

Precursors-Derived Ceramic Membranes for High-Temperature Separation of Hydrogen

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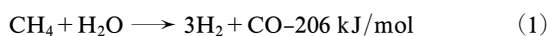
This review describes recent progress in the development of hydrogen-permselective ceramic membranes derived from organometallic precursors. Microstructure and gas transport property of microporous amorphous silica-based membranes are briefly described. Then, high-temperature hydrogen permselectivity, hydrothermal stability as well as hydrogen/steam selectivity of the amorphous silica-based membranes are discussed from a viewpoint of application to membrane reactors for conversion enhancement in the methane steam reforming reaction, which leading to development of a novel highly efficient hydrogen production system. Novel nickel (Ni)-nanoparticles dispersed amorphous silica-based membranes with a unique hydrogen permselectivity, and polymer-derived amorphous Si-(B)-C-N membranes having enhanced thermal and chemical stability are also discussed to develop novel ceramic membranes for high-temperature separation of hydrogen.

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1. Introduction

BECAUSE of concerns about global warming, increasing attention has been directed towards finding an alternative to fossil fuels, of which hydrogen is rapidly becoming one of the leading candidates. Hydrogen can be used in combustion devices and fuel cells without production of polluting greenhouse gases. Today, most hydrogen is produced through steam reforming of natural gas, described by the reaction:



This reaction is endothermic, and the methane (CH_4)/hydrogen (H_2) conversion efficiency is limited by thermodynamic equilibrium. Generally, the reactor is operated at approximately 1073 K. The synthesis gas then proceeds to a water-gas shift reactor where steam and carbon monoxide (CO) can be converted into more H_2 and carbon dioxide (CO_2). Finally, H_2 must be separated from the mixed gas using an adsorption technology such as pressure swing adsorption (PSA). Due to the higher operation temperature and several complicated purification steps, the cost to produce H_2 with these current technologies is too high for it to be an alternative to the conventional hydrocarbon fuels.

It is well known that the application of high-temperature membrane reactors to this steam reforming step has the potential to achieve the same conversion efficiencies as those attained in conventional reactors at a significantly lower temperature of about 773 K.^{1)–4)} In addition, membrane reactors may simplify the process of producing H_2 from natural gas and purifying it by combining these processes into a single step, leading to development of a novel highly efficient hydrogen production system.

For application to high-temperature membrane reactors, two types of inorganic membranes are considered: dense palladium-based membranes and porous ceramic membranes. Palladium-based membranes, while exhibiting excellent H_2 permselectivity, suffer from a number of drawbacks: they are very expensive, susceptible to poisoning by sulfur and prone to formation of pinholes or cracks as a result of hydrogen embrittlement. Organometallic precursors-derived ceramic membranes with micropores smaller than one nano-

meter have great potential for gas separation. Compared with polymer membranes, microporous ceramic membranes with molecular sieve-like properties have relatively high gas permeances and a good stability at higher-temperatures, and they have been expected to use in membrane reactors for the conversion enhancement in dehydrogenation of hydrocarbons⁵⁾ as well as in the methane steam reforming reaction mentioned above. The present review describes recent progress in the development of precursors-derived microporous ceramic membranes for high-temperature separation of hydrogen, especially focused on amorphous silica-based membranes, novel amorphous silica-based nanocomposite membranes with a unique H_2 -permselectivity, and polymer-derived thermally and chemically stable amorphous Si-(B)-C-N membranes.

2. Microporous amorphous silica-based membranes

2.1 Microstructure and gas transport property

Precursors-derived microporous amorphous silica-based membranes are well known for their H_2 permselectivity, and generally fabricated as a thin film on a permeable alumina (Al_2O_3) porous support. The Al_2O_3 support has a graded and layered porous structure with macropores in $\alpha\text{-Al}_2\text{O}_3$ support layers to mesopores in a $\gamma\text{-Al}_2\text{O}_3$ surface thin layer. The pore size of the Al_2O_3 support decreases layerwise from several hundred nanometers to an average pore size of about 4 nm for the $\gamma\text{-Al}_2\text{O}_3$ surface thin layer.^{6),7)} A typical transmission electron micrograph (TEM) of a focused ion beam cross section of a microporous ceramic membrane on a porous Al_2O_3 support⁸⁾ is shown in **Fig. 1**.

The overall gas transport properties of a porous support are examined to study the effect of defect formations such as pinhole and cracks in the microporous ceramic membranes, and gas transport resistance in the porous support. Possible gas transport mechanisms are Knudsen's diffusion, viscous flow, and molecular diffusion. The dominant mechanism for the gas transport properties depends on the Knudsen's number (K_n):

$$K_n = \frac{\lambda}{D_p}; \quad \lambda = \frac{kT}{\sqrt{2} \sigma p} \quad (2)$$

where λ is the mean free path length of a gas molecule, D_p the

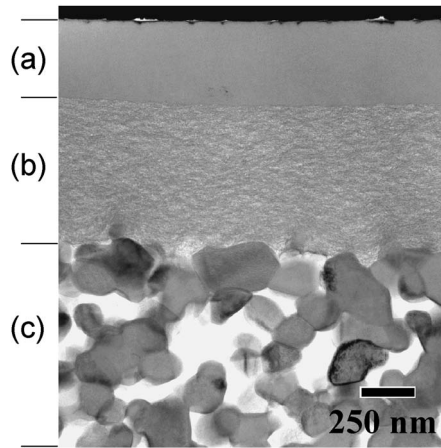


Fig. 1. Cross-sectional TEM image of a precursor-derived microporous ceramic membrane fabricated on a porous support. (a) microporous membrane, (b) mesoporous γ - Al_2O_3 thin layer and (c) α - Al_2O_3 macroporous support.

