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SEPARATION SCIENCE AND TECHNOLOGY, 37(5), 1031–1039 (2002)

SEPARATION OF NITROGEN FROM OXYGEN USING A TITANOSILICATE MEMBRANE PREPARED ON A POROUS α-ALUMINA SUPPORT TUBE

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ABSTRACT

A zeolite membrane was formed on a porous α-alumina support tube by hydrothermal reaction using a solution which was appropriate for the synthesis of ETS-4 zeolite. The morphology and x-ray diffraction pattern of the top surface of the support tube were consistent with those of the ETS-4 zeolite. The permeances to single-component H_2, CO_2, O_2, N_2, and CH_4 were in the range $(0.8–2.5) \times 10^{-8}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$, while those to *n*-$C_4H_{10}$ and *iso*-C_4H_{10} were less than $10^{-11}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$. This suggests that the membrane functioned as a molecular sieve with pores smaller than 0.4 nm. At a permeation temperature of 310K, the ideal N_2/O_2 separation factor was 2.8, and the N_2/O_2 separation factor was 2.3 and 3.2 for a mixture of $N_2/O_2 = 1$ and 4, respectively. Thus, the membrane is nitrogen-selective and can be used to enrich the oxygen level in air, which is fed on the pressurized side, without much loss of compression energy.

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INTRODUCTION

A number of polyimide-based membranes and carbon membranes have been developed for the purpose of separating air, and such membranes show high O_2/N_2 separation factors at relatively high permeation rates (1). If the outlet flow (retentate flow) on the feed side at high pressure is used as the sweep flow on the permeate side at low pressure, the concentration of oxygen in the retentate flow can be decreased. If this procedure is repeated several times in a cascade operation, compressed oxygen-free nitrogen is produced at the outlet on the feed side. When compressed oxygen-enriched air is the desired product, on the other hand, a membrane whose N_2/O_2 separation factor is higher than unity is required. However, most solid-state membranes, which have been produced to date, are oxygen-selective, as reported by Koros and Mahajan (1).

A microporous zeolite-type titanium silicate ETS-4 [$Na_9Si_{12}Ti_5O_{38}(OH)\cdot 12H_2O$] was synthesized by Kuznicki (2). While the framework of A (LTA), ZSM-5 (FAU), and Y (MFI) zeolites is composed of tetrahedral units, the framework of ETS-4 is composed of corner-sharing SiO_4 tetrahedra and TiO_6 octahedra (3–8). It has been reported that the pore size of ETS-4 is 0.3–0.4 nm, and that ETS-4 is adsorptive to H_2O, N_2, NH_3, H_2S, and SO_2 and essentially nonadsorptive to molecules which are larger than 0.5 nm (2). These properties suggest that ETS-4 might be suitable for the separation of small-sized molecules.

Braunbarth et al. (9) fabricated ETS-4 membranes on different porous supports, and reported that an alumina-based support was not suitable, since aluminum was dissolved from the support, leading to poor reproducibility of the membrane properties. These investigators used a porous titania disc as the support, and applied the synthesized ETS-4 membrane to separate water from water–ethanol mixtures by a pervaporation technique. The water flux through the ETS-4 membrane was comparable to or higher than the water flux through A (LTA), X (FAU), and Y (FAU) zeolite membranes. However, the effect of the chemical composition of such porous supports on the permeation properties of membranes has not been investigated fully. Sasaki et al. (10) reported on a detailed study of the structure of a ZSM-5 (MFI) zeolite membrane, which had been formed in the macropores of a porous α-alumina support. High-resolution transmission electron microscopy (TEM) images showed that crystal grains of the zeolite were connected directly to one another, as well as to the α-alumina grains, and that no grain boundary phases were evident. The Al/Si ratio in the zeolite, which was formed in the macropores, was different from that in the zeolite layer, which was formed on the outer surface of the support. These investigators suggested that some dissolution of aluminum from the support might play an important role in the densification of the zeolite grains.

