Network engineering of a BTESE membrane for improved gas performance via a novel pH-swing method

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Abstract

Organosilica microporous membranes were fabricated from 1, 2-bis (triethoxysilyl) ethane (BTESE)-derived sols prepared in acidic pH via the pH-swing method. This method includes two steps whereby a specific amount of NH_3 was added into the acid sols and switched to acid after a reaction of several minutes. We found that the size of the BTESE-derived sols by pH-swing could be controlled via the H_2O /BTESE molar ratio and the reaction time in alkali. Under the same H_2O /BTESE ratio of 60, the BTESE-derived sols prepared in the pH-swing method showed an increase sol size in contrast with the acid method, and the sol size was easily controlled by the dominating reaction in alkali pH — the condensation reaction. Gas permeation results showed that some gases (He , H_2 , N_2 , C_3H_8 , SF_6) permeated the membrane that was prepared using the pH-swing sols (pH-swing membrane) at approximately twice the rate shown by the membrane prepared using acid sols (acid membrane); H_2

23 permeance levels of the pH-swing membrane and the acid membrane were 3.4×10^{-6}
24 and $1.6 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 200 °C, respectively. The pH-swing membrane also
25 maintained similar $\text{H}_2/\text{C}_3\text{H}_8$ permeance ratios of ranging from 2,600~5,800,
26 confirming that pH-swing processing is an innovative method for improvement in the
27 gas permeance of BTESE-derived organosilica membranes. One possible reason for
28 these results could be that the membranes prepared using the pH-swing sols increased
29 the size of the sols, which reduced the sol penetration into the intermediate layer.
30 Moreover, the high cross-linking that was caused by pH-swing increased the
31 thermostability of the BTESE-derived organosilica networks. The CO_2/CH_4 and
32 CO_2/N_2 permeance ratios for the pH-swing membrane were as high as 90 and 28,
33 respectively, at 50 °C.

34 **Keywords:**

35 Organosilica; pH-swing; sol size; gas permeation; thermostability.

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1. Introduction

Hydrogen is considered a source of clean energy and is expected to play a significant role in the reduction of the emissions of greenhouse gases for the environment [1]. To reduce fossil fuel consumption, highly efficient separation processes should be developed to obtain high-grade H_2 production on a large scale, but many fundamental scientific and technological challenges are yet to be overcome.

A feasible approach to efficient hydrogen purification is to use inorganic membranes, particularly the silica-based versions [2-4]. These membranes have attracted considerable attention for excellent molecular sieving effect and the thermostability, which enables their applicability to gas separation under conditions where polymeric membranes cannot be used [5, 6]. The purification of hydrogen from organic compounds (such as CH_4 , C_3H_8) could be one of the most important applications. Tetraethoxysilane (TEOS) is the most commonly used silicon precursor for the preparation of sol-gel derived silica membranes due to its excellent selectivity [7]. However, the low stability of the silica structure to water severely limits its application in many industrial processes that include hydrothermal conditions [8]. In addition, molecular simulation has revealed that most of the membrane pores are smaller than H_2 molecules and only a small number of pores are available for H_2 permeation, which results in poor gas permeance [9].

A possible approach to improving the hydrothermal stability and gas permselectivity of silica membranes is to incorporate organic functional groups in the silica networks. The shape, flexibility and length of the organic units in a hybrid silica network are known to influence the membrane pore size, structure and affinity [10]. Recently, a new class of organoalkoxysilanes with double silicon and linking organic groups, such as 1, 2-bis (triethoxysilyl) ethane (BTESE), was used as a precursor to prepare organic-inorganic hybrid membranes for the pervaporation dehydration of aqueous solutions. The pore sizes of the BTESE-derived networks were enlarged due to the existence of the linking units compared with TEOS, which was proposed as a spacer technique for tuning subnanopores [11]. BTESE-derived membranes were

66 reportedly applied to pervaporation [12], reverse osmosis [13] and membrane
67 reactors[14, 15]. The formation of a loose structure and improved hydrothermal
68 stability have clearly been due to the presence of a Si-C-C-Si unit in silica networks
69 [16]. BTESE-derived network pore sizes have been successfully controlled via the
70 water ratio [17]. With an increase in the H₂O/BTESE ratio of from 6 to 240, the
71 membrane permeance for H₂ was decreased from $2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to 1×10^{-6}
72 $\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, while the permeance ratio of H₂/C₃H₈ was increased from 40 to 6,000.
73 In addition, the pore sizes of BTESE networks has been controlled via the acid ratio
74 [18]. By optimizing the acid ratio, BTESE membranes obtained a H₂/N₂
75 permselectivity that ranged from 50 to more than 400 [19].

