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Preparation and characterization of methyl-modified hybrid silica membranes for gas separation

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ABSTRACT

The methyl-modified hybrid silica sols with methyltriethoxysilane and tetraethoxysilane were successfully prepared using alkaline (NH_3 and tetra-methyl-ammonium hydroxide (TMAH)) and acid catalysts (HCl and CH_3COOH) and characterized with thermogravimetric analysis, Fourier transform infra-red, and water contact angle. The methyl-modified silica film showed hydrophobic property with water contact angles over 90° under alkaline or acid catalyst. The methyl-modified silica membranes were fabricated and evaluated with He, H_2, N_2, C_3H_8, and SF_6 at 200℃. He gas permeance for hybrid silica membranes was in the range of 0.61–$1.91 \times 10^{-6}\,\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}\,\text{Pa}^{-1}$, while He/SF_6 and N_2/SF_6 permeance ratios of acid-catalyzed membranes was quite higher than those of alkaline catalyzed. Pore size (d_p) of membranes were evaluated with normalized Knudsen-based permeance method, and the order of pore size for methyl-modified silica membranes can be estimated as follows: HCl-catalyzed membrane < acetic acid-catalyzed membrane < TMAH-catalyzed membrane < ammonium-catalyzed membrane. Judging from the order of pore size for methyl-modified silica membranes, the pore size of methyl-modified silica membranes can be tuned by controlling of catalyst during the sol–gel processing.

Keywords: Hybrid silica membrane; Sol–gel; Methyltriethoxysilane (MTES); Gas separation; Normalized Knudsen-based permeance (NKP)

1. Introduction

Microporous silica membranes have a great potential for gas separation and pervaporation at high temperatures in chemically aggressive environments and show high fluxes for small gas molecules such as H_2, CO_2, and O_2 and considerable selectivities for these gases over large molecules such as SF_6 and hydrocarbons [1–3]. Generally, silica membranes are formed by chemical vapor deposition [4–9] or sol–gel technique [1–3,10–12] of silica precursors on the ceramic supports. However, pure silica membranes cannot be used due to dissolution into aqueous solutions and

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are not stable even in humid environment because of the highly hydrophilic silanol groups in the silica structure. The density of amorphous silica membranes can be increased by rearrangement of the silanol groups, reducing the performance of the silica membranes. Therefore, the organic–inorganic hybrid silica membranes have been developed to improve the hydrothermal stability of silica membranes [13–18]. Hydrophobic silica prepared using methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) is one of the most popular organic–inorganic hybrid silica materials [13–15]. Methyl groups in hybrid silica network can lead to elimination of the surface silanol groups. Recently, the research group in Twente University developed hybrid silica membranes by sol–gel technique using a bridged alkoxide precursor such as bis(triethoxysilyl) ethane (BTESE) and bis(triethoxysilyl) methane (BTESM), and MTES [16–18]. BTESE and BTESM hybrid silica membranes showed good hydrothermal stability in comparison with MTES/TEOS-derived silica membranes because of the incorporation of organic linking groups (Si–C–Si, Si–C–C–Si units) into the silica networks.

MTES/TEOS-derived hybrid silica membranes were developed not only for the improvement of hydrothermal stability but also for the control of silica network size. Brinker et al. first reported the controlled silica network size created by the organic-template method using MTES/TEOS hybrid membranes in 1995 [19]. The type of catalyst, the molar ratio of water to Si precursor, the molar ratio of MTES/TEOS, etc. affect the colloidal size during the preparation of MTES/TEOS hybrid silica sol by sol–gel technique. The ability to control the size of the colloidal particles is so important because colloidal size is a crucial for the determination of membrane pore sizes [20,21].