pore radius, k the Boltzmann constant, T the temperature, σ the collision cross section of a gas molecule, and p the gas pressure. Knudsen's diffusion dominates at the $Kn \gg 1$, and the permeance (Q) can be described by following equation:⁹⁾

$$Q = \frac{\varepsilon D_p}{\tau L} \left(\frac{8}{9\pi MRT} \right)^{1/2} \quad (3)$$

where ε is the porosity, D_p the pore diameter, τ the tortuosity, L the mean membrane thickness, R the gas constant, T the temperature, and M the molecular weight.

The gas diffusion resistance of the mesoporous γ - Al_2O_3 surface thin layer is much larger than that of the macroporous α - Al_2O_3 support. Therefore, the overall gas transport properties of the Al_2O_3 porous support are considered to be governed mainly by the transport properties of the mesoporous γ - Al_2O_3 surface thin layer. The ratios of the lengths of mean free paths of the gas molecules such as H_2 , CO_2 , CO and CH_4 , and the mean pore size of the mesoporous γ - Al_2O_3 surface thin layer are approximately 30 to 120.¹⁰⁾ The gas permeation behaviors through the mesoporous γ - Al_2O_3 -coated α - Al_2O_3 porous support have been experimentally confirmed to show Knudsen's diffusion characteristics as predicted.^{10),11)}

To study the gas transport properties of a microporous amorphous silica-based membrane on a porous Al_2O_3 support systematically, a mesoporous anodic alumina capillary (MAAC) tube having highly oriented radial mesopore channels was used as an ideal alumina-based support with a graded and layered porous structure (Fig. 2). The mean pore diameters of region I, II and III in Fig. 2(c) were about 3–4 nm, 6 nm and 16 nm, respectively.^{12),13)} Single gas permeance through the MAAC tube was evaluated for helium (He), H_2 , CO_2 , argon (Ar) and nitrogen (N_2) at 773 K. As shown in Fig. 3(a), the gas permeance was proportionate to the reciprocal of the square root of the molecular weight (M). The H_2/He permselectivity given by the ratio $Q_{\text{H}_2}/Q_{\text{He}}$ was 1.4, which was well consistent with the theoretical value (1.41) based on the Knudsen's diffusion. The dominant mechanism for the gas permeation behaviors through the MAAC tube could be well explained by the Knudsen's diffusion, which indicating that the MAAC tube was defect-free, and the gas molecules could permeate only through the radial mesopore channels in the MAAC tube.¹²⁾

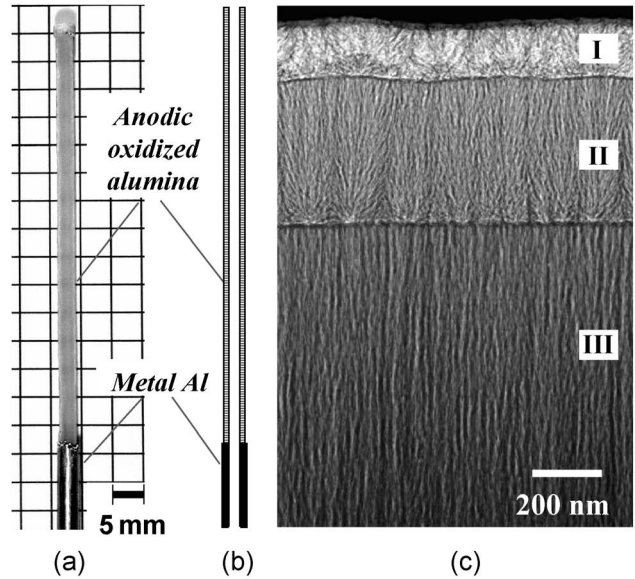


Fig. 2. Mesoporous anodic alumina capillary (MAAC) tube synthesized by a novel pulse sequential anodic oxidation technique: (a) Optical microscope image, (b) Schema, and (c) Cross sectional TEM image of the near outer surface area fabricated by changing the anodizing voltage in steps.

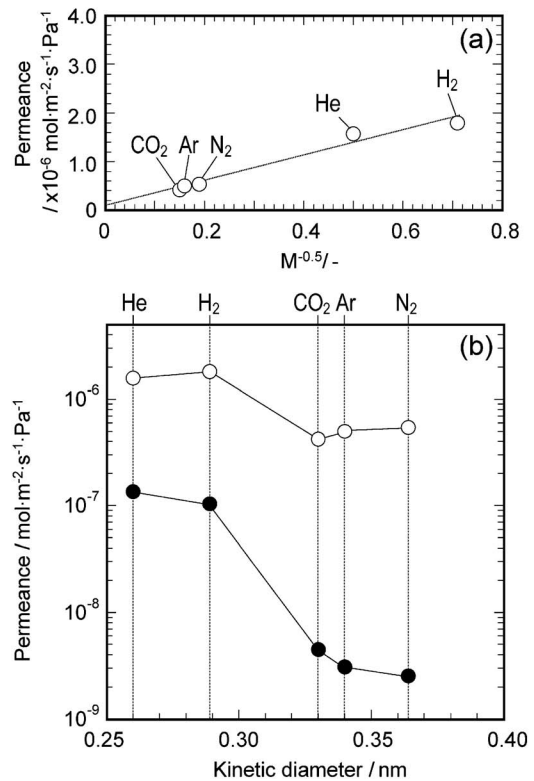


Fig. 3. Gas permeation behaviors at 773 K of a MAAC tube and a sol-gel derived amorphous silica membrane fabricated on the MAAC tube. (a) Variation of gas permeances through a MAAC tube with $M^{-0.5}$, and (b) Gas permeances as a function of kinetic diameter of gas molecules. \circ : MAAC tube, \bullet : amorphous silica membrane.