76 In general, for the fabrication of inorganic membranes, a separation layer is coated
77 onto an intermediate layer, as shown in Fig.1 (a). When the pore size of the
78 intermediate layer is larger than the size of BTESE-derived sols, these would
79 penetrate the mesoporous intermediate layer and decrease the gas performance.
80 Therefore, if it is possible to increase the sol size enough to prevent penetration, as
81 shown in Fig. 1 (b), it would be possible to increase the gas permeance of
82 BTESE-derived membranes with a thin film coating. The hydrolysis and condensation
83 reaction rates of alkoxysilanes are known to be dependent on pH [20]. The size and
84 shape of sols is controlled by pH in the sol-gel method [21-23]. The rate of hydrolysis
85 in a BTESE reaction is high in an acidic pH, while that of condensation is high under
86 an alkali pH. Therefore, it should be possible to enlarge the size of BTESE-derived
87 sols by increasing the condensation rate in an alkali pH. In addition, through
88 condensation cross-linking network could affect the thermostability and gas
89 permeability of organosilica membranes.

90 In the present study, we attempted to control the sols by adjusting the pH during
91 their preparation. Three types of BTESE-derived sols were prepared: acid sols,
92 acid-alkali sols and pH-swing sols. The pH-swing is a novel process where sol pH is
93 manipulated from acidic to alkali, and returned to acidic. This process was
94 investigated for its ability to tune the colloid sol sizes for BTESE-derived membranes
95 in terms of the H₂O/BTESE molar ratio and pH values in BTESE hydrolysis and

condensation. BTESE-derived sols were prepared by manipulating the pH of a sol from acid (pH=2) to alkali (pH=10) with H₂O/BTESE ratios of 60 and 240, respectively. The sols were characterized by DLS, small-angle X-ray scattering, NMR, TGA, FT-IR, and N₂ adsorption. The gas permeation properties were also examined to investigate the effect of sols on gas separation.

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Fig. 1 Schematic structure of small and large size sols-derived membranes.

2. Materials and Methods

2.1. Preparation of BTESE sols

1, 2-bis (triethoxysilyl) ethane (BTESE) as a precursor was purchased from Aldrich, and used without further purification. Ethanol (minimum 99.5%) was used as a solvent without further purification. The amount of water contained in ethanol was assumed to be 0.5%. HCl and NH₃ were used as catalysts. Three types of BTESE-derived sols were prepared as shown in Fig. 2: acidic, acid-alkali and pH-swing (acid-alkali-acid). To prepare “acid sols,” BTESE was hydrolyzed and condensed with water and hydrochloric acid at 50 °C for 1 h with molar ratios of BTESE/HCl/H₂O=1/0.1/ (6-240). To prepare “acid-alkali sols,” a specific amount of NH₃ was added to the acid sols with agitation at 25 °C to adjust the NH₃/HCl molar ratios from 1.56 to 12. To prepare the ‘pH-swing sol,’ NH₃ was added to the acid sols and maintained for 3–20 min at 0 °C, followed by the addition of HCl (HCl/NH₃=0.8) to return the pH to approximately 2 at 25 °C. The sizes of BTESE sols were controlled by adjusting the pH values and reaction time in alkali. The concentration of BTESE in all three types of BTESE-derived sols was kept at 5.0 wt% in the final compositions.

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124 Fig. 2 A schematic procedure of acid, acid-alkali and pH-swing sols preparation.

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127 2.2. Characterization of BTESE-derived gels and powders

128 The colloid size of BTESE-derived sols was determined via Dynamic Light
 129 Scattering (DLS) using a Malvern Zetasizer Nano ZS (Malvern Instruments, Ltd.) at
 130 25 °C. Small-angle X-ray scattering (SAXS) was evaluated using a Nano-viewer
 131 (Rigaku Co., Japan).

