1. Introduction

Aromatic hydrocarbons, including benzene, toluene, and xylene, are fundamental feedstocks for numerous chemical industrial processes. These basic aromatic hydrocarbons are conventionally produced by catalytic reforming of naphtha and hydrocarbon pyrolysis. However, other processes, such as aromatization of light alkanes, have been widely studied to cope with the steadily growing market demand. Conversion of light alkanes to aromatic hydrocarbons is an attractive process because of the vast abundance and low cost of natural gas. In particular, nonoxidative CH₄ aromatization to produce benzene over Mo loaded zeolite catalysts has been widely studied. Catalysts have shown high selectivity for the formation of aromatic hydrocarbons, but thermodynamics calculations have demonstrated that direct nonoxidative conversion of CH₄ to aromatics can only achieve about 14% yield at 700 °C. The main challenges in this reaction process are the thermodynamic limitations that constrain CH₄ conversion at low temperature and the inherent coke deposition over the active sites of the catalysts leading to fast deactivation. Use of H₂-permeable membrane reactors to improve aromatics yield has been examined. Study of a dense ceramic H₂-permeable membrane reactor found the yield of aromatics could be increased compared to the fixed-bed reactor, but 10% more coke was formed. Although the yield of aromatics could be increased compared to reaction conducted in the fixed-bed reactor, 10% more coke was formed than the fixed-bed reactor. Removal of H₂ by a membrane resulted in accelerated coking on a catalyst. Microwave-assisted reactors were developed using a SiC monolith coated with Mo/zeolite catalysts. The catalysts could be selectively heated under microwave irradiation, and a gas-solid temperature gradient was established that prevents the formation of coke from aromatics in the gas phase. Solid super acid catalysts were also examined by several groups. Oligomerization of CH₄ was reported at temperatures as low as 200 °C over an AlBr₃/zeolite catalyst. However, further development is required for industrial adoption of nonoxidative CH₄ aromatization.

This study focused on the development of aromatics-selective membranes. Aromatic hydrocarbons are not only the desired products but also the precursors of...
Ionic liquids (ILs) are organic molten salts with superior physical and chemical properties, such as low volatility, thermal stability and ability to dissolve CO2 and a large range of organic molecules24),25). By utilizing these features, ILs have been widely studied in the membrane separation process for various gases and vapors such as CO226), N2 adsorption measurement, gas/vapor permeation tests and 7.5 mL of NH3 aqueous solution (1 mol/L, FUJIFILM Wako Pure Chemical Corp.), and dried under vacuum at 40 °C. The precipitate (KCl) was washed 5 times with diethyl ether (FUJIFILM Wako Pure Chemical Corp., extraction grade) and dried under vacuum to remove dichloromethane, and then the obtained solution was dried under vacuum to remove acetonitrile. For further purification, the obtained SipbenzylimTf2N was dissolved in dichloromethane and an appropriate amount of water was added to remove unreacted SipbenzylimCl as well as remaining KCl and KTf2N. This procedure was repeated 10 times. Dehydration was conducted by adding an appropriate amount of magnesium sulfate, and the added magnesium sulfate was removed by filtration. Finally, the obtained solution was dried under vacuum to remove dichloromethane, and obtained purified SipbenzylimTf2N. Mass spectrometry (JEOL Ltd., JMS-700) and ATR-IR (Shimadzu Corp.), and IRaffinity-1S) characterizations were performed to confirm the structure of the resulting SipbenzylimTf2N (Fig. S2). Mass spectrometry confirmed that Cl anion could not be detected from purified SipbenzylimTf2N.

2.2. Preparation of SipbenzylimTf2N-derived Organosilica Sol and Membrane

A mixture of synthesized SipbenzylimTf2N (0.1 mol), ethanol (25 mL, FUJIFILM Wako Pure Chemical Corp.), and 7.5 mL of NH3 aqueous solution (1 mol/L, Kanto Chemical Co., Inc.) was stirred at 20 °C for 24 h, to obtain SipbenzylimTf2N-derived organosilica sol.

