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ARTICLE TYPE

Tuning the pore sizes of novel silica membranes for improved gas permeation properties via *in-situ* reaction between NH₃ and Si-H groups**Masakoto Kanezashi,^{*a} Rui Matsugasako,^a Hiromasa Tawarayama,^b Hiroki Nagasawa,^a Tomohisa Yoshioka,^a and Toshinori Tsuru^a**⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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A new concept was proposed to control the pore size in a novel silica membrane. The tuning of the pore sizes in triethoxysilane (TRIES)-derived membranes was successfully conducted via an *in-situ* reaction between NH₃ and Si-H groups at high temperatures. The formation of Si-NH₂ and/or Si-NH groups in the silica structure enhanced the hydrogen selectivity.

It is well known that amorphous silica networks via CVD and sol-gel methods that utilize a tetraethoxysilane (TEOS) have a silica network size that ranges from 0.3-0.35 nm.^{1,2} Only He (kinetic diameter: 0.26 nm) and H₂ (0.289 nm) can permeate amorphous silica networks, and amorphous silica membranes show high perm-selectivity for H₂/N₂ (0.364 nm) and H₂/CH₄ (0.38 nm) due to the molecular sieving separation.^{1,3,4} However, a TEOS-derived amorphous silica structure is not appropriate for other separation systems that are used for separations such as CO₂ (0.33 nm)/N₂, O₂ (0.346 nm)/N₂, CO₂/CH₄, C₂-C₄, and C₃H₆ (0.468 nm)/C₃H₈ (0.506 nm), due to the small network size as well as to a weak affinity between adsorptive molecules such as CO₂, C₂H₄ and C₃H₆, and silica (silanol groups).⁴ Control of the affinity between preferentially adsorbed molecules and silica is important in order to achieve a high degree of separation performance by blocking the permeation of non-adsorptive molecules by preferentially adsorbed molecules under binary separation (CO₂/N₂, CO₂/CH₄, C₃H₆/C₃H₈, etc.).^{5,6} Thus, if the gas separation properties of a separation system are to be improved, the precise tuning of the network size as well as an enhancement of the adsorption properties between permeating molecules and silica are paramount issues.

The utilization of organoalkoxysilane, which can be classified as either a bridged-type⁶⁻¹¹ or a pendant-type¹²⁻¹⁴ alkoxide, was effective for the control of amorphous silica network sizes. For example, bridged-type alkoxides, such as bis (triethoxysilyl) ethane (BTESE) and bis (triethoxysilyl) methane (BTESM), contain a functional group between 2 silicon atoms, while pendant-type alkoxides have organic groups such as methyl and phenyl that are directly connected with a Si atom. Organosilica membranes have amorphous networks that are looser than those of TEOS-derived membranes, because of the presence of organic groups.⁸⁻¹⁰ For instance, BTESE membranes (Si-C-C-Si unit) showed a H₂ permeance (6×10^{-6} - 1×10^{-5} mol m⁻² s⁻¹ Pa⁻¹) that was higher than that of TEOS (=Si-O) membranes, as well as a

high H₂/SF₆ permeance ratio (1,000-3,000) with a low H₂/N₂ permeance ratio (~10) due to a larger average pore size.^{8,10}

To accomplish an improved membrane affinity for CO₂ separation at low temperature, Xomeritakis et al.^{15,16} proposed an aminosilicate membrane with fixed amine ligands incorporated in the silica structure. The aminosilicate membrane showed CO₂ permeance (~10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) with a CO₂/N₂ separation factor of 24-27.2 at 22 °C (Feed composition: CO₂: 50 vol.%). Aminosilica sols are synthesized by the co-polymerization of TEOS with a 3-aminopropyl triethoxysilane (APTES), which is a pendant-type alkoxide with a large amount of HCl to avoid gelation, because of the basic properties of -NH₂ groups in an APTES precursor. Thus, the removal of HCl from -NH₂ groups was essential in reactivating the amine groups, which would be the most critical factor for improved CO₂ perm-selectivity. The aminosilicate membranes would be good candidates for CO₂ separation membranes, although in a later publication Xomeritakis et al.¹⁶ also reported difficulty in simultaneously controlling the pore size and the porosity of an aminosilicate framework, perhaps because aminopropyl (-CH₂CH₂CH₂NH₂) groups are long-branched structures.

