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Trial for Preparation of Glass Capillary Membranes by Elution of Alkali Metal Ions

K. KURAOKA*
OSAKA NATIONAL RESEARCH INSTITUTE
AIST
MIDORIGAOKA, IKEDA CITY, OSAKA 563, JAPAN

Z. QUN
NANJING FIBERGLASS RESEARCH & DESIGN INSTITUTE
INORGANIC MATERIALS SCIENCE SUB-INSTITUTE
ANDELI, WEST YUHUA ROAD, NANJING 210012, PEOPLE'S REPUBLIC OF CHINA

K. KUSHIBE
AKAGAWA KOSHITU GLASS KOGYOSHO CO.
IKUE, ASAHI-KU, OSAKA 535, JAPAN

T. YAZAWA
OSAKA NATIONAL RESEARCH INSTITUTE
AIST
MIDORIGAOKA, IKEDA CITY, OSAKA 563, JAPAN

ABSTRACT

The gas separation characteristics of ultramicroporous glass capillary membranes were investigated. Glass capillary membranes which had ultramicropores (pore diameter less than 1 nm) were prepared by elution of alkali metal ions from glass capillaries. It was found from elution treatment that alkali metal ions of 3.5 Na (composition: 77.8 SiO_2, 22.2 Na_2O mol%) and 3.5 K (composition: 77.8 SiO_2, 22.2 K_2O mol%) glass capillaries were completely eluted after 90 and 10 minutes with 3 mol/L HNO_3, 240 and 10 minutes with 3 mol/L CH_3COOH and 3 mol/L H_3PO_4, respectively. Permeations of N_2, He, and CO_2 were measured at 298, 373, and 473 K. Permeation rates of the 3.5 Na and 3.5 K glass capillary membranes were $1–10^{-1}$ ($cm^3(STP)\cdot cm^{-2}\cdot s^{-1}\cdot cmHg^{-1}$). The ratios of permeation rates, CO_2/N_2 and He/N_2, were similar to the theoretical Knudsen values.

* To whom correspondence should be addressed.

Key Words. Glass capillary membranes; Elution of alkali metal ion; Gas separation; Ultramicro porous membranes; Inorganic membranes

INTRODUCTION

Due to their stability in organic solvents and at high temperatures, inorganic membranes recently attracted the attention of many investigators and much research has been done. In particular, glass membranes show promise because they can be shaped into glass capillaries. The glass capillary shape has the following advantages: 1) A large membrane area may be obtained for a small module size, 2) there is flexibility, and 3) the high shaping rate permits the mass production of glass capillary membranes without difficulty.

Ma et al. (1) and Way et al. (2) reported microporous glass hollow fiber membranes which had high selectivities for gases. It was proposed that the transport mechanisms of these membranes were mainly surface flow and molecular sieving. However, the composition of the glass and the formation process of the ultramicropores were not investigated.

It is well known that alkali metal ions in glass are easy to diffuse compared with other metal ions (for example, Al^{3+} and B^{3+}) (3), and they are easily eluted by water and acid solution. It can be considered that pores made by elution of alkali metal ions are ultramicropore.

In this paper, glass capillary membranes with ultramicropores (pore diameter of less than 1 nm) were prepared by elution of alkali metal ions. We try to explain the formation of micropores in terms of elution of alkali metal ions from glass capillaries. We also report gas separation characteristics.

EXPERIMENTAL

Preparation of Glass Capillary Membrane

Glass capillary membranes with an outer diameter of 0.30 mm and an inner diameter of 0.24 mm were made from glass capillaries. The glass capillaries were prepared as follows. First, glass tubes which had an outer diameter of 5 mm and inner diameter of 4 mm were made of glass melts. Second, the glass tubes were shaped into glass capillaries by redrawing. The glass capillaries compositions of 3.5 Na and 3.5 K are 3.5 $SiO_2 \cdot Na_2O$ and 3.5 $SiO_2 \cdot K_2O$, respectively. The glass capillaries were cut to approximately 100 mm lengths. Then they were immersed in solutions of 3 mol/L HNO_3, 3 mol/L CH_3COOH, and 3 mol/L H_3PO_4 at 371 K for a certain time until the alkali metal ions were completely eluted. After that, they were washed with distilled water and dried at room temperature.