Figure 3(b) shows gas permeation behaviors at 773 K of a sol-gel derived amorphous silica membrane fabricated on the MAAC tube.¹⁴⁾ The gas permeance order apparently

changed, and followed the kinetic diameter of the gas molecules, He (0.260) > H₂(0.289) > CO₂(0.330) > Ar (0.340) > N₂ (0.364).¹⁵ The permeances of the smaller gas molecules below 0.3 nm (He and H₂) were much higher than those of other gas molecules with larger dimensions. This could be recognized as the molecular sieve-like property of microporous amorphous silica membranes.

Recently, Oyama et al. analyzed and discussed on the selectivity and transport mechanism for the smaller gas molecules (He and H₂) through amorphous silica membranes synthesized by the chemical vapor deposition (CVD) method.¹⁶ They employed a permeation mechanism of molecular diffusion in which gas molecules adsorb in the solubility sites and then diffuse through the amorphous silica by jumping to adjacent solubility sites under the driving force of a concentration gradient. The solubility sites were thought to be approximately 0.3 nm in diameter, and formed from cavities in the amorphous silica similar to a disordered form of β -cristobalite containing 5 to 8 membered rings.¹⁷ The well controlled size of the solubility site in the amorphous silica could restrict sorption of the larger gas molecules above 0.3 nm in kinetic diameter, which resulted in the excluding passage of CO₂, CO and CH₄ through the amorphous silica membranes.

The theory for the permeation mechanism of He and H₂ could be adapted from an existing classical statistical mechanics treatment for vitreous silica glasses.¹⁸⁾⁻²⁰⁾ A monatomic gas permeance through silica glass has been expressed by the following equation,

$$Q = \frac{1}{6L} \left(\frac{d^2}{h} \right) \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \times \frac{N_s/N_A}{(e^{h\nu^*/2kT} - e^{-h\nu^*/2kT})^2} e^{-\Delta E_K/RT} \quad (4)$$

where Q is the permeance of a monatomic gas, L the membrane thickness, d the jump distance, h the Planck's constant, k the Boltzmann constant, m the mass of the species, N_s the number of solubility sites available/m³ of glass volume, N_A the Avogadro's number, ν^* the vibrational frequency of gas molecules on the doorway sites, R the gas constant, T the temperature, and E_K the activation energy for hopping between sorption sites.²⁰ This permeance model could be applied to H₂ in a similar form taking into account loss of rotational freedom at the doorway sites through the factor $\{\sigma h^2 / (8\pi I k T)\}^{1/2}$,^{0.2} where σ is the symmetry factor (2) for H₂, I is its moment of inertia, and the exponent, 0.2 is empirical. The two key parameters of d and N_s obtained by the Perkus-Yevick treatment of their experimental data were 0.8 nm and 10²⁶ m⁻³, respectively, which could be physically realistic to explain the CVD-derived lower dense amorphous silica network structure compared to the vitreous silica glasses.¹⁶⁾

2.2 High-temperature hydrogen permselectivity

Figure 4 shows the H₂ permselectivity of the amorphous silica-based membranes synthesized by the CVD or chemical vapor infiltration (CVI),²¹⁾⁻³⁴⁾ sol-gel,³⁵⁾⁻³⁷⁾ and polymer pyrolysis³⁸⁾ methods. The literature data measured at permeation temperatures ranging from 573 to 873 K were taken and plotted. The amorphous silica-based membranes generally exhibit a trade-off relationship between the H₂/N₂ selectivity and H₂ permeance, and there is an empirical upper bound in performance shown by a broken line in Fig. 4. Compared with the higher-performance of palladium-based membranes, the amorphous silica-based membranes need to surpass this bound. Furthermore, hydrothermal stability and H₂/steam selectivity of the amorphous silica-based membranes are also

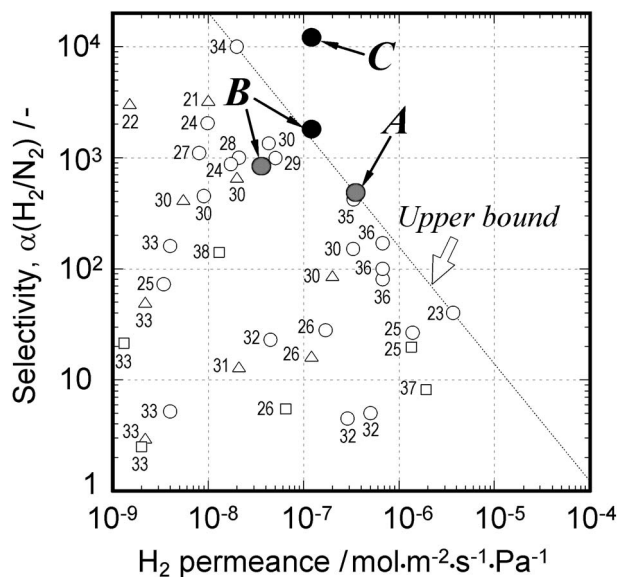


Fig. 4. H₂ permselectivity of precursors derived microporous amorphous silica-based membranes measured under ●: dry condition at 773–798 K, ●: hydrothermal condition at 773 K (steam 75–90 kPa). The literature data^{21–38} measured under dry condition at permeation temperatures ranging from □: 573 K ≤ T < 673 K, △: 673 K ≤ T < 773 K and ○: 773 K ≤ T ≤ 873 K were taken and plotted.

important properties to apply for steam reforming reactions as a hydrogen permselective membrane reactor.