Guan et al. (11) investigated N_2/O_2 separations using NaY-type zeolite membranes. High N_2/O_2 ideal separation factors were obtained when single-component N_2 and O_2 were fed, but the N_2/O_2 separation factor decreased in the case of mixed feeds. The N_2/O_2 separation through the NaY-type zeolite membranes is dependent largely on differences in the adsorptivity of N_2 and O_2 on the micropore walls. The effect of pore size is not a dominant factor, since the pores of NaY-type zeolite are much larger than the molecular sizes of N_2 and O_2. The ETS-4 zeolite possesses pores that are smaller than the Y-type zeolite and adsorbs N_2 to a greater extent than CH_4 (7). Thus the ETS-4 zeolite, which can adsorb N_2 over O_2, would be expected to be useful for the separation of N_2 from O_2. In the present study, a titanosilicate membrane was prepared on a porous α-alumina support tube via a hydrothermal synthesis using a solution which was used normally for the synthesis of ETS-4. The separation properties of the membrane were then investigated for mixtures of N_2 and O_2.

EXPERIMENTAL

The solution was prepared from water glass, titanium (IV) butoxide, sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2) (8). Titanium (IV) butoxide was added to the aqueous NaOH solution under stirring. The white precipitate was then dissolved by adding an aqueous solution of H_2O_2, resulting in a bright yellow solution. Water glass was then dissolved in this solution under stirring. The initial composition of the solution used for preparing the ETS-4 powder was $Ti : Si : Na : H_2O_2 : H_2O = 0.9 : 10 : 14 : 8 : 675$ on a molar basis. The hydrothermal synthesis was performed at 180°C for 72 hr in an autoclave. The powder was filtered, washed with deionized water, and dried at 40°C. The outer surface of a porous α-alumina support tube (NOK Corporation, Tokyo, Japan; outer diameter = 2.8 mm, inner diameter = 1.9 mm, average pore size = 150–170 nm) was rubbed with the prepared ETS-4 powder for purposes of seeding. The membrane was prepared using a solution which had an initial composition of $Ti : Si : Na : H_2O_2 : H_2O = 1.0 : 10 : 13 : 6 : 675$. The conditions for the membrane preparation were the same as those used for the powder preparation. The morphology of the membrane was observed by scanning electron microscopy (SEM, Hitachi Ltd, Tokyo, Japan, S-900). The crystal structure was determined by x-ray diffraction (XRD, Rigaku International Corporation, Tokyo, Japan, RINT-2500 KS), and an elemental analysis was obtained using an energy-dispersive x-ray analyzer (EDX, Kevex Delta Class). A gas permeation test was performed using single-components and binary mixtures of O_2 and N_2, as described in the literature (12). The partial pressure of the permeants on the permeate side was maintained below 1 kPa by varying the sweep flow rate. The total pressure on the feed and permeate sides was 101 kPa, and helium was used as the sweep gas on the permeate side in order to decrease the partial pressure of the permeants. The separation factor, α, was determined as the ratio of N_2 and O_2 permeances by neglecting the partial pressures of the permeants on the permeate side.

RESULTS AND DISCUSSION

The powder, which was synthesized by a reaction at 180°C for 72 hr, was composed of plate-like crystals (crystal length on the c-axis $= 15\,\mu$m) and globular particles (diameter $\sim 1\,\mu$m). The morphology of the crystals was similar to that reported by Braunbarth et al. (9). Fig. 1(a) shows the XRD pattern of the as-synthesized powder. By comparing with the XRD patterns reported by Philippou and Anderson (3), Fig. 1(b), and Braunbarth et al. (4), Fig. 1(c), the powder was identified as ETS-4. Figure 2 shows the outer surface and a fractured section of the membrane. The outer surface of the support tube was rubbed with the zeolite powder, but the inner surface was not. The outer surface was covered completely with plate-like crystals as shown in Fig. 2(a), but the inner surface