132 BTESE-derived powders ($H_2O/BTESE=60$, acid and pH-swing) were prepared via
 133 the quick-drying method where the BTESE-derived sols were dried quickly at 180 °C
 134 under air, similar to the membrane fabrication, followed by calcination at 200 °C
 135 under an air atmosphere for 30 min, and ground using a mortar. The
 136 thermogravimetric analysis (TG) was provided by TG-MASS (TG-DTA-410s, Rigaku
 137 Co). He/O₂ mixed gas (He: 80 mol%, O₂: 20 mol%) was used as a carrier, and the
 138 temperature was increased at a ramping rate of 10 °C min⁻¹ to 1,000 °C. The
 139 adsorption isotherms of N₂ for BTESE-derived powders fired at 300, 400 and 500 °C
 140 under an air atmosphere were measured at 77 K (BELMAX, BEL Japan INC). The
 141 surface area of the samples was calculated using the BET equation. The chemical
 142 structures were characterized at room temperature by Fourier transform infrared
 143 spectroscopy (FT-IR-4100, JASCO). The surface of the membranes was examined by
 144 Field Emission Scanning Electron Microscopy (FE-SEM, S-4800, HITACHI). The
 145 ²⁹Si-NMR spectra were recorded at 119.17 MHz on a Varian 600 PS solid NMR
 146 spectrometer.

147 *2.3. Preparation of BTESE-derived membranes*

148 BTESE-derived membranes were prepared as reported elsewhere [14, 17]. Porous
149 α -alumina tubes (porosity of 50%, an active outer diameter of 10 mm and an average
150 pore diameter of 2 μ m) were used as supports for the BTESE-derived membranes.
151 Two types of α -Al₂O₃ particles (average diameter: 3.0, and 0.2 μ m) were coated onto
152 the outer surface of a porous support using a silica-zirconia colloidal sol (SiO₂-ZrO₂,
153 Si/Zr=1/1, which was prepared from TEOS and zirconium tetrabutoxide) as the binder
154 [24], and fired at 550 °C for 15 min to smooth the surface. These procedures were
155 repeated several times to cover any large pores that might have resulted in pinholes in
156 the final membrane. Silica-zirconia colloidal sol diluted to 0.5 wt%, was coated onto
157 the substrate to form an intermediate layer with pore sizes of several nanometres,
158 which was followed by firing at 550 °C for 15 min. Finally, a BTESE-derived sol was
159 coated onto the intermediate layer to serve as a separation layer, followed by drying
160 and calcination at 300 °C [25] for 1 h under air. The coating and firing of the
161 BTESE-derived sols was repeated 2-4 times.

162 *2.4. Single-gas permeation measurement*

163 Fig. 3 shows a schematic diagram of the experimental apparatus for a single-gas
164 permeation measurement. Single-gas permeation tests were carried out at a given
165 temperature from 50 to 250 °C. He, H₂, CO₂, N₂, CH₄, C₃H₈ and SF₆ were fed to the
166 outside (upstream) of a cylindrical membrane, with a transmembrane pressure of
167 0.15-0.2 MPa, while the permeate stream was maintained at atmospheric pressure.
168 The gas flow rate through the membrane was measured using a bubble film flow
169 meter (SF-U, Horiba, Co. Ltd., Japan).

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1. Pure gas cylinder	8, 10. 3-way cock
2, 5, 12. Stop valve	11. Needle valve
3. Pressure controller	13. Soap film meter
4, 9. Pressure gauge	14. Thermocouple
6. Membrane module	15. Membrane
7. Temperature controller	

Fig. 3 Schematic diagram of the experimental apparatus for single-gas permeation measurement

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3. Results and discussion

3.1. Characterizations of BTESE sol structure

BTESE sols were prepared via three routes: acid, acid-alkali and pH-swing (acid-alkali-acid). Fig. 4 (a) shows the sol size distribution as determined by the dynamic light scattering of acid and pH-swing sols prepared with a water ratio of 60. In the preparation of acid sols, pH was controlled approximately at 2. The pH-swing sols were prepared with a reaction time of 2 min in alkali with a NH_3/HCl ratio of 12. The sizes of the acid and pH-swing sols were 1.7 and 3.0 nm, respectively, which indicated a larger size for pH-swing sols than that for acid sols. Fig. 4 (b) shows the time courses of three types of BTESE-derived sol sizes. The size of acid sols increased to ~ 1.8 nm after 1 h of reaction time, and then remained stable at 1.8 nm for several days. In the acid-alkali route, NH_3 ($\text{NH}_3/\text{HCl}=12$) was added into acid sols, and this resulted in a pH of about 10. Before finally gelling, the sol size became large with time — 2 nm to 30~40 nm after 30 min reaction. Therefore, no membrane was

190 prepared using an acid-alkali sol due to the instability. In the pH-swing route, after
 191 adding NH_3 into acid sols, the sol sizes increased from 2 nm to 4 and 8 nm for
 192 reaction times of 3 and 20 min in alkali steps, respectively. Then, after adding acid
 193 into the acid-alkali sols, the sol size remained stable for several days. The sizes of the
 194 sols prepared for the pH-swing route were larger than those in the acid route,
 195 confirming that the pH-swing process enlarged the size of the BTESE-derived sols.