In our previous study, colloidal sols were prepared with alkaline catalyst and were discussed the effect of the molar ratio of MTES/TEOS, initial concentration of MTES/TEOS and the water molar ratio to MTES/TEOS. MTES/TEOS hybrid silica sols with a particle size of <40 nm were successfully prepared [20]. In this study, MTES/TEOS hybrid silica sols were prepared with alkaline (NH_3 and tetramethyl-ammonium hydroxide (TMAH)) and acid (HCl and CH_3COOH) catalyst and applied for the control of pore size of silica membranes. The single gas permeation for MTES/TEOS hybrid silica membranes was evaluated at 200˚C, and the pore size was estimated using normalized Knudsen-based permeance (NKP) method, which was proposed for the determination of membrane pore sizes less than 1 nm [22,23].

2. Experimental

2.1. Preparation of methyl-modified hybrid silica sols and membranes

Methyl-modified silica sols were prepared by the hydrolysis and condensation reaction of MTES ($CH_3Si(OC_2H_5)_3$) and TEOS ($Si(OC_2H_5)_4$). Ammonium and TMAH, and hydrochloric acid and acetic acid were used as alkaline and acid catalysts in the preparation of hybrid silica sols, respectively. The concentration of alkaline catalyst of ammonium and TMAH was 0.4 and 0.005 wt.%, respectively, while that of acid catalyst of hydrochloric acid and acetic acid was 0.13 and 0.2 wt.%, respectively. The concentration of total was kept at 5 wt.% with molar ratios of MTES/TEOS (M/T) ranging from 0 to 3. The reactants were mixed in an ice bath for <5 min and then reacted at 50˚C with stirring for various reaction times in the range of several to 40 h [20].

A porous α-alumina support (OD = 10.0 mm, pore size = 1 μm, porosity: 50%) was used as a support for the methyl-modified hybrid silica membranes. α-alumina particles (average particle diameter: 0.2, 1.84 μm) were coated on the outer surface of a support using silica-zirconia colloidal sol as the binder, and the support was fired at 550˚C for 30 min to make the surface smooth. These procedures were repeated several times to cover large pores. Then, 2.0 wt.% of silica–zirconia (Si/Zr = 1) sol was coated on the support to form an intermediate layer with the pore size of <3 nm [24]. After coating of intermediate layer, the membrane was fired at 550˚C for 30 min in air atmosphere. And then, methyl-modified hybrid silica membranes were prepared by hot coating with MTES/TEOS sol, followed by drying and firing at 400–550˚C in air and N_2 atmosphere, respectively, for 30 min.

2.2. Characteristics of methyl-modified hybrid silica sol and membranes

The methyl-modified hybrid silica gel was prepared by drying the sol at 40˚C in air and grinded using a mortar. The weight loss of methyl-modified silica powder was measured for the evaluation of gel characteristics with a ramping rate of 10˚C min^{-1} up to 1,000˚C in nitrogen and air (30 cc min^{-1}) using thermogravimetric analysis (TGA-50, Shimadzu, Japan). Before TG measurement, powder was pretreated at 100˚C for 1 h to remove adsorbed water and ethanol. The hydrophobic property for hybrid silica films, which were coated on the glass slide by firing at 400˚C in N_2 atmosphere, was evaluated by measuring water contact angle (DM-300, Kyowa, Japan). The hybrid silica film coated on the KBr plate was fired at 400℃ for 15 min in nitrogen atmosphere and characterized by Fourier transform infra-red (FT-IR) spectroscopy (FTIR-8300, Shimadzu, Japan).

Fig. 1 shows a schematic diagram of experimental apparatus for gas permeation measurement. Single gas permeation characteristics (He, N_2, CO_2, C_3H_8, and SF_6) for hybrid silica membranes were evaluated at 200℃. After membranes were pre-treated with a helium flow at 300℃ overnight, the permeation flow rate was measured by a soap film flow meter.