In the present study, a triethoxysilane (TRIES) that had never been used for membrane preparation was used as a Si precursor. A new concept was proposed for control of the pore size and the affinities of TRIES-derived novel silica membranes via *in-situ* reactions between NH₃ and Si-H groups at high temperatures. Hydrosilyl groups (Si-H) in TRIES have generally been used to create Si-C-C-Si units via a hydrosilylation reaction with vinyl groups (Si-CH=CH₂),¹⁷ but NH₃ has never been used to control the pore size of silica networks. The concept for the formation of NH₂ groups in silica networks by *in-situ* reaction is shown in Fig. 1. A silsesquioxane (SQ) sol was prepared via a sol-gel method using a triethoxysilane (TRIES) for the formation of Si-O-Si networks. Next, an *in-situ* NH₃ reaction was carried out to form NH₂ groups in silica networks, which were expected to form by the reaction of hydrosilyl groups and NH₃ for improved gas permeation. The details of the fabrication procedure are described in the supplementary information. Gas permeation through TRIES-derived membranes before and after *in-situ* reactions was evaluated to discuss the effect of the *in-situ* reaction between NH₃ and Si-H groups on the silica structure and the affinity between NH₂ groups and CO₂ molecules.



Fig. 1 Schematic image of controlling the pore size and the affinities of TRIES-derived membranes via an *in-situ* reaction between NH_3 and Si-H groups.

Fig. 2 (a) shows the FT-IR transmission spectra of TRIES-derived films calcined at 400 to 650 °C under N_2 . All samples showed Si-O-Si asymmetric stretching vibrations at approximately 1,100 cm^{-1} that were caused by the hydrolysis and condensation of Si-OEt and Si-OH groups, which suggested the formation of silica networks.¹⁸ A small peak of CH_3 -groups that originated from the unreacted ethoxide groups (2,974 cm^{-1})¹⁹ was observed in the TRIES-derived film that was calcined at only 400 °C, since ethoxide groups can decompose at temperatures above 450 °C under a N_2 atmosphere.^{10,20} The hydrosilyl (Si-H) groups were observed at 2,250 cm^{-1} ,²¹ and showed almost the same peak intensity ratio as that of Si-O-Si, irrespective of calcination temperatures. Thus, hydrosilyl groups were expected to be present in the amorphous structure even at high temperatures under an N_2 atmosphere.

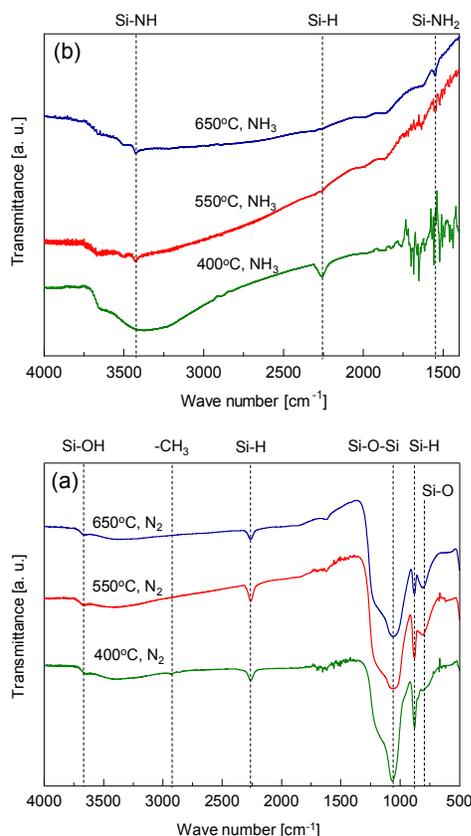


Fig. 2 FT-IR transmission spectra of TRIES-derived films calcined at 400-650 °C under N_2 before and after exposure to NH_3 ((a) before exposure to NH_3 , (b) after exposure to NH_3 at 400-650 °C for 1h).