The SipbenzylimTf2N-derived organosilica membrane was formed on a nanoporous Al2O3 tube by a sol-gel method. Firstly, a γ-Al2O3 layer was formed on an α-Al2O3 porous tube (purchased from Noritake Co., Ltd.) with a length of 30 mm, a diameter of 10 mm, a thickness of 1 mm and a pore size of 150 nm. The tube was coated twice with a boehmite/polyvinyl alcohol sol, and calcined at 500 °C, resulting in the γ-Al2O3 layer with a pore diameter of 7 nm. The boehmite solution was supplied by Kawaken Fine Chemicals Co., Ltd. The pore size of the γ-Al2O3 layer was determined by a nanopermporometry method (Fig. S3). The permeances of H2 through the nanoporous Al2O3 tube was 2.2 × 10-6 mol m2 s-1 Pa-1. The organosilica membrane was prepared by dip-coating of the SipbenzylimTf2N-derived sol on the supported γ-Al2O3 tube.
followed by heating at 180 °C for 3 h.

For comparison, a SILM was also prepared using IL, 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (benzylimimTf2N, io-li-tec, > 98 %). A polyvinylidene difluoride (PVDF) membrane with a diameter of 47 mm, an average pore size of 0.2 μm and a typical thickness of 127 μm (Pall, FluoroTrans® PVDF membrane) was employed as a support. The PVDF membrane was impregnated with 0.5 mL of benzylimimTf2N for 5 min. After complete impregnation, the excess IL was removed from the surface of membrane using KimTowel.

2.3 Characterization of SipbenzylimTf2N-derived Gel and Membrane

ATR-IR characterizations were performed to identify the structural changes between as-made SipbenzylimTf2N and SipbenzylimTf2N-derived organosilica gel. The gel was obtained by hydrolysis and condensation after thermal treatment at 180 °C. Sorption isotherms of toluene vapor and methane were measured on the organosilica gel at 25 °C using the BELSORP-max (MicrotracBEL Corp.). To discuss the membrane’s structure, we measured N2 adsorption isotherms of the Sipbenzylim-derived organosilica gel and silica powder using the BELSORP-max. The SipbenzylimTf2N-derived silica powder was obtained by removing the IL group through high temperature calcination treatment. The preparation procedure is described below. Si substrate was coated with the SipbenzylimTf2N-derived sol, followed by calcination at 500 °C under O2 flow. In addition, the SipbenzylimTf2N membrane was characterized by nanopermporometry for evaluation of the structure and permeation mechanism. Hydrogen and n-hexane were used as the non-condensable and condensable components, respectively. The characterization was conducted at 22 °C. Scanning electron microscopy (SEM) and an energy dispersive X-ray spectrometry (EDS) were performed with JEOL JCM-6000Plus/JED-2300 Analysis Station Plus on membrane cross-sections to examine the thickness of prepared membranes.

2.4 Gas and Vapor Permeation Tests

The performance of the SipbenzylimTf2N membrane was characterized by single gas permeation and toluene/CH4 mixture separation. A schematic diagram of the separation test apparatus is shown in Fig. S4. The membrane was held in a membrane module for a tubular type membrane with cylindrical O-rings. The effective membrane area of the organosilica membrane was 6.28 cm². The permeation performance of the membrane was evaluated using permeance (mol m⁻² s⁻¹ Pa⁻¹), permeability (mol m⁻² s⁻¹ Pa⁻¹) and separation factor. The separation factor was calculated as the ratio of permeances. The detection limit was 10⁻¹² mol m⁻² s⁻¹ Pa⁻¹. Single gas permeation tests were conducted at 50 °C, with the feed side pressure maintained at 150 kPa. Various gases with different kinetic diameters were measured as follows: H2 (0.289 nm), CO2 (0.33 nm), CH4 (0.38 nm) and SF6 (0.55 nm). Separation tests for the toluene/CH4 mixture were conducted at temperatures ranging from 50 to 170 °C. Total feed side pressure was maintained at atmospheric pressure. CH4 gas was passed through toluene to make the binary mixture gas, with partial pressure of toluene of 3.4 kPa. The permeate gases and vapors were carried on He or N2 flows. The total pressure on the permeate side was kept constant at atmospheric pressure. The permeated stream was analyzed by gas chromatography with a thermal conductivity detector (Shimadzu GC-8A). The flow rate of permeate gas was calculated using the relational expressions of GC peak areas and flow rate ratios of the objective gases and carrier gases.