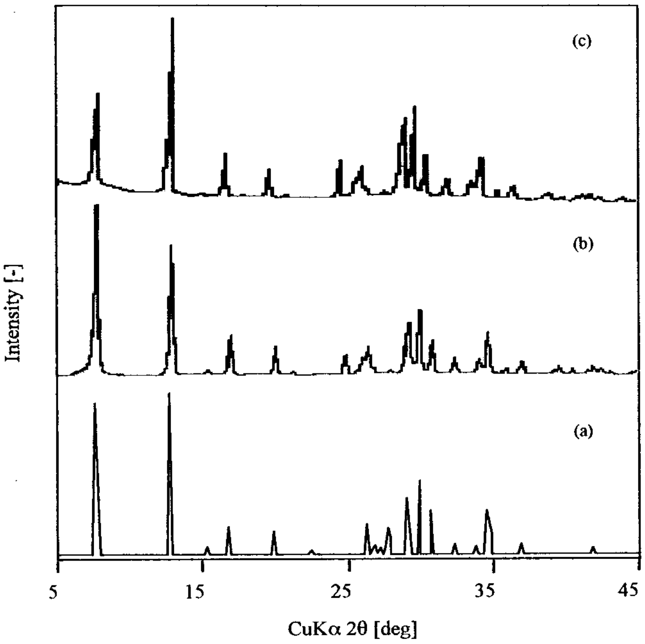
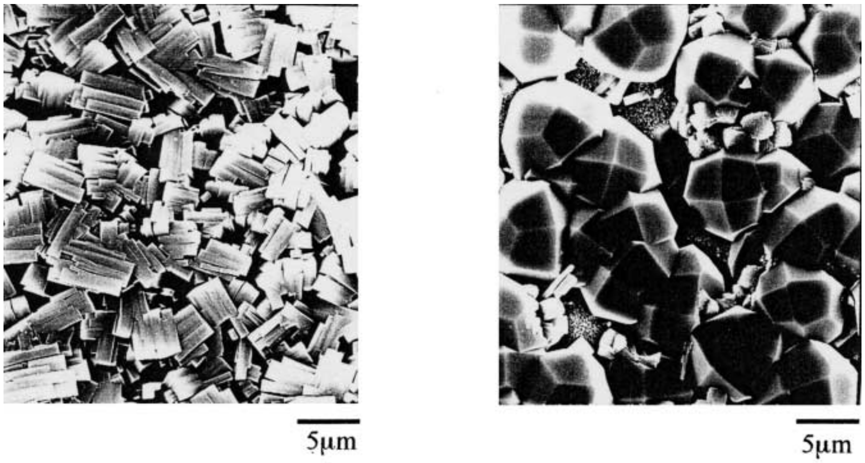
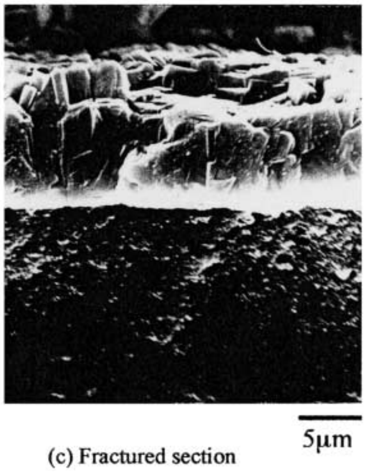


Figure 1. X-ray diffraction patterns of titanosilicate samples. (a) The sample obtained in this study; (b) Philippou and Anderson (3); (c) Braunbarth et al. (4).



(a) Outer surface (b) Inner surface



(c) Fractured section

Figure 2. The SEM images of the titanosilicate membrane: (a) outer surface; (b) inner surface; (c) fractured section.

was covered incompletely with large grains as can be seen in Fig. 2(b). The zeolite layer on the outer surface had an overall thickness of 10 μm, as shown in Fig. 2(c). However, the effective zeolite layer is estimated to be less than 5 μm in thickness, since the outer part of the layer contained a number of large defects. Figure 3 shows the EDX spectrum of the outer surface of the membrane. The atomic ratio is calculated to be Na : Si : Ti = 30 : 55 : 15, which is not greatly

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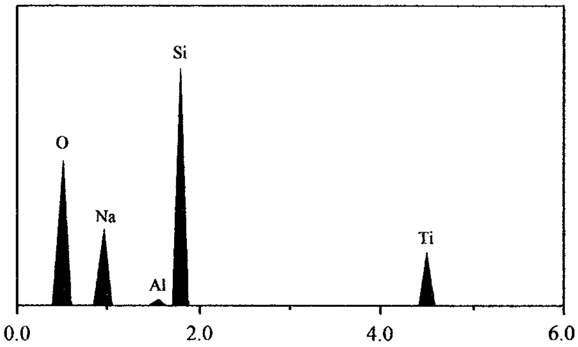

Figure 3. Elemental analysis of the outer surface of the membrane.

different from the ratio in the chemical form of ETS-4, Na : Si : Ti = 35 : 46 : 19. However, the dense layer, which was formed in the macropores of the support was not analyzed in the present study, and may have a different composition because of the solubilization of aluminum from the support.