Recently, Kanezashi and Asaeda studied on the hydrothermal stability and H₂/steam selectivity of sol-gel derived nickel (Ni)-doped amorphous silica membranes having Si/Ni atomic ratios ranging from 4/1 to 1/1.³⁹⁾ The membranes were fabricated on a porous α -Al₂O₃ support coated with hydrothermally stable zirconium-doped amorphous silica.⁴⁰⁾ After hydrothermal treatment at 923 K, the amorphous silica-based membrane with Si/Ni=2/1 showed H₂ permeance of 3.5 × 10⁻⁷ [mol·m⁻²·s⁻¹·Pa⁻¹] at 773 K, while H₂/N₂ permselectivity was measured to be 480 (A in Fig. 4). Even after the hydrothermal treatment (steam: 90 Pa) at 773 K for one week, the membrane exhibited relatively high H₂ permeance, 2.0 × 10⁻⁷ [mol·m⁻²·s⁻¹·Pa⁻¹] with H₂/N₂ permselectivity of 400. The H₂/steam selectivity was also found to be dependent on the Ni content, giving a maximum observed selectivity of 37 for the Ni-doped amorphous silica membrane (Si/Ni = 1/1).³⁹⁾

Nomura et al. also developed stable amorphous silica membranes by using the counter diffusion CVD method where two kinds of reactants, tetramethylorthosilicate [Si(OCH₃)₄, TMOS] and oxygen (O₂) were supplied from the opposite side of the mesoporous γ -Al₂O₃-coated α -Al₂O₃ porous support.^{41),42)} At 773 K, the H₂ permeance and H₂/N₂ permselectivity of the CVD-derived amorphous silica membrane achieved 1.2 × 10⁻⁷ [mol·m⁻²·s⁻¹·Pa⁻¹] and 1800, respectively. Even under a severe hydrothermal condition of steam/N₂=3 at 773 K, the H₂/N₂ permselectivity was kept over 800 for 82 h (B in Fig. 4), and the H₂/steam selectivity was found to be 290.⁴²⁾

Further study on the microstructure refinement for the counter diffusion CVD-derived amorphous silica membranes has been performed as a collaboration research work between The University of Tokyo and JFCC. The performance of the amorphous silica membrane could successfully reach above

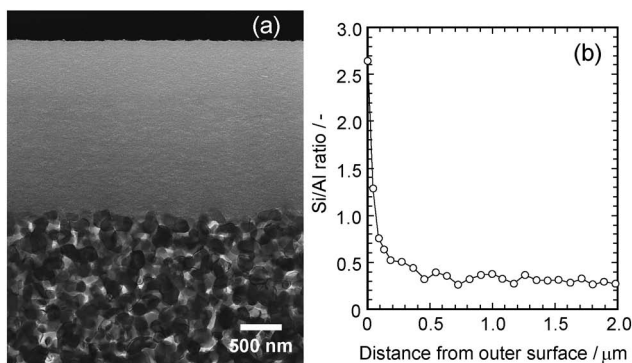


Fig. 5. High-performance microporous amorphous silica membrane synthesized by the counter diffusion CVD method. (a) Typical cross-sectional TEM image of the membrane fabricated on a mesoporous γ - Al_2O_3 -coated α - Al_2O_3 porous support, and (b) Distribution of Si/Al ratios for the mesoporous γ - Al_2O_3 surface thin layer by EDS analysis.

the upper bound, the H_2 permeance and H_2/N_2 permselectivity at 798 K were measured to be 1.2×10^{-7} [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$] and 12200, respectively (C in Fig. 4).¹¹ A typical cross-sectional TEM image of the high-performance amorphous silica membrane fabricated on a mesoporous γ - Al_2O_3 -coated α - Al_2O_3 porous support is shown in Fig. 5(a). The mesoporous γ - Al_2O_3 was observed as a defect-free surface thin layer having a thickness of approximately $2.3 \mu\text{m}$. The results of EDS analysis showed that the entire surface thin layer was composed of aluminum, silicon and oxygen, and the amorphous silica membrane was found to be formed at the contact points of TMOS and O_2 inside the mesoporous γ - Al_2O_3 surface thin layer. The Si/Al atomic ratios of the surface thin layer evaluated by the EDS analysis are shown in Fig. 5(b). For minimizing pressure drop, the mesoporous γ - Al_2O_3 surface thin layer was gradually modified with amorphous silica as designed, and the effective amorphous silica membrane thickness for gas separation could be estimated to be 180 nm .¹¹