3. Results and discussion

3.1. Characteristics of hybrid silica gel powder and film

Fig. 2 shows the TG curves of MTES/TEOS-derived silica powder with acid catalyst in air and N_2 atmosphere. The weight loss between 100 and 400℃ was attributed to dehydration by polycondensation between silanol groups and/or decomposition of unreacted ethoxy groups in the silica networks [20,22]. The residual weight of MTES/TEOS-derived silica at 1,000℃ in N_2 atmosphere is apparently higher than that of in air due to oxidation of organic groups such as ethoxy and methyl groups. In N_2 atmosphere, methyl groups are reported to form Si-C-Si groups, resulting in higher residual weight. In air atmosphere, most of the weight loss of MTES/TEOS-derived silica gel powder at temperatures >350℃ was from decomposition of methyl groups, while methyl groups showed thermal stability below 550℃ in nitrogen in the silica networks [22]. Therefore, methyl group in the methyl-modified silica networks was stable below 350℃ in air atmosphere, but methyl group was stable below 550℃ in nitrogen atmosphere.

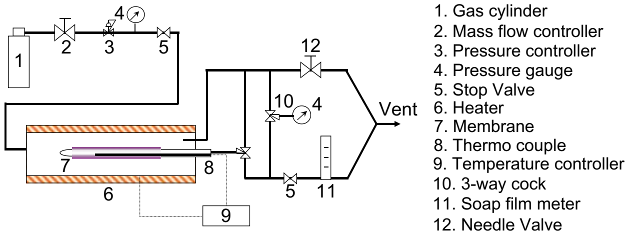

Fig. 1. A schematic diagram of experimental apparatus for gas permeation measurement.

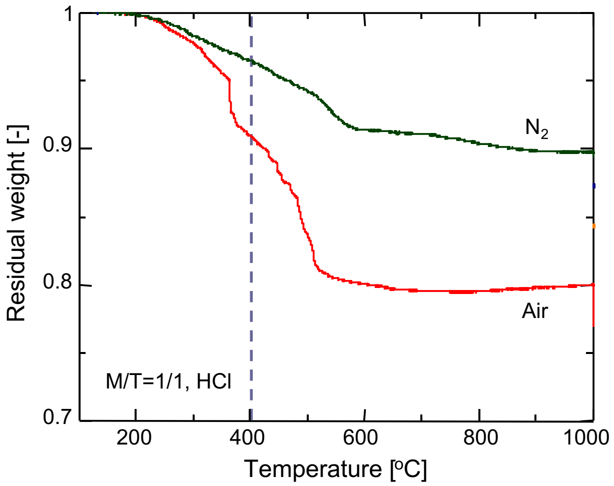

Fig. 2. The TG curves of MTES/TEOS-derived silica powder with acid catalyst in air and N_2 atmosphere (MTES/TEOS = 1/1).

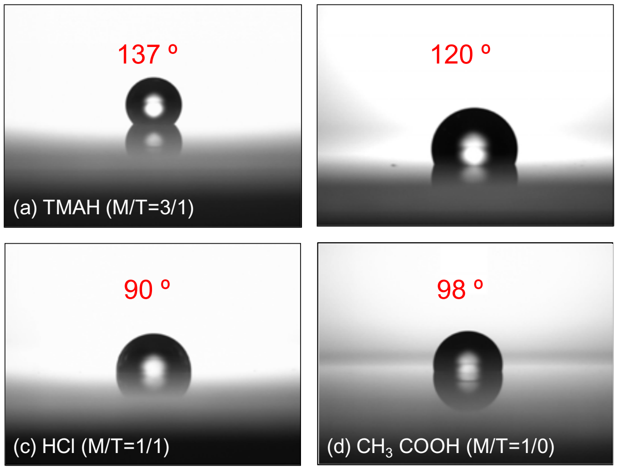

Fig. 3. The photographs of water contact angle for methyl-modified hybrid silica films with different catalysts on the glass slide.