196 Fig. 5 shows the small-angle X-ray scattering (SAXS) of the acid sols
 197 ($\text{H}_2\text{O}/\text{BTESE}=60$) and the pH-swing sols ($\text{H}_2\text{O}/\text{BTESE}=60$, $\text{NH}_3/\text{HCl}=12$) as a
 198 function of q , which was the scattering angle vector. DLS analysis of these two types
 199 of sols are shown in Fig. 4 (a). The SAXS patterns exhibited a power-law relationship,
 200 $I - q^{-\beta}$ at $q \geq 1 \text{ nm}^{-1}$ [26, 27]. The value β is known to indicate the degree of the
 201 structure branching [26]: $\beta=1$ for an infinitely long rod, $\beta=2$ for an infinitely thick
 202 disk, $\beta=4$ for a sphere [28]. An infinitely thick disk and an infinitely long rod could
 203 be differentiated by the surface-to-volume ratio (S/V). The S/V was $1/H$ and $2/R$ for a
 204 disc and a rod, respectively [29]. H is half the thickness, and R is the radius of the
 205 sphere (see Supplementary Data, SD-1). Table 1 summarizes the sizes of the sols and
 206 the values of β . The β value of the acid sol (1.85) suggested it was a long and thick
 207 disk structure instead of hard-sphere packed, while the β value of the pH-swing sol
 208 (2.63) suggested an elliptical structure. The scattering intensity of the pH-swing sol
 209 was higher than that of acid, due to the larger sol size and the shape. Based on the
 210 growth mechanism of silica-derived sols that showed a high reaction rate for
 211 hydrolysis in an acidic pH and a high reaction rate for condensation in an alkali, it is
 212 strongly suggested that sols grown via pH-swing will assume a three-dimensional
 213 structure through condensation reaction.

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216 Fig. 4 (a) Dynamic light scattering for pH-swing sol (reacted 2 min in alkali, $\text{NH}_3/\text{HCl}=12$) and
 217 acid sols. (b) Time course of BTESE-derived sols in acid (dotted curve), acid-alkali (black solid
 218 line curve) and acid-alkali-acid (red and blue solid line curve). ($\text{H}_2\text{O}/\text{BTESE}=60$)

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220

221 Table 1 Analytical data for BTESE-derived sols: the diameter determined with DLS and exponent
 222 β of the power-law relationship $I \sim q^{-\beta}$.

sol	$\text{H}_2\text{O}/\text{BTESE}$ [-]	NH_3/HCl [-]	d [nm]	β
acid	60	-	1.7	1.85
pH swing	60	12	3.0	2.63

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224

225 Fig. 5 Small-angle X-ray scattering pattern of acid ($\text{H}_2\text{O}/\text{BTESE}=60$) and pH-swing
 226 ($\text{H}_2\text{O}/\text{BTESE}=60$, $\text{NH}_3/\text{HCl}=12$) sols.

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229 3.2 Improved thermal stability of BTESE gel

230 Fig. 6 shows the ^{29}Si -NMR spectrum for BTESE-derived powders prepared by the
 231 drying of acid and pH-swing BTESE-derived sols, which will be referred to as acid
 232 and pH-swing powders, respectively. Each of the powders was fired under air and N_2
 233 conditions at 300°C . The T was observed at -60 ppm of the chemical shift and was
 234 referred to as CSiO_3 [30]. Q appeared at -100 to -110 ppm and was referred to as SiO_4
 235 [30]. The T/ (T+Q) area ratios of BTESE-derived powders fired under air and N_2 are
 236 summarized in Table 2. The ^{29}Si -NMR results showed that there was no Q peak for
 237 either acid or pH-swing BTESE-derived powders when fired under N_2 . This result
 238 confirmed that calcination under N_2 could prevent the oxidation of Si-C-C-Si and the
 239 combustion of unreacted ethoxide groups [16]. On the other hand, for powders fired
 240 under air, the T peak% of the pH-swing powder was larger than that of the acid
 241 powder. In a comparison of the T (Si-C-C-Si) and Q peaks (Si-O-Si), a larger amount
 242 of the Si-C-C-Si peak remained in the pH-swing BTESE-derived powder, indicating
 243 that pH-swing was more stable due to a higher degree of condensation.