3. Results and Discussions

3.1 Membrane Morphology

The cross-sectional SEM images and EDS chemical maps for Al and Si atoms of the SipbenzylimTf2N membrane are shown in Fig. 1. Color changes in the chemical maps represent the concentration ratio of each atom. Al and Si atoms were highly detected in the light color regions. The results indicated that the silylated IL formed a composite layer with the γ-Al₂O₃.
The total thickness of SipbenzylimTf₂N-derived layer including the composite layer was about 5 μm.

3.2. Microstructure and Permeation Mechanism of SipbenzylimTf₂N Membrane

Toluene vapor and CH₄ sorption of the SipbenzylimTf₂N-derived organosilica gel were measured at 25 °C prior to membrane preparation and evaluation. The gel showed selective sorption of toluene vapor against CH₄ (Fig. 2). CH₄ is significantly less soluble in ILs compared with other hydrocarbons.²⁵ The IL molecular structure was chemically stabilized on the silica network in the SipbenzylimTf₂N-derived gel. Although the organosilica gel has different structure from standard ILs, the SipbenzylimTf₂N-derived gel showed IL-like properties.

Permeances of gases and toluene vapor through the SipbenzylimTf₂N membrane at 50 °C are plotted as a function of kinetic diameter of molecules in Fig. 3. The toluene permeance was 8.7 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹, a higher value than those of gases, regardless of kinetic diameter. As expected from the sorption result, the membrane showed selective permeation of toluene against CH₄. The SipbenzylimTf₂N membrane achieved a toluene/CH₄ selectivity of 13. Porous membranes such as zeolite, silica and carbon membranes have been developed as molecular sieve-based membranes. Small molecules selectively permeate through these membranes. On the other hand, such membranes also show reverse-selectivity, in which larger molecules selectively permeate through the membranes. Separation properties of several zeolite membranes were evaluated in a binary methanol/H₂ mixture system.⁵¹,⁵² Hydrogen permeation through FAU-type and NaZSM-5 zeolite membranes was decreased in the presence of methanol. Preferential adsorption of methanol in the micropores of zeolite hindered the permeation pathways of H₂. Consequently, these zeolite membranes showed reverse-selectivity. Similar permeation and separation properties have been reported for silica membranes.⁵³ However, the value of CH₄ permeance did not change significantly in the presence of toluene. Selective permeation of toluene against CH₄ through the membrane could not be explained by only the preferential adsorption/pore blocking effect.

The ATR-IR spectra of as-made SipbenzylimTf₂N and IL after hydrolysis and thermal treatment are compared in Fig. S5. A peak at 960 cm⁻¹ is assigned to the ethoxy group.⁵⁴,⁵⁵ Additionally, the peak of the Si-O-Si band (1130 cm⁻¹)⁵⁶ appeared after the treatments, indicating that SipbenzylimTf₂N molecules were well hydrolyzed, and the organosilica network was formed via cross-linking of the hydrolyzed IL molecules. N₂ adsorption measurements were also performed to investigate the microstructure of the SipbenzylimTf₂N membrane. The SipbenzylimTf₂N-derived gel did not adsorb N₂ molecules like CH₄ molecules, but the SipbenzylimTf₂N-derived silica powder, obtained by removing the IL group through calcination treatment, adsorbed N₂ molecules (Fig. 4). Pore size distribution was calculated from the isotherms by the SF method. The silica powder had less than 1 nm-sized pores. The pore size distribution of the membrane was not equal to that of the SipbenzylimTf₂N-derived silica powder because of the difference in thermal treatment temperature. These results indicate that the SipbenzylimTf₂N membrane has micropores derived from the organosilica network like other molecular sieve-organosilica membranes, but the micropores are covered and/or occupied by the branched IL. The outer surface of the SipbenzylimTf₂N membrane is covered
Gas and vapor molecules dissolve in the membrane, and diffuse through the membrane, resulting in the SILM-like properties. Thus, the selective permeation of toluene against CH$_4$ through the SipbenzylimTf$_2$N membrane resulted from the difference in solubility of toluene and CH$_4$ in the IL.