In order to determine when the alkali metal ions were completely eluted, a portion of the acid solutions in which the glass capillaries were immersed was removed at certain time intervals and the Na^+ or K^+ concentrations were measured with an atomic absorption/flame emission spectrophotometer (Shimadzu AA-180, Shimadzu). Inductively coupled plasma spectrometry (ICP spectrometry: SPS-1200, Seiko) was used to detect the elution of Si ion when the alkali ions were completely eluted.

Pore Size Measurement

Samples were prepared as described above. The specific surface areas and the pore size distribution of samples were measured by nitrogen adsorption (Belsorp 28, Bel Japan Inc.). The specific surface areas were determined by BET plots (4), and the pore size distributions were analyzed by MP methods (5).

Measurement of Gas Permeation

Single gas permeations of the membranes were measured using He, N_2, and CO_2 by a procedure described previously (6). One side of the capillary membranes was sealed and the other side was connected to a Pyrex glass tube with epoxy resin. This membrane were supported in a gas flow cell. The pressure difference of the gases through the membranes was kept at 1 atm (1 atm $= 1.013 \times 10^5$ Pa), and the permeation rates at 298, 373, and 473 K were measured with a mass flow meter.

RESULTS AND DISCUSSION

Elution Rates of Alkali Metal Ions

In an alkali-silicate glass, alkali metal ions are located between SiO_2 networks as shown in Fig. 1 (7). The ionic crystal radii of Na^+ and K^+ are 0.102 and 0.155 nm, respectively (8). In an acidic solution, H^+ ions diffuse into the glass and replaced the alkali metal ions. Alkali ions are also easily moved in glass, and therefore they are eluted in solution and create pores whose diameters are about the diameter of alkali metal ions.

The elution rates of alkali metal ions from 3.5 Na glass capillaries are shown in Fig. 2, and those of the 3.5 K glass capillaries are shown in Fig. 3. Alkali metal ions of the 3.5 Na and 3.5 K glass capillaries were completely eluted after 90 and 10 minutes with 3 mol/L HNO_3, and 240 and 10 minutes with 3 mol/L CH_3COOH and 3 mol/L H_3PO_4, respectively. The elution rates of the 3.5 K glass capillaries were much faster than those

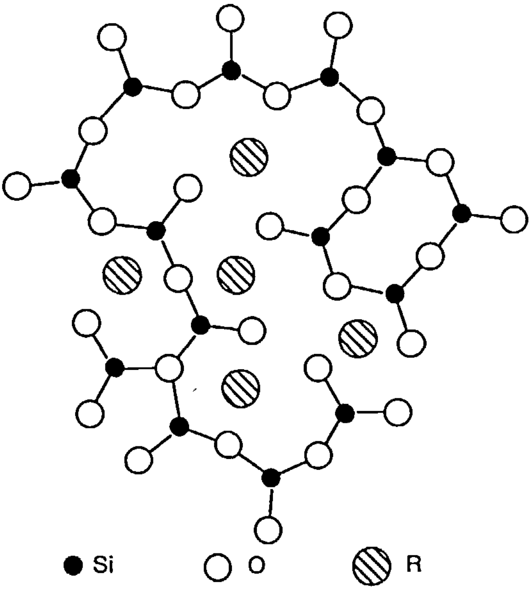

FIG. 1 Schematic representation of the structure of alkali-silicate glass.