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245
246 Fig. 6 ^{29}Si -NMR spectra of BTESE-derived powders fired at 300 °C in N_2 or air. Acid gel:
247 $\text{H}_2\text{O}/\text{BTESE}=60$, pH-swing gel: $\text{H}_2\text{O}/\text{BTESE}=60$, $\text{NH}_3/\text{HCl}=12$. Blue line: N_2 condition, red line:
248 air condition.

249

250 Table 2 T/(T+Q) area ratio of BTESE-derived silica powder fired at 300 °C in air.

Sol	T/(T+Q) area ratio [-]	
	in air	in N_2
acid	0.36	1.00
pH-swing	0.58	1.00

251

252

253 Fig. 7 (a) shows the TG curves for pH-swing and acid BTESE-derived powders.

254 TG, normalized by weight after drying for 1 h at 100 °C, showed residual weights of

268 67.1 and 85.8% for the pH-swing and acid powders at 1,000 °C, respectively. At a
 269 temperature of 200 °C, the pH-swing powder showed a drastic weight loss of 15.9%,
 270 which can be ascribed to the decomposition of ammonium chloride. As shown in Fig.
 271 7(b), a large endothermal peak, which could be ascribed to the decomposition of
 272 ammonium chloride, was observed at 200 °C only for the pH-swing powders. In order
 273 to examine the impact of the amount of NH_4Cl on TG, TG curves of the acid and the
 274 pH-swing gel were calculated by normalizing the weight at 250 °C where all NH_4Cl
 275 was decomposed. The remaining weight of the pH-swing gel at 1,000 °C was about
 276 88.4 wt% (the red dash line in Fig. 7 (a)), which approximately overlapped the
 277 remaining weight of the acid gel at 83.6 wt% (the black dash line in Fig. 7 (a)). The
 278 weight and heat flow had similar trend curves for a water ratio of 240 shown in
 279 Supplementary Data, SD-2. Therefore, it could be concluded that NH_4Cl had a small
 280 effect on the weight loss of the BTESE-derived network.

269

270
 272 Fig. 7 Thermogravimetric weight and heat flow for BTESE-derived acid and pH-swing gels.
 273 ($\text{He}/\text{O}_2=8/2$, pH-swing: red-line, $\text{H}_2\text{O}/\text{BTESE}=60$, $\text{NH}_3/\text{HCl}=12$, acid: black-line,

272 H₂O/BTESE=60)

273

274

275 Fig. 7 (b) shows the heat flow of acid and pH-swing powders. As discussed
276 previously, the endothermic peak observed (a-peak) at 200 °C could be ascribed to the
277 decomposition of NH₄Cl. On the other hand, exothermic peaks, the b-peak and c-peak,
278 which can be ascribed to the decomposition of Si-C-C-Si, were observed at 350 and
279 400 °C for acid and pH-swing powders, respectively, showing a 50 °C shift towards
280 high temperature for pH-swing sol-derived powders. It was confirmed that the
281 pH-swing method increased the thermostability of the Si-C-C-Si bonds of BTESE.

282 The nitrogen adsorption and desorption isotherms at 77 K for the BTESE-derived
283 powders are shown in Fig. 8. After firing BTESE powders at 300, 400 and 500 °C
284 under air, all the samples were degassed in vacuum at 200 °C for 4 h prior to
285 measurement. The specific surface areas are summarized in Table 3. For the powders
286 fired at 300 °C, the acid gel showed a higher BET surface area than the pH-swing gel.
287 This is probably because pH-swing promoted the condensation of Si-OH and
288 Si-OC₂H₅ to a Si-O-Si bond, leading to the formation of dense silica networks. When
289 the firing temperature was increased, the BET specific surface areas of both
290 BTESE-derived powders were decreased. The higher temperature accelerated the
291 decomposition of the Si-C-C-Si structure, and the surface area was reduced by the
292 sintering that followed, which is well known even for SiO₂ powders derived from
293 TEOS [6]. Interestingly, for the powders fired at 400 and 500 °C, the pH-swing gel
294 showed a higher BET specific area than that of the acid gel. This can be ascribed to an
295 enhancement of the network stability via the pH-swing method.

296 From the experiments indicated in the sol and gel characterizations, stronger
297 BTESE-derived networks were formed in pH-swing sols as a result of a higher degree
298 of condensation and cross-linking ($\equiv\text{Si-O-Si}\equiv$), which was clarified by the DLS and
299 SAXS. The powders derived from pH-swing BTESE sols showed a higher level of
300 thermostability, which was confirmed by NMR, TGA and BET. All the
301 characterizations were consistent.