The structure of the SipbenzylimTf$_2$N membrane is close to those of mixed-matrix membranes. The membrane has two types of permeation pathways; gas and vapor molecules diffuse through (1) only the dense IL regions and (2) both the micropores and the dense IL regions. The permeation mechanism of the former pathway involves the solution-diffusion mechanism as well as SILMs. The permeation mechanism of the latter permeation pathways is similar to porous membranes, including surface diffusion flow and Knudsen diffusion flow. Nanopermporometry was performed for further characterization of the permeation mechanism and microstructure of the SipbenzylimTf$_2$N membrane.

Nanopermporometry is an effective method to evaluate active pores, which contribute to the permeability of porous membranes. In this study, H$_2$ permeance was monitored in the presence of capillary condensation of $n$-hexane vapor. Figure 5 shows the dimensionless permeance of H$_2$ as a function of the Kelvin diameter. The H$_2$ permeance through the organosilica membrane sharply decreased with Kelvin diameter less than 1 nm, suggesting that SipbenzylimTf$_2$N contained about 1 nm-sized micropores. Nanopermporometry can detect the preferential adsorption/pore blocking effect, but this effect was not observed in the toluene/CH$_4$ separation test (Fig. 3). Prominent differences in the capillary condensation/pore blocking effect of $n$-hexane and toluene may be due to the difference in permeation temperature. Capillary condensation of toluene would not occur in the micropores due to the higher temperature.

The result of nanopermporometry agreed with that of N$_2$ adsorption for the SipbenzylimTf$_2$N-derived silica powder. Although the H$_2$ permeance decreased with higher Kelvin diameter, the value did not decrease to “zero” with Kelvin diameter of about 24 nm. About 22 % of H$_2$ permeance (= 3.3 $\times$ 10$^{-10}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$) was still observed. In this study, the organosilica membrane was prepared on the $\gamma$-Al$_2$O$_3$ layer, with pore size of 7 nm determined by nanopermporometry (Fig. S3). Therefore, the SipbenzylimTf$_2$N membrane would not possess 24 nm-sized pores. As mentioned above, we concluded that the organosilica membrane has two types of permeation pathways; gas and vapor molecules diffuse through (1) only the dense IL regions and (2) both the micropores and the dense IL regions. The latter permeation pathway would be blocked by condensation of $n$-hexane in the pores.
above results, we considered that 78 % of H₂ molecules would permeate through pathway-2 (both micropores and dense IL regions), and the remaining 22 % of H₂ molecules would permeate through pathway-1 (only dense IL regions) by the solution-diffusion mechanism.

To assess the adequacy of the estimated H₂ permeance, H₂ permeability through the SipbenzylimTf2N membrane was compared with that for the benzylmimTf2N/PVDF membrane. The benzylmimTf2N/PVDF membrane was a typical SILM prepared by the impregnation method, and H₂ permeation through the membrane depends on the solution-diffusion mechanism. Due to its similar molecular structure with SipbenzylimTf2N, benzylmimTf2N was selected as for comparison in this study. Membrane thickness and H₂ permeability of both membranes are summarized in Table 1. The values of estimated H₂ permeability of the organosilica membrane through permeation pathway-2 was of the same order as that of the SILM, indicating that 22 % of H₂ molecules permeated through the dense IL regions in the SipbenzylimTf2N membrane through the solution-diffusion mechanism. Therefore, nanopermporometry could successfully evaluate the micropore size in the silylated IL-derived organosilica membrane, and the contributions of the two permeation pathways to gas permeation.

3.3. Separation Performance of SipbenzylimTf2N Membrane

The temperature dependence of the permselectivity of the organosilica membrane in the toluene/CH₄ binary mixture system is shown in Fig. 6. The partial pressure of toluene in the feed stream was 3.4 kPa in these tests. The maximum toluene/CH₄ separation factor of 13 was obtained at 50 °C. The toluene and CH₄ permeances were 8.7 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹ and 6.6 × 10⁻¹¹ mol m⁻² s⁻¹ Pa⁻¹, respectively. Both permeances increased with higher temperature, and the rate of CH₄ permeance increased faster than that of toluene permeance. As a result, the separation performance of the SipbenzylimTf2N membrane decreased with higher temperature. However, the membrane still showed selectivity of 4.8 toward toluene against CH₄ at temperatures up to 170 °C. The Arrhenius equation was adapted to calculate the activation energies of permeation (Eₚ,i) through the organosilica membrane in the temperature range from 110 to 170 °C. The Eₚ,i value of toluene (8.1 kJ/mol) was smaller than that of CH₄ (29 kJ/mol), regardless of the higher molecular weight and size. These results suggest that the branch ILs in