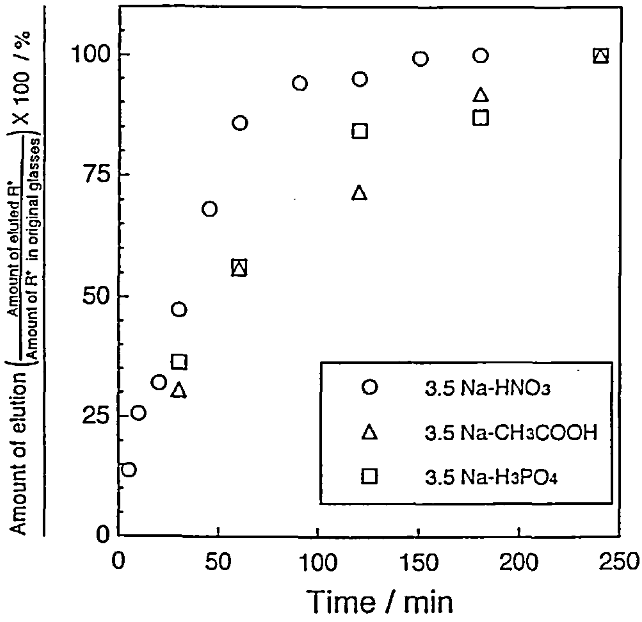

FIG. 2 Elution rate of Na^+ from the 3.5 Na glass capillaries eluted with 3 mol/L HNO_3 (3.5 Na-HNO_3), 3 mol/L CH_3COOH (3.5 Na-CH_3COOH), and 3 mol/L H_3PO_4 (3.5 Na-H_3PO_4).

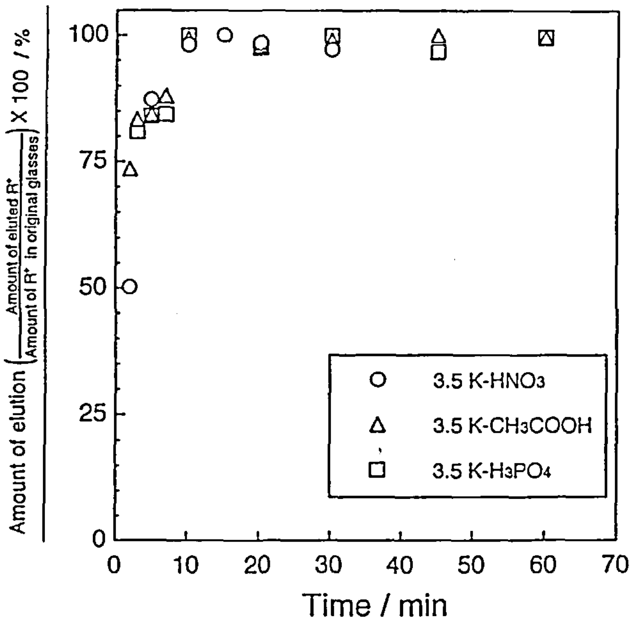

FIG. 3 Elution rate of K^+ from the 3.5 K glass capillaries eluted with 3 mol/L HNO_3 (3.5 K-HNO_3), 3 mol/L CH_3COOH (3.5 K-CH_3COOH), and 3 mol/L H_3PO_4 (3.5 K-H_3PO_4).

of the 3.5 Na capillaries. Many studies on the elution of alkali metal ions from alkali silicate glasses in water have been reported (9–11). These papers observed that the elution of K^+ from potassium silicate glasses was much faster than that of Na^+ from sodium silicate glasses. There are two important processes for alkali diffusion in glass: 1) the ionic bonds between the alkali cations and the anionic nonbridging oxygens ($Si—O^-$) must be broken, and 2) the alkali cations must have unobstructed pathways to migrate between sites in the glass (12). In potassium silicate glasses, ionic bonds of K^+ between $Si—O^-$ are weaker than those of Na^+ between $Si—O^-$ in sodium silicate glasses. One reason is because the ionic field strength of K^+ is smaller than that of Na^+. Therefore, Process 1) occurs easily. Potassium silicate glasses have a larger void volume than do sodium silicate glasses because the ionic radius of K^+ is larger than that of Na^+ and the molar volume of potassium silicate glasses is larger than that of sodium silicate glasses in the same molar ratio of alkali oxide/silica. This means that Process 2) easily takes place. In addition, hydration of the glass during elution treatment can change both the bonding interaction and the void volume in the glass, thereby exerting a significant influence on alkali diffusion in the glass (12). Consequently, the above two important processes for alkali diffusion in glass are satisfied, so the elution of alkali ions from potassium silicate glasses is much faster than that from sodium silicate glasses. Bansal reported a similar difference of alkali elution in alkali silicates, and he concluded that the most likely reason for this result is that hydronium ions have a higher mobility in potassium silicate than in sodium silicate glasses because potassium and hydronium ions have about the same effective radius (0.13 nm) (13). Although our case is in acid solutions, it is considered that the elution behavior is similar but without silica dissolution. Silica easily dissolves in a solution of pH > 9, but it dissolves only slightly in a solution of pH < 9. For the 3.5 Na and 3.5 K glass capillaries, the amounts of elution of Si as determined with ICP spectrometry were less than 1.8% at the point where the alkali ions were completely eluted. The effects of various acids on the amount of elution of these glass capillaries have not been determined for this paper, but we are planning further experiments to elucidate these effects.