Figure 4 shows the relationship between the permeances of the zeolite membrane and the kinetic diameters of the permeating gases. The data on kinetic diameters represent literature values (13). The permeation experiments were carried out at 310K, and the permeances to H_2, CO_2, O_2, N_2, and CH_4 were relatively high and in the range $(0.8\text{–}2.5) \times 10^{-8}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$.

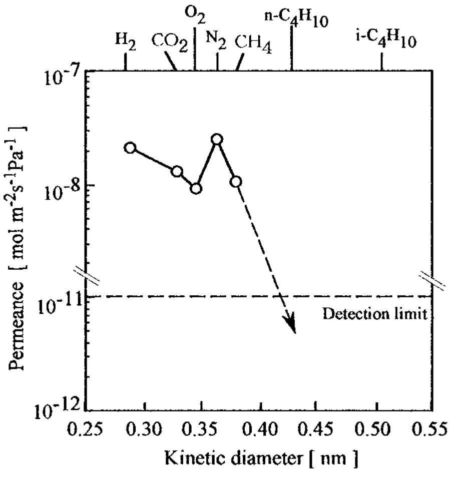

Figure 4. Permeances to single-component gases at 310K.

The concentration of n-C_4H_{10} and i-C_4H_{10} on the permeate side was below the detection limit, and their permeances were less than $10^{-11}\,\mathrm{mol\,m^{-2}\,sec^{-1}\,Pa^{-1}}$. Since the kinetic diameters of n-C_4H_{10} and i-C_4H_{10} are reported to be 0.43 and 0.50 nm, respectively, the pore size of the membrane is estimated to be less than 0.43 nm and roughly equivalent to the pore size of ETS-4 (ca. 0.4 nm). Permeance to N_2 was the highest of all the gases measured in the present study, and the ideal separation factors of N_2/O_2 and N_2/CH_4 were 2.8 and 2.1, respectively, at 310K.

Figure 5 shows the permeances through the membrane for single-component O_2 and N_2, as well as binary mixtures thereof at a permeation temperature of 310K. When the N_2/O_2 molar ratio in the mixed gas was 4, the N_2/O_2 separation factor was 3.2, which was larger than that for the single-component systems. Figure 6 shows the effect of permeation temperature on the permeances to N_2 and O_2. The permeances increase, and the N_2/O_2 separation factor decreases with increase in temperature, but the N_2/O_2 separation factor was as high as 1.6 at a permeation temperature of 330K. The NaY-type zeolite membranes, which were synthesized by Guan et al. (11), showed an N_2/O_2 ideal separation factor of 18.1 for single-component feeds. However, the separation factor decreased to 1.6 when an equimolar mixture of N_2 and O_2 was fed, and approached unity when a mixture of a molar ratio $N_2 : O_2 = 4 : 1$ was fed. The above results suggest that the high N_2/O_2 separation factor obtained in the present study might be the result of a combination of the adsorptivity of N_2 and the small pore size of the membrane.

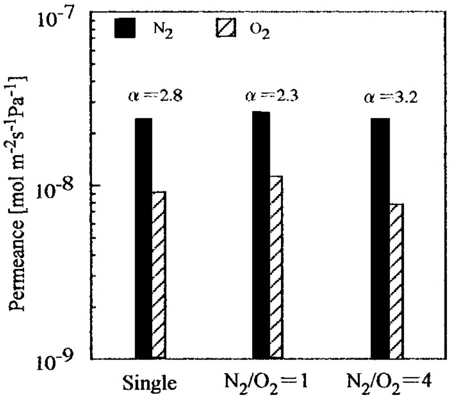

Figure 5. N_2/O_2 separation factor at 310K as a function of the N_2/O_2 ratio in the feed gas.