Fig. 3 shows the photographs of water contact angle for methyl-modified hybrid silica films with different catalysts on the glass slide. In this study, methyl-modified hybrid silica sols were prepared with alkaline (TMAH, NH_3) and acid catalysts (HCl and CH_3COOH). Regarding alkaline catalysts, the water contact angles for hybrid silica film with TMAH and ammonium catalyst were 137° and 120°, respectively. The water contact angles for hybrid silica film with HCl and acetic acid catalyst were 90° and 98°, respectively. All of the methyl-modified silica film showed hydrophobic properties due to methyl groups originated from MTES structure, which was confirmed by FT-IR as shown in Fig. 4. The peak of methyl groups (3,000, 1,400, 1,260 cm^{-1}) was observed in the methyl-modified hybrid silica film except pure silica film [20–22].

The sol–gel process is divided into the polymeric sol–gel route and colloidal sol–gel route. In the colloidal route, the hydrolysis and condensation reaction is

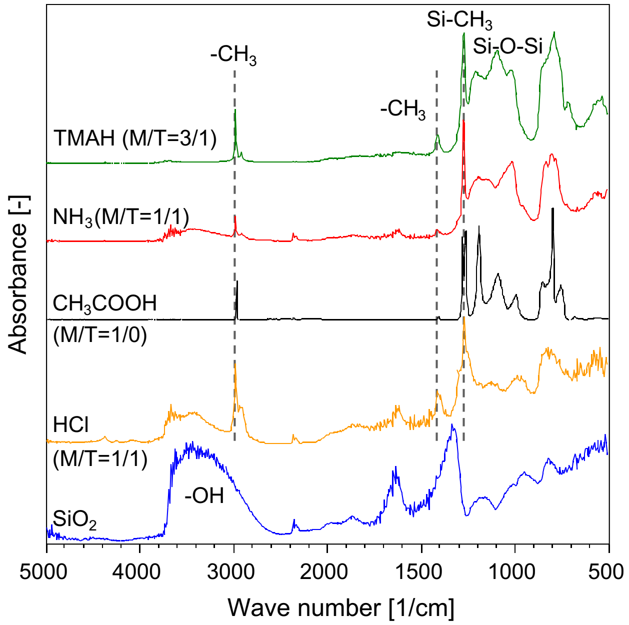

Fig. 4. FT-IR spectra for methyl-modified silica films coated on the KBr plate and fired at 400℃ in N_2 atmosphere.

fast compared with the polymeric route, and the rapid condensation reaction causes particulates growth and/or the formation of precipitates. On the other hand, the hydrolysis reaction in the polymeric route is slower and linear inorganic polymer is formed [25]. It is generally agreed that alkoxides are slowly hydrolyzed and entangled linear chains are formed in acid systems, while hydrolysis reaction was relatively fast and it is easy to form colloidal sols in alkaline solutions. Furthermore, the reaction rate of TEOS is much higher than that of MTES in alkaline conditions, while the reaction rate of MTES is much faster than TEOS under acid conditions [13]. In alkaline solution, TEOS formed colloidal sols at the initial reaction stage, and MTES gradually reacted with silanol groups on the outer surface of the colloidal silica sols. Since the reaction rate of TEOS is faster than that of MTES in alkaline solutions, the most probable structure of hybrid silica sols is a core–shell structure (core: TEOS, shell: MTES) [20,21]. Therefore, the water contact angle of alkaline-catalyzed sol was higher than that of acid-catalyzed sol due to higher density of hydrophobic functional groups on the surface of core–shell sols.

3.2. Gas permeation characteristics of hybrid silica membranes

Methyl-modified hybrid silica membranes were prepared with various firing temperature and catalyst, and single gas permeation at 200℃ was evaluated with He, N_2, CO_2, C_3H_8, and SF_6 in this study. Table 1 summarizes the preparation condition for methyl-modified hybrid silica membranes and the He gas permeation and permeance ratios of He/SF_6 and N_2/SF_6 at 200℃. Fig. 5 shows gas single gas permeation at 200℃ for methyl-modified silica membranes prepared with ammonium and HCl-catalyzed solution. In the case of NH_3-catalyzed membranes, M-2 membrane fired at 450℃ in nitrogen atmosphere showed high He permeance of $1.64 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$ with low He/SF_6 and N_2/SF_6 permeation ratio of 6.9 and 2.6, respectively, which were close to Knudsen ratio. On the other hand, M-4 membrane fired at 550℃ in nitrogen atmosphere showed a low He permeance of $9.01 \times 10^{-7}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$ with moderate He/SF_6 and N_2/SF_6 permeation ratio of 82 and 18,