3. Novel amorphous silica-based nanocomposite membranes

As mentioned in the previous section, amorphous silica-based composite membranes have been investigated in order to enhance their thermal and hydrothermal stabilities for practical application, and the composite membrane with a mixed-oxide system such as Si-Ni-O showed a better hydrothermal stability.³⁹ Recently, another type of composite membranes, nanoparticle-dispersed amorphous silica-based membranes have been designed and synthesized. Some metals with high-temperature H_2 affinity have been selected for the nanoparticles. This is expected to be essential to enhance the high-temperature H_2 permselectivity of the amorphous silica-based membranes. Based on the design concept mentioned above, novel Ni nanoparticle-dispersed amorphous silica membranes have been synthesized by an in-situ compositing method composed of three main processes:⁴³ (1) preparation of a homogeneous solution precursor for the Si-Ni-O system, (2) dip-coating of the solution precursor on a MAAC tube (Fig. 2), and (3) heat treatment at 873 K in air, followed by an additional heat treatment at 773 K under a H_2 flow. A cross-sectional TEM image of an as-synthesized membrane is shown in Fig. 6(a). The precursor-derived amorphous Si-Ni-O layer was located on a MAAC tube with a thickness of about 400 nm. During the 773 K-heat treatment under flowing H_2 ,

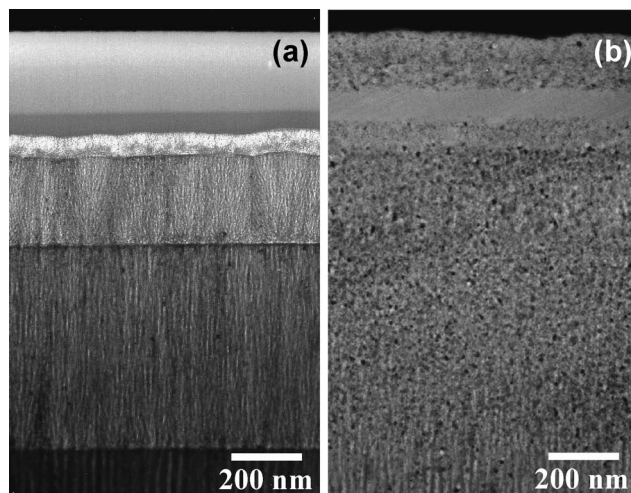


Fig. 6. Cross-sectional TEM images of a precursor-derived Si-Ni-O membrane [$\text{Ni}/(\text{Si} + \text{Ni}) = 0.3$] on a MAAC tube. (a) As-synthesized, and (b) After heat treatment in hydrogen.

nanometer-sized Ni particles having a size range of about 5–10 nm were found to be in-situ formed both within the Si-Ni-O layer and mesopore channels of the MAAC tube (Fig. 6(b)).

The novel nanocomposite membranes having Ni/(Si + Ni) ratios ranging from 0.1 to 0.3 showed a molecular sieve-like property, and the permeances of He and H_2 were apparently higher than those of other larger gas molecules. However, as shown in Fig. 7(a), the H_2 permeance at 773 K of the composite membranes increased selectively with increasing the Ni content, i.e. Ni/(Si + Ni) ratio. As a result, the H_2 permeance reached the highest value of 1.3×10^{-7} [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$] at the Ni/(Si + Ni) ratio of 0.3, and the permselectivities of H_2/He and H_2/CO_2 were measured to be 5 and 89, respectively (Fig. 7(b)).

To study the mechanism for the unique H_2 permselectivity, H_2 chemisorption isotherm analysis was performed on the powdered samples of the precursors-derived Ni-nanoparticle dispersed amorphous silica, Ni, and Ni-free amorphous silica.⁴⁴ At the first step, an isotherm analysis at 773 K was performed to measure a total amount of adsorbed H_2 , which was the sum of the strongly and weakly adsorbed H_2 on the sample. Then, the sample was exposed to high vacuum at 773 K to remove the weakly (reversibly) adsorbed H_2 from the sample. Then, the second isotherm analysis was performed to evaluate the amount of the reversibly adsorbed H_2 . The results are summarized and shown in Fig. 8. An apparent reversible H_2 adsorption was observed for the Ni-nanoparticle dispersed amorphous silica powder, while the Ni powder exhibited only irreversible strong H_2 adsorption, and the Ni-free amorphous silica powder showed no interaction with H_2 . Subsequent research work on the effect of Ni content on the high-temperature H_2 adsorption property revealed that there was no simple proportionality between the Ni content and the amount of reversibly adsorbed H_2 . The highest amount of the reversibly adsorbed H_2 was achieved at around the Ni/(Ni + Si) atomic ratio of 0.20 to 0.33, when Ni nanoparticles approached to saturate in the amorphous silica matrix.⁴⁵ Consequently, the reversible H_2 adsorption could be an important property for the selective enhancement in the H_2 permeance at 773 K of the novel Ni-nanoparticle dispersed amorphous silica membranes. Study on other amorphous silica-based nanocomposite systems for further enhancement in the H_2 permeance is under in-