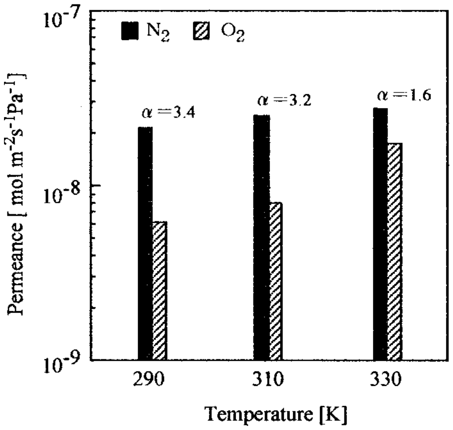

Figure 6. N_2/O_2 separation factor for the mixture of $N_2 : O_2 = 4 : 1$ as a function of permeation temperature.

CONCLUSIONS

A titanosilicate membrane, which was formed on a porous α-alumina support, showed an N_2/O_2 separation factor of 3.2 at 310K for a molar ratio of $N_2 : O_2 = 4 : 1$. This suggests that the membrane has the potential for producing oxygen-enriched air without totally losing the energy required for compression of the feed gas. However, the N_2 permeance of the prepared membranes was relatively low for practical use. Procedures for optimizing the preparation of thin, defect-free titanosilicate membrane are underway currently.

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REFERENCES

1. Koros, W.J.; Mahajan, R. Pushing the Limits on Possibilities for Large Scale Gas Separation: Which Strategies? J. Membr. Sci. **2000**, *175* (2), 181–196.

2. Kuznicki, S.M. Preparation of Small-Pored Crystalline Titanium Molecular Sieve Zeolite. US Patent 4,938,939, July 3, 1990.
3. Philippou, A.; Anderson, M.W. Structural Investigation of ETS-4. Zeolites **1996**, *16*, 98–107.
4. Braunbarth, C.; Hillhouse, H.W.; Nair, S.; Tsapatsis, M. Structural of Strontium Ion-Exchanged ETS-4 Microporous Molecular Sieves. Chem. Mater. **2000**, *12*, 1857–1865.
5. Valtchev, V.; Mintova, S.; Mihailova, B.; Konstantinov, L. Comparison of Physicochemical Properties of Zorite and ETS-4. Mater. Res. Bull. **1996**, *31* (2), 163–169.
6. Cruciani, G.; De Luca, P.; Nastro, A.; Pattison, P. Rietveld Refinement of the Zorite Structure of ETS-4 Molecular Sieves. Microporous Mesoporous Mater. **1998**, *21*, 143–153.
7. Kuznicki, S.M.; Bell, V.A.; Petrovic, B.T.; Desai, B.T. Small-Pored Crystalline Titanium Molecular Sieve Zeolites and Their Use in Gas Separation Processes. US Patent 6,068,682, May 30, 2000.
8. Bal, R.; Chaudhari, K.; Srinivas, D.; Sivasanker, S.; Ratnasamy, P. Redox and Catalytic Chemistry of Ti in Titanosilicate Molecular Sieves: an EPR Investigation. J. Mol. Catal. A: Chem. **2000**, *162*, 199–207.
9. Braunbarth, C.M.; Boudreau, L.C.; Tsapatsis, M. Synthesis of ETS-4/TiO_2 Composite Membranes and Their Preparation Performance. J. Membr. Sci. **2000**, *174* (1), 31–42.
10. Sasaki, Y.; Shimizu, W.; Ando, Y.; Saka, H. Microstructure Analysis with TEM for Zeolite Layer Formed in Pore of Porous Alumina Substrate. Microporous Mesoporous Mater. **2000**, *40* (1), 63–71.
11. Guan, G.Q.; Kusakabe, K.; Morooka, S. Separation of N_2 from O_2 and Other Gases Using FAU-Type Zeolite Membranes. J. Chem. Eng. Jpn. **2001**, *34* (8), 990–997.
12. Kusakabe, K.; Kuroda, T.; Murata, A.; Morooka, S. Formation of a Y-Type Zeolite Membrane on a Porous α-Alumina Tube for Gas Separation. Ind. Eng. Chem. Res. **1997**, *36* (2), 649–655.
13. Breck, D.W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974; 636.

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