Table 1
The preparation condition for methyl-modified hybrid silica membranes and the He gas permeation and permselectivity at 200℃

Membrane	Sol molar ratio (MTES/TEOS)	Catalyst	Firing temp. (℃)	He permeance at 200℃ ($\mathrm{mol\ m^{-2}\ s^{-1}\ Pa^{-1}}$)	Permeance ratio	
					He/SF_6	N_2/SF_6
M-l	0/1	HC1	550	1.080×10^{-6}	1,595	157
M-2	1/1	NH_3	450	1.639×10^{-6}	6.9	2.6
M-3	1/1	NH_3	500	1.428×10^{-6}	39	11
M-4	1/1	NH_3	550	9.006×10^{-7}	82	18
M-5	1/1	HCl	450	1.909×10^{-6}	2,616	474
M-6	3/1	TMAH	400	8.496×10^{-7}	28	8.8
M-7	1/0	CH_3COOH	400	1.657×10^{-7}	158	51

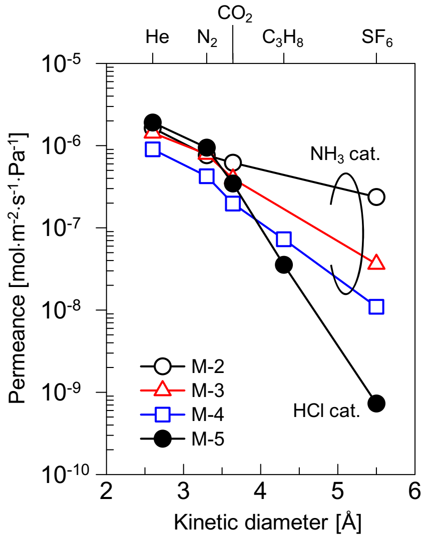

Fig. 5. Single gas permeance at 200°C for methyl-modified silica membranes prepared from NH_3 and HCl-catalyzed silica sols and fired at various temperatures.

respectively, in comparison with M-2 membrane. These results suggest that the pore size distribution shifted to a smaller size with the increase in firing temperature due to sintering of the amorphous silica structure under alkaline catalyst.

M-2 and M-5 membranes, which were prepared by firing at 450°C in nitrogen atmosphere, showed similar helium permeances of 1.64×10^{-6} and 1.91×10^{-6} mol $m^{-2}s^{-1}Pa^{-1}$, respectively. However, the permeance ratios of He/SF_6 and N_2/SF_6 for M-5 membrane were higher than M-2 membrane. Since the structure of hybrid silica sols in alkaline and acid catalyst is a colloidal sol with core–shell structure and a linear polymer, respectively, HCl-catalyzed sol is more preferable for the formation of silica networks of smaller pore size [23].

Fig. 6 shows single gas permeation at 200°C and their NKP plots for TEOS and methyl-modified hybrid silica membranes with alkaline and acid catalysts. The tendency of gas permeation between alkaline (NH_3, TMAH) and acid (HCl, CH_3COOH) catalyzed membranes in Fig. 6(a) was similar to that in Fig. 5. He gas permeance for each membranes were in the range of 0.85–1.91×10^{-6} mol $m^{-2}s^{-1}Pa^{-1}$, but He/SF_6 and N_2/SF_6 ratios of acid-catalyzed membranes, were quite higher than those of alkaline-catalyzed membranes. Pore size, d_p, was estimated by NKP fitting curves as shown in Fig. 6(b). Judging from NKP fitting curves for each silica membranes, the order of pore size can be estimated as follows: M-1 (SiO_2 membrane with HCl catalyst, $d_p = 5.2$ Å) < M-5 (HCl catalyst, $d_p = 6.0$ Å) < M-7 (CH_3COOH catalyst, $d_p = 7.5$ Å) < M-6 (TMAH catalyst, $d_p = 11$ Å) < M-2 (NH_3 catalyst, $d_p > 50$ Å). It can be concluded that the pore size of methyl-modified silica membranes can be tuned by controlling of catalyst during the sol–gel processing, because the structure of hybrid silica sols in alkaline and acid catalyst are a core–shell structure and linear polymer, respectively.