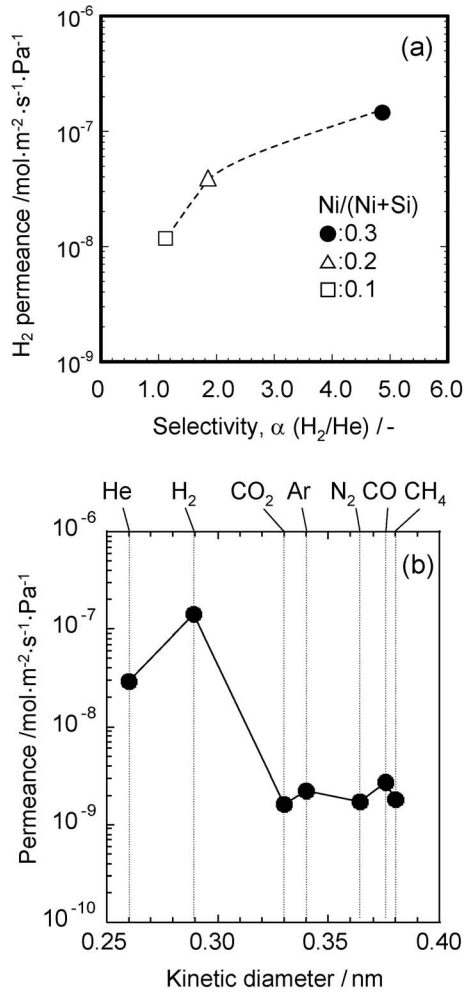


Fig. 7. Gas permeation behaviors at $T=773$ K of Ni nanoparticle-dispersed amorphous silica membranes. (a) Relation between H₂ permeance and H₂/He permselectivity of membranes with Ni/(Si+Ni) atomic ratios ranging from 0.1 to 0.3, and (b) Gas permeation behaviors evaluated for the membrane [Ni/(Si+Ni)=0.3] showing selective enhancement of H₂ permeance by Ni nanoparticles dispersion.

vestigation.

4. Polymer-derived amorphous Si-(B)-C-N membranes

Organometallic precursors-derived amorphous silicon carbide (Si-C-N) ceramics were found to show enhanced thermal stability compared to the binary Si-N or Si-C amorphous ceramics,⁴⁶⁾ and amorphous Si-C-N ceramics with a C/Si atomic ratio, $R > 0.5$ can remain in the amorphous state up to 1673–1773 K.⁴⁷⁾ They also exhibit excellent oxidation⁴⁸⁾ and creep resistance⁴⁹⁾ at very high temperatures due to the absence of metal oxide additives. Incorporation of hetero element into the ternary Si-C-N system also strongly influences the crystallization behavior of amorphous Si-C-N ceramics to thermodynamically stable silicon nitride/silicon carbide (Si₃N₄/SiC) ceramics. Especially, boron (B) can stabilize the amorphous state of Si-C-N ceramics at 1973–2073 K.⁵⁰⁾⁻⁵²⁾ These findings indicate that the amorphous Si-(B)-C-N ceramics are candidate materials for high temperature applications.

Recently, novel polymer precursors have been designed and synthesized for the fabrication of thermally stable amorphous Si-(B)-C-N membranes at Technische Univer-

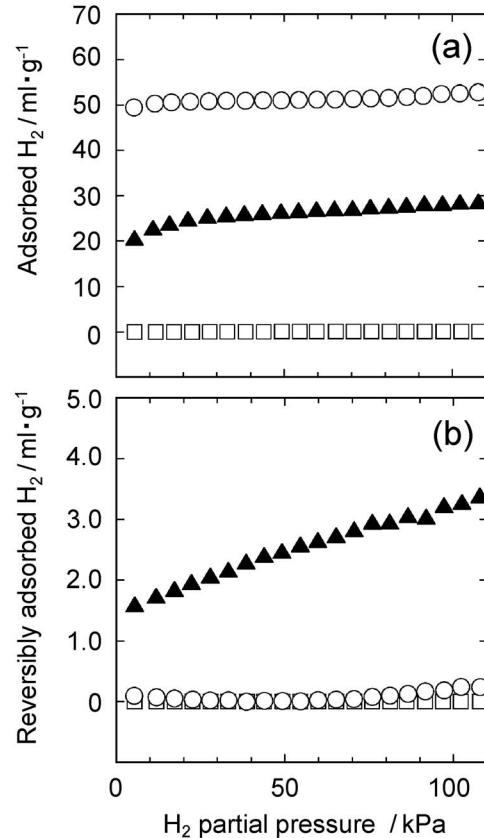
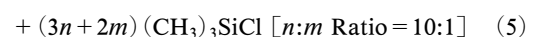
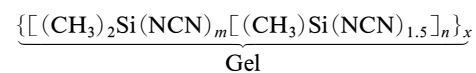
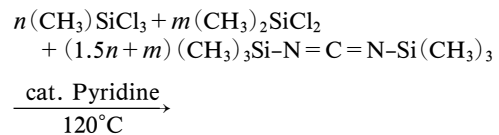


Fig. 8. Hydrogen chemisorption isotherms at 773 K of precursor-derived powdered samples showing (a) Total amount of H₂ adsorption, and (b) Reversibly adsorbed H₂. ○: Ni, ▲: Ni-nanoparticle dispersed amorphous silica with Ni/(Si+Ni)=0.3, and □: Ni-free amorphous silica.

sitat Darmstadt, Germany. Volger et al. synthesized a novel poly(silyl)carbodiimide⁵³⁾ for the ternary amorphous Si-C-N ceramics by a non-oxide sol-gel process based on reactions of bis(trimethylsilyl)carbodiimide with chlorosilanes.^{54),55)} The gelation process as well as the viscosity of the poly(organosilyl)carbodiimide was adjusted for spin coating on a porous membrane support by reacting dimethyldichlorosilane [(CH₃)₂SiCl₂] and methyltrichlorosilane [(CH₃)SiCl₃] in a molar ratio of 10:1 with bis(trimethylsilyl)carbodiimide [(CH₃)₃Si-N=C=N-Si(CH₃)₃] using pyridine as catalyst.