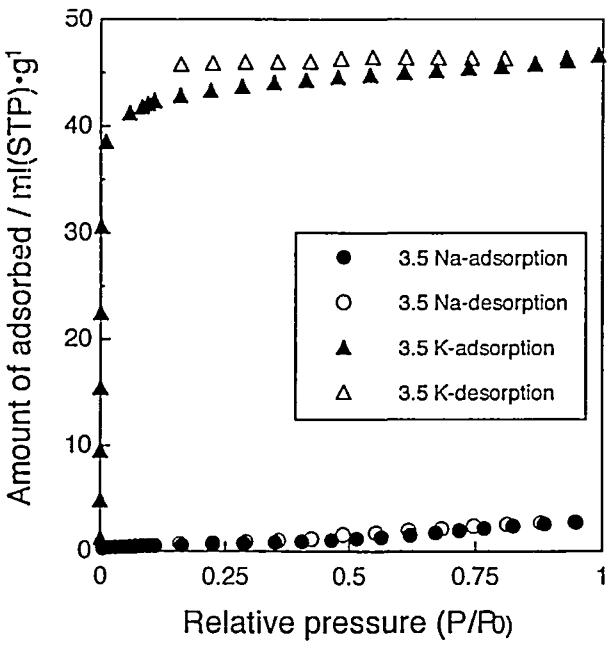

FIG. 4 N_2 adsorption-desorption isotherms at 77 K of the 3.5 Na and 3.5 K glass capillary membranes eluted with 3 mol/L HNO_3.

Pore Size Distribution

Typical N_2 adsorption–desorption isotherms of the 3.5 Na and 3.5 K glass capillary membranes eluted with 3 mol/L HNO_3 are shown in Fig. 4. The isotherms of other membranes were similar to these. All the isotherms of 3.5 Na were of the so-called Type IV isotherm but the adsorption amounts were very small. Those of 3.5 K were near the Type I isotherm but a hysteresis loop were observed. These hysteresis loops indicate the existence of mesopores. These mesopores are probably caused by dissolution and deposition of silica in the leached layer during elution treatment.