| Membrane                        | Membrane thickness [µm] | H₂ permeability [mol m⁻² s⁻¹ Pa⁻¹] |
|---------------------------------|-------------------------|-----------------------------------|
| SipbenzylimTf2N-derived organosilica | 5                       | 1.6 × 10⁻¹⁵                      |
| BenzylmimTf2N/PVDF              | 127                     | 3.2 × 10⁻¹⁵                      |
was performed at 150 °C. The SipbenzylimTf2N membrane could stably separate toluene from CH4 for 3 h.

This investigation of the application of IL-based membranes for separation of aromatics and CH4 found that silylated IL-derived organosilica membrane is promising for selective recovery of aromatic hydrocarbons from CH4.

4. Conclusions

A silylated IL, SipbenzylimTf2N-derived organosilica membrane was fabricated on porous Al2O3 substrate by the sol-gel method. The permselectivity in binary toluene/CH4 mixture system, and ATR-IR, N2 adsorption and nanopermoporometry were performed to evaluate the microstructure and permeation mechanism of the organosilica membrane. These characterizations revealed that the membrane depended on two permeation pathways, “only the dense IL regions” and “organosilica network-derived micropores + dense IL regions.” Nanopermoporometry revealed that the Sipbenzylim Tf2N membrane contained about 1 nm-sized pores, and successfully evaluated the contribution of the two permeation pathways to gas permeation. The results indicated that about 80 % of H2 molecules permeated through “both dense IL regions and micropores,” and the remaining 20 % molecules permeated through only dense IL regions through the solution and diffusion mechanism. These findings of detailed microstructure and permeation mechanism will be useful for the future design of silylated-IL derived organosilica membranes.

The organosilica membrane showed selectivity for toluene against CH4 at low concentration of toluene in the feed streams and high temperature up to 170 °C. The separation tests showed that silylated-IL derived organosilica membranes are promising membranes for the selective recovery of aromatic hydrocarbons in the nonoxidative CH4 aromatization process. Improvements of thermal stability and permselectivity at high temperature are future challenges.

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Supporting Information

Supplementary data associated with this article can be found, in the online version, at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.63.213).