Thermal gravimetric analysis of this preceramic polymer exhibited extraordinary high ceramic yield of 91% after pyrolysis up to 1473 K in Ar. The novel polymer precursor film on a Si₃N₄ porous support was fabricated by solvent-free dip coating. The precursor film was successfully converted into an amorphous Si-C-N thin film by pyrolysis at 1273 K in Ar. The SEM observation revealed that a thin layer with a thickness of about 500 nm was homogeneously deposited on

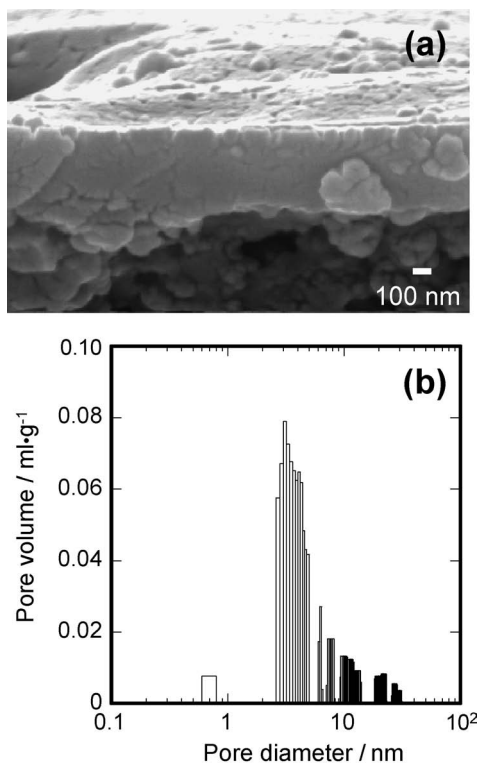
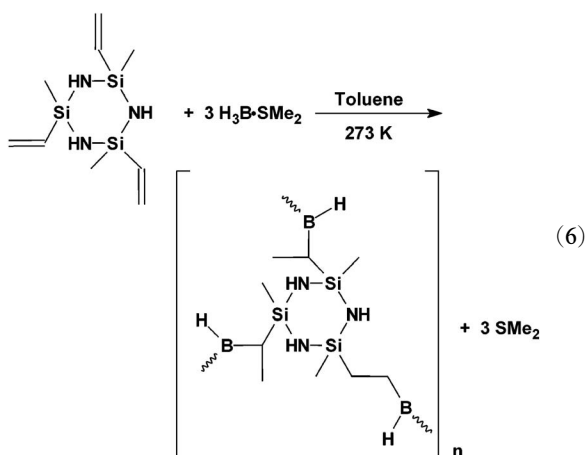


Fig. 9. Amorphous Si-C-N thin film synthesized from a novel sol-gel process-derived poly(organosilyl)carobodiimide. (a) SEM image, and (b) Pore size distribution of the amorphous Si-C-N thin film fabricated on a porous Si_3N_4 support.

the porous support surface (Fig. 9(a)). The N_2 sorption isotherm analysis of the thin layer showed the existence of a certain amount of mesopores of 2–5 nm in size (Fig. 9(b)).

Hauser et al. synthesized a novel preceramic polymer for the thermally stable quaternary Si-B-C-N amorphous ceramics by hydroboration reaction of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisilazane with borane dimethylsulphide.⁵⁶⁾



The polymer-to-ceramic conversion was achieved at 1323 K under Ar atmosphere, and a relatively high ceramic yield of 65% was achieved. The polymer-derived amorphous Si-B-C-N ceramics showed a high thermal stability up to 2073 K, and an excellent oxidation resistance at 1673 K. Using the dip-coating technique, the amorphous Si-B-C-N ceramic thin film was fabricated directly on a macroporous $\alpha\text{-Al}_2\text{O}_3$ support. As shown in Fig. 10(a), A crack-free amorphous Si-B-

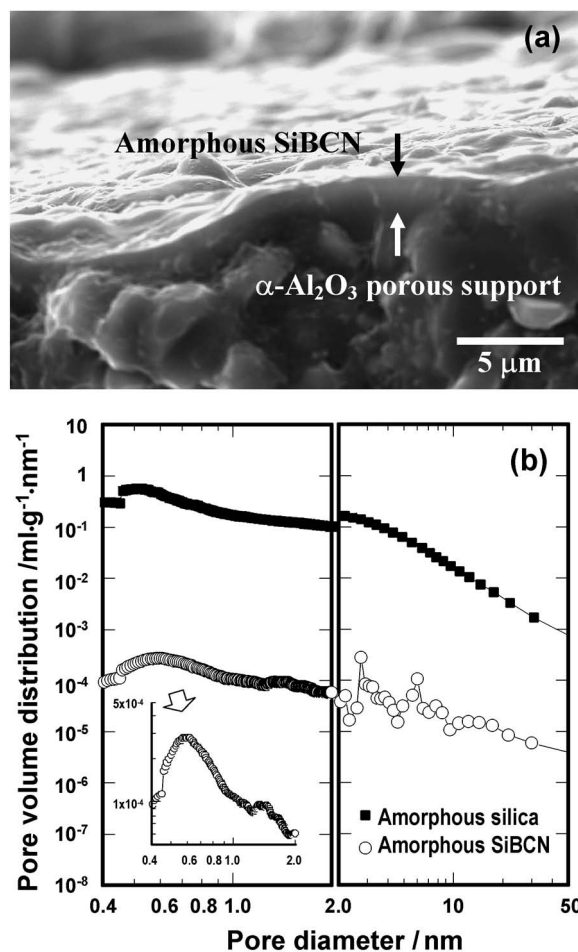


Fig. 10. Amorphous Si-B-C-N thin film derived from poly(borosilazane). (a) Cross sectional SEM image, and (b) Pore size distribution of the SiBCN thin film fabricated on a porous $\alpha\text{-Al}_2\text{O}_3$ in comparison with a polysilazane-derived amorphous silica membrane.³⁸⁾

C-N layer was formed with a thickness of approximately 2.5 μm . Obviously, no precursor solution was soaked up into the porous support and filled or sealed the pores.