Fig. 2 (b) shows the FT-IR transmission spectra of TRIES-derived films after NH_3 reaction at 400 to 650 °C. It should be noted that NH_3 reaction was conducted for samples pretreated at the same temperature under a N_2 atmosphere (Fig. 2 (a)). A film with a NH_3 reaction at 400 °C showed almost the same FT-IR spectra as before the NH_3 reaction (Fig. 2 (a)), indicating no reaction had occurred. The films with NH_3 reactions at 550 and 650 °C showed no peak intensities of Si-H groups, and Si- NH_2 (1,550 cm^{-1}) and Si-NH (3,420 cm^{-1}) groups were confirmed.^{22,23} These results suggest that Si-H groups can be reacted with NH_3 at temperatures higher than 550 °C, and that the Si- NH_2 and/or Si-NH groups were created with a silica structure.

Fig. 3 shows the molecular size dependence of gas permeance at 400 °C for a TRIES-derived membrane (TM-1) before and after thermal stability testing at 550 °C. A TM-1 immediately following fabrication at 550 °C under N_2 showed a H_2 permeance of approximately $6.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with permselectivities for H_2/CO_2 at 10, for H_2/CH_4 at 24, and for H_2/CF_4 at 100 with a temperature of 400 °C. A TM-1 showed high thermal stability at 550 °C under a N_2 atmosphere for 12 h, and no appreciable change in permeance was confirmed for any gas. After confirming the thermal stability of TM-1, an *in-situ* NH_3 reaction at 550 °C was conducted for 1 h.

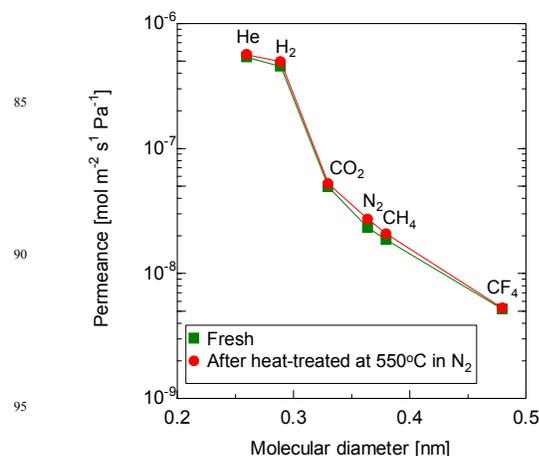


Fig. 3 Molecular size dependence of gas permeance at 400 °C for a TRIES-derived membrane (TM-1) before and after thermal stability testing at 550 °C.

Fig. 4 shows molecular size dependence of gas permeance at 400 °C for a TM-1 before and after *in-situ* NH_3 reaction at 550 °C. The permeance of both He and H_2 was decreased approximately 40% of the initial values, but He was more permeable than H_2 after exposure to NH_3 . CO_2 permeance was decreased by approximately 80%, and the decreased ratio of CO_2 permeance was larger than that of either He or H_2 , resulting in an increase in H_2/CO_2 selectivity of from 9.5 to 20. NH_3 permeance, which was measured at 550 °C during the *in-situ* reaction, showed good agreement with the molecular size dependence of gas permeance. The large decrease in CO_2 permeance could have been due to the fact that CO_2 (0.33 nm) molecules have an effective molecular size that is similar to that of NH_3 (0.326 nm).²⁴ Thus, the network pores seemed to be densified by the reaction of the hydrosilyl groups and NH_3 , and

this is where most of the permeation by NH_3 and CO_2 molecules took place. On the contrary, there was no change in CF_4 permeance either before or after the reaction with NH_3 , which has a larger molecular size than either He or H_2 . The measured permeance after the NH_3 reaction, except for that of He, H_2 and NH_3 , was in good agreement with Knudsen permeation based on CF_4 permeance. These results suggest that a TRIES-derived membrane reacted with NH_3 creates a bimodal structure with amorphous networks that He and H_2 can permeate, but fewer large pores that CF_4 molecules can permeate by Knudsen diffusion.