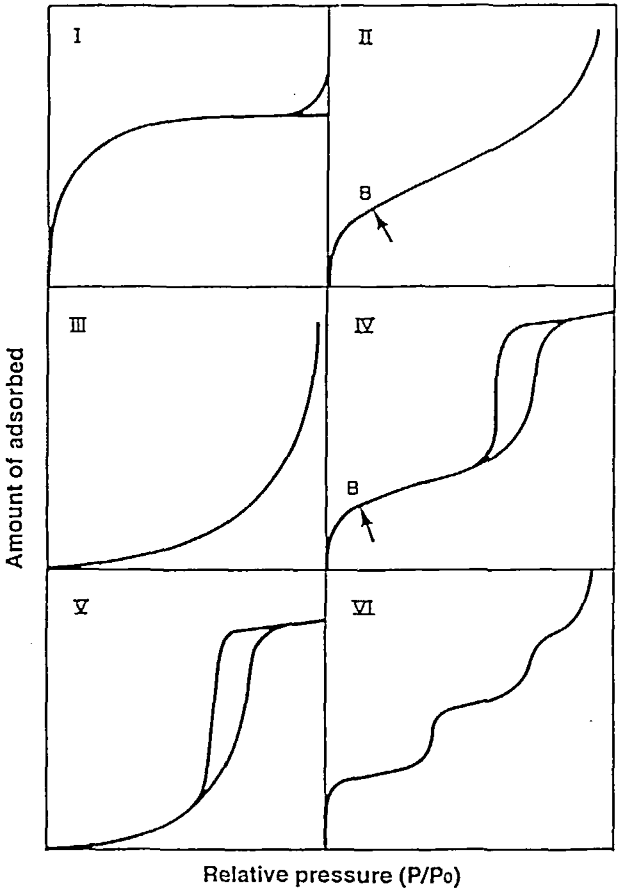

FIG. 5 The five types of adsorption–desorption isotherm, I to V, in the BDDT classification, together with Type VI, the stepped isotherm (15).

Type I and Type IV isotherms follow the BDDT classification, which is shown in Fig. 5 and was originally proposed by Brunaer, Deming, Deming, and Teller (14, 15). Type I isotherms are often found with a solid which contains micropores. They are characterized by a large amount of adsorption at a low relative pressure and a plateau which is nearly horizontal. Type IV isotherms are characteristic of a mesoporous solid and are characterized by a hysteresis loop. Specific surface area values based on BET plots of 3.5 Na and 3.5 K glass capillary membranes with various elution treatment are presented in Table 1. The 3.5 Na glass capillary membrane eluted with 3 mol/L CH_3COOH had a larger value than other 3.5 Na samples, but the reason for this large value is not clear. The specific surface areas of 3.5 K glass capillary membranes eluted with 3 mol/L CH_3COOH and 3 mol/L H_3PO_4 were slightly larger than that of the 3.5 K glass capillary membrane eluted with 3 mol/L HNO_3. It is assumed that those values were slightly large due to dissolution and deposition of silica in the leached layer during elution treatments, because those samples needed a longer time to eluate the alkali ions completely. The adsorption amounts of 3.5 Na glass capillary membranes were smaller than those of 3.5 K, and the specific surface areas of 3.5 Na were also much smaller those of 3.5 K. It has been reported by some researchers (16, 17) that the adsorption amounts of N_2 on ultramicroporous materials were also very small. Based on these results it is believed that the pores formed by elution of Na^+ are so small that N_2 cannot adsorb on the pores, and therefore the values of the 3.5 Na glass capillary membranes are small.

Figure 6 shows the pore size distribution of the 3.5 K glass capillary membrane eluted with 3 mol/L HNO_3. The mean pore radius was about 0.4 nm. This pore radius is in agreement with the order of the ionic crystal

TABLE 1
Specific Surface Areas of the 3.5 Na and 3.5 K Glass Capillary Membranes Eluted with 3 mol/L HNO_3 (3.5 Na-HNO_3 and 3.5 K-HNO_3), CH_3COOH (3.5 Na-CH_3COOH and 3.5 K-CH_3COOH), and H_3PO_4 (3.5 Na-H_3PO_4 and 3.5 K-H_3PO_4).

Samples	Specific surface area ($m^2 \cdot g^{-1}$)
3.5 Na-HNO_3	2.3
3.5 Na-CH_3COOH	15.3
3.5 Na-H_3PO_4	4.0
3.5 K-HNO_3	133.3
3.5 K-CH_3COOH	187.8
3.5 K-H_3PO_4	179.7