References

1) Wang, L., Tao, L., Xie, M., Xu, G., Huang, J., Xu, Y., Catal. Lett., 21, 35 (1993).
2) Hagen, A., Roessner, F., Catal. Rev.-Sci. Eng., 42, 403 (2000).
3) Ma, S., Guo, X., Zhao, L., Scott, S., Bao, X., J. Energy Chem., 22, 1 (2013).
4) Sun, K., Ginosar, D. M., He, T., Zhang, Y., Fan, M., Chen, R., Ind. Eng. Chem. Res., 57, 1768 (2018).
5) Velebná, K., Horúček, M., Jorík, V., Hudec, P., Čaplovičová, M., Čaplovíč, L., Micropor. Mesopor. Mater., 212, 146 (2015).
6) Morejudo, S. H., Zanon, R., Escolastico, S., Yuste-Tirados, I., Malerod-Fjeld, H., Vestre, P. K., Coors, W. G., Martinez, A., Norby, T., Serra, J. M., Kjolseth, C., Science, 353, 563 (2016).
7) Gao, K., Yang, J., Seidel-Morgenstern, A., Hamel, C., Chem. Eng. Tech., 88, 168 (2016).
8) Xue, J., Chen, Y., Wei, Y., Feldhoff, A., Wang, H., Caro, J., ACS Catal., 6, 2448 (2016).
9) Kee, B., Karakaya, C., Zhu, H., DeCaluwe, S., Kee, R. J., Ind. Eng. Chem. Res., 56, 3551 (2017).
10) Julian, I., Ramirez, H., Hueso, J. L., Mallada, R., Santamaria, J., Chem. Eng. J., 377, 119764 (2019).
11) Rezgui, S., Liang, A., Cheung, T.-K., Gates, B. C., Catal. Lett., 53, 1 (1998).
12) Hua, W., Goeppert, A., Sommer, J., Appl. Catal. A: Gen., 219, 206 (2001).
13) Martins, R. L., Schmal, M., Appl. Catal. A: Gen., 308, 143 (2006).
14) Kanitkar, S., Carter, J. H., Hutchings, G. J., Ding, K., Spivey, J. S., ChemCatChem, 10, 5019 (2018).
15) Deng, S., Liu, T., Sourirajan, S., Matsuura, T., Farnard, B. A., J. Polyommer Eng., 14, 219 (1995).
16) Cha, J., Malik, V., Bhaanick, D., Li, R. H., Sirkar, K. K., J. Membr. Sci., 128, 195 (1997).
17) Sohn, W.-I., Ryu, D.-H., Oh, S.-J., Koo, J.-K., J. Membr. Sci., 175, 163 (2000).
18) Yang, W., Zhou, H., Zong, C., Li, T., Jin, W., Sep. Purif. Technol., 200, 273 (2018).
19) Aguado, S., Polo, A. C., Bernal, M. P., Coronas, J., Santamaria, J., J. Membr. Sci., 240, 159 (2004).
20) Sui, G., Li, J., Ito, A., Sep. Purif. Technol., 68, 283 (2009).
21) Ozturk, B., Kuru, C., Aykac, H., Kaya, S., Sep. Purif. Technol., 153, 1 (2015).
22) Hirota, Y., Maeda, Y., Furusawa, T., Nishiyama, N., Ito, A., AIChE J., 62, 624 (2016).
23) Ranjbaran, F., Kamio, E., Matsuyma, H., Sep. Purif. Technol., 53, 2840 (2018).
24) Camper, D., Becker, C., Koval, D., Noble, R., Ind. Eng. Chem. Res., 44, 1928 (2005).
25) Lei, Z., Dai, C., Chen, B., Chem. Rev., 114, 1289 (2014).
26) Scovazzo, P., Kief, J., Finan, D. A., Koval, C., DuBois, D., Noble, D. R., J. Membr. Sci., 338, 57 (2004).
27) Bara, J. E., Lessmann, S., Gabriel, C. J., Hatakeyama, E. S., Norby, D. R., Gin, D. L., J. Membr. Sci., 238, 159 (2004).
28) Scovazzo, P., Kieft, J., Finan, D. A., Koval, C., DuBois, D., Noble, D. R., J. Membr. Sci., 338, 57 (2004).
29) Won, J., Kim, D. B., Kang, Y. S., Choi, D. K., Kim, H. S., J. Jpn. Petrol. Inst., Vol. 63, No. 4, 2020
要 旨
シリル化イオン液体由来オルガノシリカ膜によるトルエン／メタン分離とその透過機構解析

大阪大学大学院基礎工学研究科化学生命工学専攻, 560-8531 大阪府豊中市待兼山町1-3

ノルゲル法により多孔質アルミナ支持体上にシリル化イオン液体由来オルガノシリカ膜を作製し、様々な温度でのトルエン／メタン混合系での透過分離能を評価した。作製した膜は170 ℃の高温下においてもメタンに対してトルエン選択透過性を示すと同時に、150 ℃において3時間、メタンからトルエンを分離する安定性を示した。膜の選択透過性はイオン液体への透過分子の親和性差により発現していることが明らかとなった。これらの結果から、シリル化イオン液体由来オルガノシリカ膜はメタンから芳香族炭化水素を選択的に回収する分離膜として有望な選択膜の一つといえる。同時に、開発した膜の構造と透過分離機構の解明を目的として、ATR-IR、窒素吸着およびナノバームポロメトリー評価を行った。これらの評価から、当該分離膜には「イオン液体密度部のみ」と「シリカネットワーク由来ミクロ孔＋イオン液体密度部」の二つの透過経路の存在が明らかとなった。開発したオルガノシリカ膜には約1 nmのミクロ孔が存在し、ガス透過における二つの透過経路の寄与率を評価することに成功した。