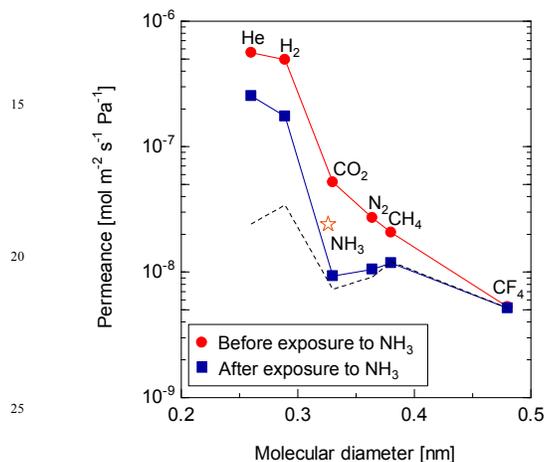


Fig. 4 Molecular size dependence of gas permeance at 400 °C for a TRIES-derived membrane (TM-1) before and after *in-situ* NH_3 reaction at 550 °C. Broken line: estimated permeance by Knudsen permeation based on CF_4 permeance.

In order to elucidate the effect that NH_3 concentration in feed gas would exert on pore size tuning properties, a He flow was used to dilute NH_3 to 10 mol%. Fig. 5 shows the permeance ratios (H_2/N_2 , H_2/CH_4 , H_2/CO_2 , CO_2/CH_4 , CO_2/N_2) and normalized permeance based on the initial permeance of each gas at 400 °C using a TRIES-derived membrane (TM-2) as a function of NH_3 reaction time (550 °C, 10 mol%). The permeance ratios of H_2/CH_4 , H_2/N_2 and H_2/CO_2 were increased by *in-situ* NH_3 reaction, but no increase in either the CO_2/CH_4 or CO_2/N_2 permeance ratios was confirmed. The decreased ratios of He and H_2 permeance were much smaller than those of either CO_2 , N_2 or CH_4 , while the decreased ratios of CO_2 , N_2 and CH_4 permeance showed almost no change, irrespective of molecular size. No appreciable change in CF_4 permeance was confirmed, which agreed with the trend shown in Fig. 4 (NH_3 concentration in feed: 100 mol%).

Gas permeation properties were evaluated by the temperature dependence of gas permeance before and after *in-situ* NH_3 reaction (550 °C, 10 mol%). Fig. 6 shows the temperature dependence of gas permeance for a TRIES-derived membrane (TM-2) before and after NH_3 reaction for 3.5 h. The permeance of He before a NH_3 reaction was constant, irrespective of temperature. The CO_2 molecules showed surface diffusion, and the CF_4 molecules showed Knudsen diffusion. After a NH_3 reaction, the He permeance increased with temperature and showed an activated diffusion. CO_2 molecules showed surface

diffusion with no appreciable changes in the slope of the temperature dependence after the NH_3 reaction. There was no change in the gas permeation properties of CF_4 molecules.