302

303

304 **Fig. 8** Nitrogen adsorption-desorption isotherm of BTESE-derived powders, acid
 305 (H₂O/BTESE=60) and pH-swing (H₂O/BTESE=60, NH₃/HCl=12). (a) and (b) were fired at 300
 306 and 400 °C, respectively.

307

308 Table 3 BET specific surface areas of acid and pH-swing BTESE (water ratio 60).

BET surface area [m ² g ⁻¹]	Temperature [°C]		
	300	400	500
acid	505	160	72
pH-swing	378	235	91

309

310 At present, we have optimized the pH-swing method with H₂O/BTESE ratios
 311 ranging from 6 to 240 and H⁺/BTESE of 0.1 and found that the size and
 312 thermostability of the BTESE sols were increased. Optimization under a wide range
 313 of water ratios (H₂O/BTESE), acid ratios (H⁺/BTESE), temperatures and types of acid
 314 conditions will be further studied.

315

316 3.3 Improved H₂ permselectivity of BTESE membranes prepared using pH-swing

317 Although partial breakage of the Si-C bonds occurred with BTESE calcination at
 318 300 °C under air according to Si-NMR, it was reported that BTESE fired at 300 °C
 319 showed the highest He permeance and He/SF₆ separation factor of about 3,000
 320 compared with BTESE membranes fired at 100 and 200 °C [25]. In addition, H₂/N₂

and $\text{H}_2/\text{C}_3\text{H}_8$ permeance ratios of pH-swing membrane fired in N_2 were approximately the same as those fired in air (Supplementary Data, SD-3). Therefore, the BTESE membranes were calcined at 300°C under air in this work.

Fig. 9 shows the SEM image of the cross-section of a pH-swing BTESE-derived membrane prepared with a $\text{H}_2\text{O}/\text{BTESE}$ molar ratio of 6 ($\text{HCl}/\text{BTESE}=0.1$, $\text{NH}_3/\text{HCl}=24$). Although the boundary of the intermediate layer and the top layer (BTESE) is not clear, the thickness of the active separation layer was estimated to be less than 500 nm .

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Fig 9. SEM micrographs displaying the cross-section of pH-swing membranes. $\text{H}_2\text{O}/\text{BTESE}=6$, $\text{HCl}/\text{BTESE}=0.1$, $\text{NH}_3/\text{HCl}=24$.

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More than 10 membranes were prepared using acid and pH-swing sols, and the details of their performance are summarized in the Supplementary Data, SD-6. Fig. 10 shows the kinetic diameter dependency of pure gas permeance at 200°C for BTESE-derived membranes, which were prepared using BTESE-derived sols with $\text{H}_2\text{O}/\text{BTESE}$ molar ratios of 60 (Fig. 10 (a)) and 240 (Fig. 10 (b)). Hereafter membranes prepared using acid and pH-swing sols will be referred to as acid and pH-swing membranes, respectively. The permeance ratio of $\text{H}_2/\text{C}_3\text{H}_8$ was drastically increased with an increase in the $\text{H}_2\text{O}/\text{BTESE}$ molar ratio, although H_2 permeance was decreased slightly. When the ratio of $\text{H}_2\text{O}/\text{BTESE}$ was 60, the values for the H_2

permeance of acid and pH-swing ($\text{NH}_3/\text{HCl}=12$) membranes were 1.6×10^{-6} and $3.4 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively; H_2 permeance of the pH-swing membrane (M-9) was twice that of the acid membrane (M-6). On the other hand, the gas permeance ratios of $\text{H}_2/\text{C}_3\text{H}_8$ for M-6 and M-9 membranes were approximately the same at 44 and 35, respectively. For a $\text{H}_2\text{O}/\text{BTESE}$ ratio of 240, the values for the H_2 permeance of acid (M-13) and pH-swing (M-16) membranes were 1.0×10^{-6} and $1.4 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. Again, the pH-swing membrane with a $\text{H}_2\text{O}/\text{BTESE}$ of 240 showed a larger value for H_2 permeance compared with that of the acid membrane. The gas permeance $\text{H}_2/\text{C}_3\text{H}_8$ ratios for acid and pH-swing membranes were 5,800 and 2,600, respectively. Under the different molar ratios of $\text{H}_2\text{O}/\text{BTESE}$ (60 and 240), the pH-swing membrane showed a higher H_2 permeance than that of the acid membrane, with similar $\text{H}_2/\text{C}_3\text{H}_8$ permeance ratios.

