature variation between 270 and 400°C. On the other hand, the H₂ permeance measured after the pretreatment at 400°C is larger than that measured after the pretreatment at 270°C, indicating thermal treatment at 270°C could not remove all the adsorbed species from pores in the zeolite membrane. Correspondingly, the H₂/*i*-C₄H₁₀ ideal selectivity at 270°C increased to be as high as 61 after the pretreatment at 400°C. This ideal selectivity is significantly higher than the value (5.4) calculated from Knudsen diffusion, indicating that the membrane has a low concentration of defects. The fact that the H₂ permeance increased while the *i*-C₄H₁₀ permeance did not after the pretreatment at 400°C indicates that *i*-C₄H₁₀ may mainly permeate through the crystal boundaries. We expected that adsorbed species in the crystal boundaries would be easily removed compared with those in the zeolitic pores. It seems that adsorbed species in the crystal boundaries have completely been removed after the pretreatment at 270°C. The pretreatment at 400°C had little effect on the size of the crystal boundaries. This may explain why the *i*-C₄H₁₀ permeances were almost unchanged after the pretreatment at 400°C. On the other hand, due to the removal of adsorbed species from zeolitic pores during the pretreatment at 400°C, the H₂ permeances increased after the pretreatment at 400°C.

Table 2 shows the *n*-C₄H₁₀ permeances and the selectivities for single gas and a 50kPa/50kPa *n*/*i*-C₄H₁₀ mixture at 200, 300 and 400°C. The *n*-C₄H₁₀ permeances for the *n*/*i*-C₄H₁₀ mixture are much smaller than the single gas permeances, indicating *i*-C₄H₁₀ inhibits the permeation of *n*-C₄H₁₀. Correspondingly, the separation factors for the mixture are smaller than the ideal selectivities over the temperature range of 200-400°C.

Table 1

Effect of the thermal pretreatment on the permeances of H₂ and *i*-C₄H₁₀ at 270°C through CS-ZSM-5 zeolite membrane

Pretreatment conditions	H ₂ permeance [mol s ⁻¹ m ⁻² Pa ⁻¹]	<i>i</i> -C ₄ H ₁₀ permeance [mol s ⁻¹ m ⁻² Pa ⁻¹]	H ₂ / <i>i</i> -C ₄ H ₁₀ ideal selectivity [-]
270°C, 2 h	1.3×10 ⁻⁷	4.4×10 ⁻⁹	30
400°C, 2 h	2.8×10 ⁻⁷	4.6×10 ⁻⁹	61

Table 2

n-C₄H₁₀ permeances and *n*/*i*-C₄H₁₀ selectivities for single gas and a 50kPa/50kPa *n*/*i*-C₄H₁₀ mixture through CS-ZSM-5 zeolite membrane at different temperatures

Temperatur e [°C]	Single gas		50kPa/50kPa mixture	
	<i>n</i> -C ₄ H ₁₀ permeance ×10 ⁸ [mol s ⁻¹ m ⁻² Pa ⁻¹]	Ideal selectivity (<i>n</i> / <i>i</i> -C ₄ H ₁₀) [-]	<i>n</i> -C ₄ H ₁₀ permeance ×10 ⁸ [mol s ⁻¹ m ⁻² Pa ⁻¹]	Separation factor, α (<i>n</i> / <i>i</i> -C ₄ H ₁₀) [-]
200	9.2	14	0.3	1.2
300	18.4	36	1.7	6.3
400	17.7	20	8.1	12.7

Table 2 also shows that the temperature dependency of the ideal selectivity is different from that of the separation factor. The ideal selectivity increases from 14 to 36 with an increase in temperature from 200 to 300°C, then it decreases with a further increase in temperature. On the other hand, the separation factor increases monotonously with temperature. At 400°C, the separation factor is as high as 12.7. Van de Graaf et al. [11] reported that the *n*/*i*-butane separation factor with a stainless steel-supported silicalite-1 disk membrane was 23.3 at 30°C, but it decreased to unity at 402°C. Coronas et al. [12] reported that the separation factor of one ZSM-5 zeolite membrane had a maximum of 55 at 117°C for a 50/50 *n*/*i*-butane mixture, but the selectivity decreased to unity at 213°C. In contrast, the *n*/*i*-butane separation factor of our membrane is as high as 12.7 at 400°C, indicating its great potential for high-temperature gas separations.

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