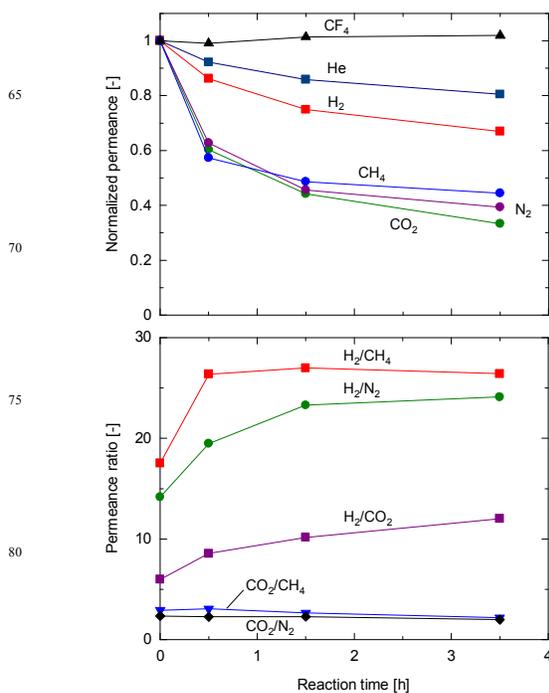


Fig. 5 Permeance ratios (H_2/N_2 , H_2/CH_4 , H_2/CO_2 , CO_2/CH_4 , CO_2/N_2) and normalized permeance based on the initial permeance of each gas at 400 °C for a TRIES-derived membrane (TM-2) as a function of the NH_3 reaction time (550 °C, 10 mol%).

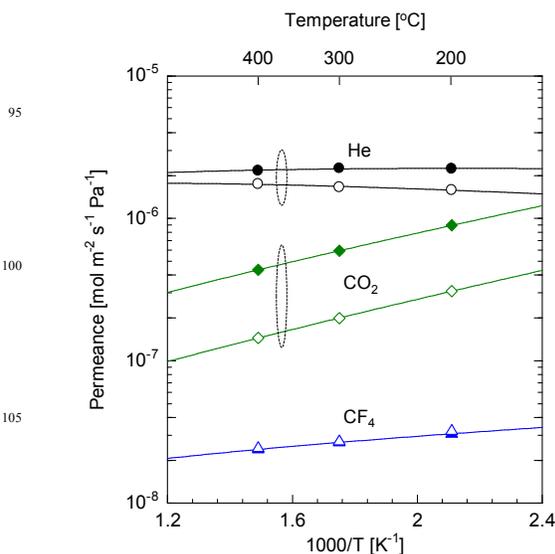


Fig. 6 Temperature dependence of gas permeance for a TRIES-derived membrane (TM-2) before and after NH_3 reaction (550 °C, 10 mol%) (closed symbols: before reaction, open symbols: after NH_3 reaction for 3.5 h).

The activation energy of permeation for He, CO_2 and CF_4 was

calculated using a modified gas translation (GT) model²⁵ and are summarized in Table S2 (supplementary information). The increased activation energy of He permeation as well as the increased He/N₂ and He/CH₄ permeance ratio after the reaction of NH₃ could have been due to the densified network structure that was caused by the formation of the Si-NH and Si-NH₂ groups. The BET surface area measured by N₂ adsorption at 77K decreased from 448 to 388 m² g⁻¹ after *in-situ* reaction (NH₃ concentration in feed: 10 mol%) for 1h, and also showed a trend in the densification of the network structure. Since the activation energy of CO₂ permeation showed only slight changes, and the CO₂/N₂ and CO₂/CH₄ permeance ratio showed a small degree of change after the reaction of NH₃, we concluded that the adsorption properties of CO₂ molecules were not enhanced, despite the presence of the Si-NH₂ groups in the membrane. The ratio of Si-NH₂/Si-O-Si for TRIES-derived film with a NH₃ reaction at 550 °C was 0.00157, which was approximately 10 times smaller than that for TEOS-APTES (TEOS/APTES molar ratio: 0.6/1)-derived film (Table S1). Thus, the densities of the Si-NH₂ groups in the membrane were insufficient, which could have been caused by the formation of a silazane structure to capture the CO₂ molecules, since 2 Si-NH₂ groups are required to capture CO₂ molecules under dry conditions.^{26,27}

In conclusion, a tuning of the pore sizes of TRIES-derived membranes was successfully conducted via an *in-situ* reaction between NH₃ and Si-H groups at high temperatures. The formation of Si-NH₂ and/or Si-NH groups in the silica structure enhanced the hydrogen selectivity, and the reaction properties were possibly controlled by the concentration of NH₃ in the feed gas.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedure, FTIR spectra, SEM, activation energy of He, CO₂ and CF₄ permeation before and after *in-situ* reaction]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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