It is noteworthy that membranes prepared with a $\text{H}_2\text{O}/\text{BTESE}$ ratio of 240 showed increased permeance ratios for H_2/N_2 (approximately 70), $\text{H}_2/\text{C}_3\text{H}_8$ (2,600~5,800), and H_2/SF_6 (11,000~17,000) with values for H_2 permeance as high as $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The effect of the water ratio on gas permeance can be explained as follows. When the $\text{H}_2\text{O}/\text{BTESE}$ molar ratio was increased, large numbers of ethoxide groups of BTESE were hydrolyzed, and the density of silanol groups was increased. Silanol groups were condensed with either another silanol group or an unreacted ethoxide group to form siloxane bonds. Therefore, a high water ratio induced a high degree of cross-linking [17]. A higher degree of cross-linking made the silica networks denser and the pore sizes smaller, which increased the permeance ratios of $\text{H}_2/\text{C}_3\text{H}_8$ and H_2/SF_6 and decreased H_2 permeance.

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Fig. 10 Kinetic diameter dependence of gas permeance for BTESE-derived membranes prepared using acid sols and pH-swing sols H₂O/BTESE of 60 (a) and 240 (b) at 200 °C. (Open: acid membrane, closed: pH-swing membrane)

Figs. 11 (a) and (b) show the trade-offs of H₂ permeance against the permeance ratios of α (H₂/C₃H₈) and α (H₂/N₂) for both acid and pH-swing-derived membranes measured at 200 °C. It should be noted that each point corresponds to one membrane prepared with a different water ratio. When the H₂O/BTESE ratio was increased from 6 to 240, the permeance ratios of α (H₂/C₃H₈) and α (H₂/N₂) of both acid and pH-swing membranes were increased, indicating a reduction in pore size. On the other hand, H₂ permeance was decreased.

The pH-swing membranes showed a higher H₂ permeance compared with acid membranes of the same water ratio, while the ratios for α (H₂/C₃H₈) and α (H₂/N₂) were approximately similar for both acid and pH-swing BTESE-derived membranes. For example, with a water ratio of 60, H₂/C₃H₈ and H₂/N₂ permeance ratios were approximately 100 and 10, respectively, for both acid and pH-swing membranes, indicating no change in pore size. On the other hand, the H₂ permeance of pH-swing membranes was higher than that of acid membranes. The average pore sizes of acid

membranes were approximately the same as those of pH-swing membranes for all H₂O molar ratios, since the permeance ratios for H₂/C₃H₈ and H₂/N₂ were approximately unchanged.

We also applied the Normalized Knudsen-based Permeance (NKP) method [31, 32] to obtain an average pore size quantitatively as shown in Supplementary Data, SD-4. In addition, a binary mixture (H₂/methylcyclohexane) for the BTESE membrane (prepared by acid sol) indicated a negligible effect for mixing at high temperature (200–300 °C), which resulted in approximately the same H₂ permeance for the single as that for the mixture [17]. This can be attributed to the different structures of the acid and pH-swing BTESE sol-derived membranes (Fig. 12). The two-dimensional (shown with beads) and three-dimensional (shown with wavy lines in the circles) structures of acid and pH-swing sols were confirmed by the SAXS results. The size of the acid sols (1 nm) was smaller than the pore size of the intermediate layer (2 nm), so the acid sols easily penetrated the intermediate layer, resulting in high resistance to gas permeation and lowered permeability. The size of pH-swing sols (5 nm) was larger than the size of the intermediate layer pores, resulting in less penetration and higher gas permeance than that of the acid membranes. The details of the XPS and SEM of acid and pH-swing films are available in the Supplementary Data (SD-5), and these confirm the concept shown in Fig. 12. Thus, BTESE membrane permselectivity was increased in the pH-swing process.

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416 **Fig.11** Trade-off of H_2 permeance and H_2/N_2 (a), H_2/C_3H_8 (b) permeance ratios for BTESE-derived
 417 membranes prepared using acid and pH-swing sols with different water ratios. Gas permeances
 418 were measured at 200 °C. Membranes prepared by acid sols: open, pH-swing sols: closed.
 419 Tabulated data are available in Supplementary Data (SD-6) that some previous findings [33] are
 420 included.

417

418 **Fig. 12** Schematic structure of the acid and pH-swing BTESE sols-derived membranes,
 420 pH-swing sols were larger in size and more spherical than acid sols.
 421

421

422

423 *3.4 Temperature dependency and CO_2 permselectivity of pH-swing membranes*

428 In the previous section, BTESE-derived hybrid organosilica membranes with high
 429 gas permselectivity were successfully prepared by carefully controlling the reactivity
 430 of the sol structure via pH-swing and water ratios in the sol. Small molecules such as
 431 hydrogen and CO_2 can be separated from larger ones, including N_2 and methane, via
 432 sieving mechanisms.