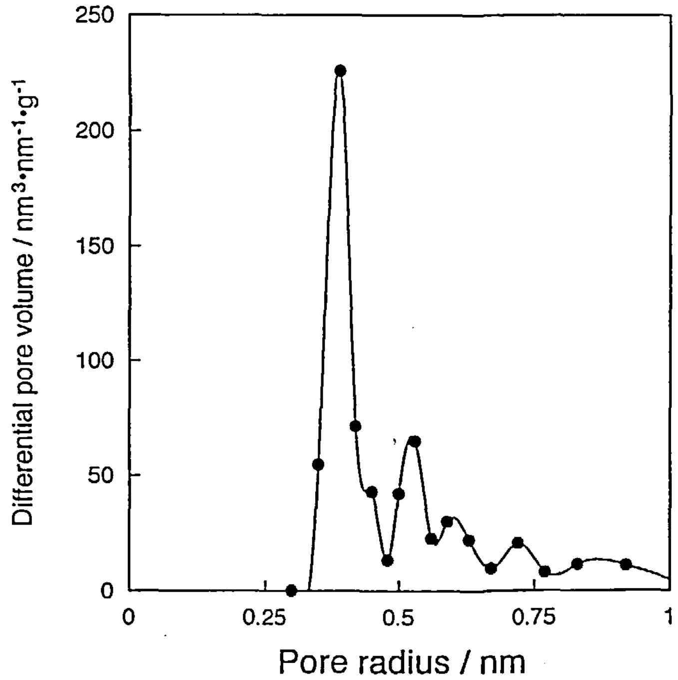

FIG. 6 Pore size distribution of the 3.5 K glass capillary membrane eluted with 3 mol/L HNO_3.

radius of K^+ as shown above. Accordingly, it seems that these pores are mainly due to elution of alkali metal ions because the ionic crystal radii of other easily eluted ions are smaller. Other samples of the 3.5 K glass capillary membranes showed almost the same pore size distributions, and they also had the same mean pore radius (about 0.4 nm). That is, they were ultramicropores (pore diameter less than 1 nm).

Gas Permeation Characteristics

Tables 2 and 3 show the ratios of the permeation rates of the 3.5 Na and 3.5 K glass capillary membranes with various elution treatments, respectively. Theoretical ratios of permeation rates based on Knudsen flow are also indicated in the Tables 2 and 3 footnates. The ratios of the permeation rates, CO_2/N_2 and He/N_2, were similar to the theoretical Knudsen value. Permeation rates of the 3.5 Na and 3.5 K glass capillary membranes are presented in Tables 4 and 5. These samples had similar values ($1-10^{-1}$

TABLE 2
The Ratio of the Permeation Rates of 3.5 Na Glass Capillary Membranes Eluted with 3 mol/L HNO_3 (3.5 Na-HNO_3), CH_3COOH (3.5 Na-CH_3COOH), and H_3PO_4 (3.5 Na-H_3PO_4)

Temperature (K)	3.5 Na-HNO_3		3.5 Na-CH_3COOH		3.5 Na-H_3PO_4	
	P_{He}/P_{N_2}[a]	P_{CO_2}/P_{N_2}[b]	P_{He}/P_{N_2}	P_{CO_2}/P_{N_2}	P_{He}/P_{N_2}	P_{CO_2}/P_{N_2}
298	2.2	0.8	2.2	0.8	2.2	0.8
373	2.1	0.8	2.2	0.8	2.2	0.8
473	2.0	0.8	2.1	0.8	2.2	0.8

[a] Theoretical separation factor based on a Knudsen flow of 2.6.
[b] Theoretical separation factor based on a Knudsen flow of 0.8.

TABLE 3
The Ratio of the Permeation Rates of 3.5 K Glass Capillary Membranes Eluted with 3 mol/L HNO_3 (3.5 K-HNO_3), CH_3COOH (3.5 K-CH_3COOH), and H_3PO_4 (3.5 K-H_3PO_4)

Temperature (K)	3.5 K-HNO_3		3.5 K-CH_3COOH		3.5 K-H_3PO_4	
	P_{He}/P_{N_2}[a]	P_{CO_2}/P_{N_2}[b]	P_{He}/P_{N_2}	P_{CO_2}/P_{N_2}	P_{He}/P_{N_2}	P_{CO_2}/P_{N_2}
298 K	2.1	0.8	2.1	0.8	2.2	0.8
373	2.1	0.8	2.1	0.8	2.2	0.8
473	2.1	0.8	2.1	0.8	2.2	0.8

[a] Theoretical separation factor based on a Knudsen flow of 2.6.
[b] Theoretical separation factor based on a Knudsen flow of 0.8.