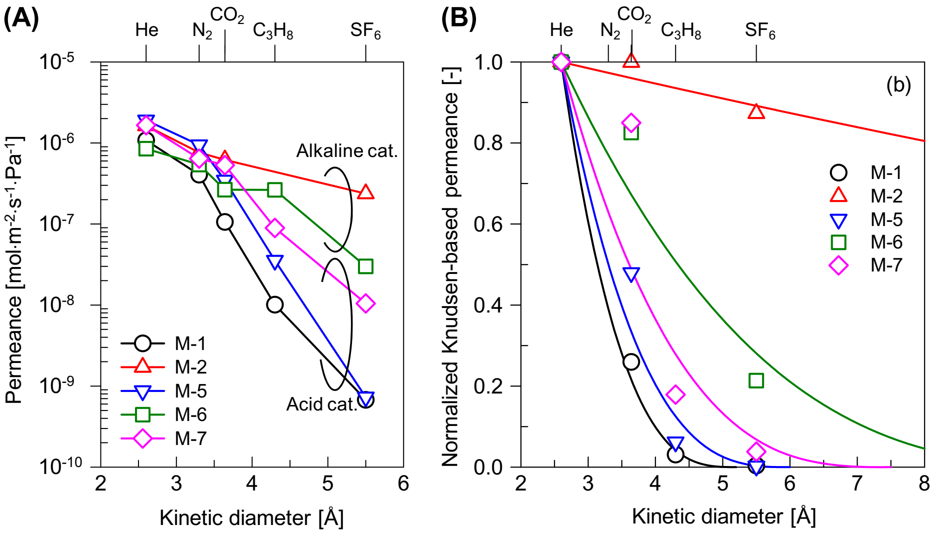

Fig. 6. Single gas permeance at 200°C and their NKP plots for TEOS and methyl-modified hybrid silica membranes with different catalysts.

4. Conclusion

Methyl-modified silica membranes were prepared by hydrolysis and condensation reaction of MTES and TEOS in ethanol as a solvent. Ammonium and TMAH, and hydrochloric acid and acetic acid were used as an alkaline and acid catalyst, respectively. Since the methyl group in the methyl-modified silica networks was stable 550℃ in nitrogen atmosphere, which was confirmed by TGA and FT-IR spectra, methyl-modified silica films prepared at 400℃ in N_2 atmosphere, showed hydrophobic property.

Methyl-modified silica membranes were prepared with MTES/TEOS hybrid silica sols and applied to single gas permeation at 200℃. He gas permeance for hybrid silica membranes was in the range of $0.61–1.91 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$, but He/$SF_6$ and N_2/SF_6 ratios of acid-catalyzed membranes were quite higher than those of alkaline-catalyzed membranes because the structure of hybrid silica sols in alkaline and acid catalyst are a core–shell structure and linear polymer, respectively. Pore size, d_p, was estimated by NKP-fitting curves, and the order of pore size can be estimated as follows: HCl-catalyzed membrane ($d_p = 6.0$ Å) < acetic acid-catalyzed membrane ($d_p = 7.5$ Å) < TMAH catalyzed membrane ($d_p = 11$ Å) < ammonium-catalyzed membrane ($d_p > 50$ Å, Knudsen diffusion). Judging from the order of pore size for methyl-modified silica membranes, the pore size of methyl-modified silica membranes can be tuned by controlling of catalyst during the sol–gel processing.

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