436 **Fig. 13** shows the temperature dependence of gas permeances for the pH-swing
 437 membrane with a $H_2O/BTESE$ ratio of 240. The permeance values of He, H_2 , N_2 and
 438 CH_4 for membranes gradually increased with increasing temperatures from 50 to 200
 439 °C, which corresponded to an activated permeation mechanism. The H_2/C_3H_8
 440 permeance ratio was higher than 1,000 at temperatures ranging from 50 to 200 °C,
 441 with the highest value reaching 2,400 at 200 °C. The permeance of C_3H_8 slightly
 442 increased with increases in temperature above 150 °C (activated diffusion), and was
 443 decreased at temperatures lower than 150 °C, showing Knudsen behavior below 150

436 °C. C₃H₈ permeation behavior could be governed by the balance of flow through
 437 activated and/or Knudsen permeation, depending on the loose pore size of the BTESE
 438 membranes. The permeance of CO₂ increased with decreases in temperature in a
 439 manner similar to that of the surface diffusion mechanism. The CO₂/N₂ and CO₂/CH₄
 440 permeance ratios increased from 8 to 30 and 20 to 90, respectively, with decreases in
 441 temperature of from 200 to 50 °C. This could be explained by a larger amount of CO₂
 442 adsorption on organosilica that could occur at a lower temperature due to a strong
 443 affinity compared with that of other gases.

444

445

446 **Fig. 13.** Temperature dependence of gas permeance and gas permeance ratios for the pH-swing
 447 BTESE-derived membrane at range of 50 to 200 °C.

448

449

450 Fig. 14 summarizes a comparison of CO₂/N₂ and CO₂/CH₄ separation through
451 BTESE prepared by pH-swing sols, silica and zeolite membranes. The data of CO₂
452 separation using BTESE-derived and zeolite membranes are available in the
453 Supplementary Data, SD-7. For BTESE-derived membranes, CO₂ permeance was
454 decreased with increases in the water ratios of from 60 to 240, while α (CO₂/N₂) was
455 increased from 8 to 30 and α (CO₂/CH₄) increased from 5 to 90. For CO₂/N₂
456 separation, BTESE-derived membranes could offer higher CO₂ permeance at a
457 H₂O/BTESE ratio of 60 and a moderate selectivity of 30 for a H₂O/BTESE ratio of
458 240 compared with that of other materials. In the case of CO₂/CH₄ separation, the
459 inorganic membranes such as DDR and SAPO-34 showed high permeance and
460 permeance ratios. While BTESE-derived membranes showed the highest selectivity of
461 90 for a H₂O/BTESE ratio of 240, the CO₂ permeance could be increased as high as
462 $2.6 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for a H₂O/BTESE ratio of 60. BTESE-derived membranes
463 demonstrated a moderate level of selectivity and a wide range of CO₂ permeance. It is
464 suggested that BTESE membranes might perform better permselectivity for CO₂/N₂
465 and CO₂/CH₄ via further optimization of the pH-swing process.
466

467
 468 **Fig. 14.** Trade-off of BTESE, silica and zeolite for CO₂/N₂ (a) and CO₂/CH₄ (b) separation at near
 469 room temperature to 50 °C. While α (CO₂/CH₄) of POSS was measured at 100 °C. References of
 470 (a): T [34], SiO₂-NH₂ [35], HZSM-5 [36] and NaZSM-5 [37-39]. References of (b): POSS [40],
 471 DDR [41], T [34, 42] and H-SAPO-34 [43-46].

472

473 4. Conclusions

474 In this study, sol-gel processing was applied to the fabrication of layers of
 475 BTESE-derived organosilica membranes formed on a SiO₂-ZrO₂ intermediate layer.
 476 The single-gas permeation properties for acid membranes and pH-swing membranes
 477 were examined to evaluate the effect of pH-swing processing on BTESE. The
 478 pH-swing process increased the condensation and cross-linking of silica networks,
 479 which improved network stability. In addition, increased sol sizes by pH-swing
 480 reduced penetration into the intermediate layer and enhanced the gas permeance
 481 compared with the acid sols. The BTESE-derived membranes also showed high
 482 permeance ratios for H₂/C₃H₈ that ranged from 2,600 to 5,800 at 200 °C with a high

483 H₂ permeance that was greater than $1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and permeance ratios for
484 CO₂/N₂ of 90 and for CO₂/CH₄ of 28 at 50 °C.

485

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