TABLE 4[a]
Permeation Rates of 3.5 Na Glass Capillary Membranes Eluted with 3 mol/L HNO_3 (3.5 Na-HNO_3), CH_3COOH (3.5 Na-CH_3COOH), and H_3PO_4 (3.5 Na-H_3PO_4)

Temperature (K)	3.5 Na-HNO_3			3.5 Na-CH_3COOH			3.5 Na-H_3PO_4		
	P_{N_2}	P_{He}	P_{CO_2}	P_{N_2}	P_{He}	P_{CO_2}	P_{N_2}	P_{He}	P_{CO_2}
298 K	1.6	3.4	1.3	2.0	4.2	1.6	1.8	3.9	1.4
373	1.6	3.2	1.2	1.7	3.7	1.4	1.6	3.5	1.3
473	1.3	2.7	1.1	1.6	3.2	1.2	1.4	3.1	1.2

[a] P_{N_2}, P_{He}, P_{CO_2}: Permeation rate × 10 (cm^3(STP)$\cdot cm^{-2}\cdot s^{-1}\cdot$cmHgSH^1).

TABLE 5[a]

Permeation Rates of the 3.5 K Glass Capillary Membranes Eluted with 3 mol/L HNO_3 (3.5 K-HNO_3), CH_3COOH (3.5 K-CH_3COOH), and H_3PO_4 (3.5 K-H_3PO_4)

Temperature (K)	3.5 K-HNO_3			3.5 K-CH_3COOH			3.5 K-H_3PO_4		
	P_{N_2}	P_{He}	P_{CO_2}	P_{N_2}	P_{He}	P_{CO_2}	P_{N_2}	P_{He}	P_{CO_2}
298	3.2	6.9	2.5	2.6	5.6	2.1	2.7	6.0	2.2
373	2.9	6.1	2.3	2.3	4.9	1.8	2.4	5.2	1.9
473	2.7	5.4	2.1	2.0	4.2	1.6	2.1	4.7	1.7

[a] P_{N_2}, P_{He}, P_{CO_2}: Permeation rate × 10 (cm^3(STP)·cm^{-2}·s^{-1}·cmHg^{-1}).

cm^3(STP)·cm^{-2}·s^{-1}·cmHg^{-1}), and no significant differences were observed. From the results it is assumed that pores created by elution with various acids did not have obvious differences in their sizes. Thus, the kinds of acids used affected the elution times but had little effect on the pore sizes after elution. A typical scanning electron microprobe (SEM) photograph of the glass capillary membrane is presented in Fig. 7. The membrane surface was smooth, and no macrocracks were observed after elution treatment and following drying. The pore diameters calculated from an N_2 adsorption measurement of the membranes were less than 1 nm. Based on these pore diameters, the membranes can be expected to

FIG. 7 SEM photograph of the glass capillary membrane.

have much higher selectivities (the ratios of the permeation rates) and lower permeation rates than were observed in the papers of Ma et al. (1) and Way et al. (2). It seems that the ratios of permeation rates indicated smaller values and the permeation rates had higher values because those membranes probably had some microcracks that couldn't be observed with SEM and N_2 adsorption measurements. When the alkali metal ions were eluted, the glasses were stressed, and so those membranes probably had some microcracks.

CONCLUSIONS

Ultramicroporous glass capillary membranes with pore diameters of less than 1 nm were prepared by elution of alkali metal ions from glass capillaries, and the gas separation properties of the membranes were measured.

N_2 adsorption measurements indicated that the membranes had ultramicropores of less than 1 nm.

The ratios of the permeation rates of 3.5 Na and 3.5 K glass capillary membranes were not high values because of the creation of microcracks during the elution treatment and following drying.

Further experiments are needed to clarify the transport mechanism in ultramicroporous glass capillary membranes.

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