Figure 10(b) presents the pore size distribution of the amorphous Si-B-C-N thin film in comparison with that of a polysilazane-derived amorphous silica membrane which was formerly studied at JFCC.³⁸⁾ The amorphous silica membrane exhibited an apparent H_2 separation property, and the H_2/N_2 permselectivity was measured to be 141. As the kinetic diameters of H_2 and N_2 are 0.289 and 0.364 nm, respectively,¹⁵⁾ the observed H_2 permselectivity was thought to be achieved by the molecular sieve-like property derived from the amorphous silica network having micropores of about 0.3 nm. As shown in Fig. 10(b), the N_2 sorption analysis of this membrane revealed the existence of micropores of about 0.5 nm, and a considerable amount of mesopores having a size range of 2 to 50 nm. A certain amount of the detected micro- and mesopores could act as defects, which lead to the degradation of the molecular sieve-like property. As a result, the H_2/N_2 permselectivity was limited to be 141. The pore size analysis of the amorphous Si-B-C-N thin film showed a trimodal distribution with maxima at 0.6, 2.7 and 6 nm, however, the total pore volume was found to be approximately three-orders of magnitude smaller than that of the amorphous silica mem-

brane.

Amorphous non-oxide ceramic membranes that can withstand very high temperatures are of great technological interest. Recent study on the preceramic polymers mentioned above present novel routes for the synthesis and fabrication of amorphous polymer-derived membranes in the Si-C-N ternary and Si-B-C-N quaternary systems, which are known to exhibit enhanced thermal and chemical stability as compared to polycrystalline oxidic counterparts. Therefore, applications of mesoporous Si-C-N especially as a surface thin layer of a macroporous membrane support or catalyst support for high-temperature membrane reactors are highly promising, while the polymer-derived amorphous Si-B-C-N is expected to use as a high-temperature H₂ separation membrane based on the intrinsic molecular sieve-like property as well as the excellent thermal stability of the Si-B-C-N amorphous network.

5. Conclusions

Precursors-derived ceramic membranes with molecular sieve-like properties exhibit relatively high gas permeances and a good stability at higher-temperatures. Moreover, they have been expected to use in membrane reactors for the conversion enhancement in the methane steam reforming reaction and dehydrogenation of hydrocarbons, which leading to development of a novel highly efficient hydrogen production system. In this paper, precursors-derived amorphous silica-based membranes, novel Ni nanoparticles-dispersed amorphous silica membranes, and non-oxide Si-(B)-C-N amorphous ceramic membranes were briefly reviewed.

Significant improvements in the stability under severe hydrothermal conditions (steam 75–90 Pa at 773 K) were successfully achieved for the sol-gel derived Ni-doped amorphous silica, and CVD-derived amorphous silica membranes. The microstructure refinement also achieved further enhancement in the high-temperature performance, the CVD-derived amorphous silica membrane exhibited a high H₂ permeance, 1.2×10^{-7} [mol·m⁻²·s⁻¹·Pa⁻¹] with an excellent H₂/N₂ permselectivity of 12200. These results show that the amorphous silica-based membranes are suitable for the application of steam reforming reactions as a membrane reactor.

Novel Ni nanoparticle-dispersed amorphous silica membranes were designed and synthesized by an in-situ compositing method. The H₂ permeance through the amorphous silica-based membrane selectively increased by the Ni-nanoparticles dispersion, and the H₂ permeance at 773 K reached 1.3×10^{-7} [mol·m⁻²·s⁻¹·Pa⁻¹]. This value was approximately five times higher even in comparison with that of a smaller gas molecule of helium. The results of H₂ chemisorption isotherm analysis revealed that the reversible hydrogen adsorption property detected for the nanocomposite membrane material could act an important role for the selective enhancement in the H₂ permeance. The nanostructure design concept for the use of H₂ affinity can be highly expected to offer an opportunity to develop novel ceramic membranes for hydrogen separation.

Novel preceramic polymers were designed and synthesized for the fabrication of non-oxide ceramic membranes of Si-C-N, and Si-B-C-N systems. A mesoporous amorphous Si-C-N thin film, and a crack-free amorphous Si-B-C-N thin film were successfully fabricated on a porous support. Amorphous Si-C-N and Si-B-C-N ceramic systems are known to exhibit enhanced thermal and chemical stability. Therefore, applications of the polymer-derived mesoporous Si-C-N, especially for high-temperature membrane reactors are highly promising, while the amorphous Si-B-C-N thin film is

expected to use as a molecular sieve membrane suitable for high-temperature separation of small gas molecules like H₂ below 0.3 nm in size. These applications are currently under investigation.⁵⁷⁾

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References

- 1) K. Jarosch and H. I. de Lasa, *Chem. Eng. Sci.*, **54**, 1455–1460 (1999).
- 2) E. Kikuchi, Y. Nemoto, M. Kajikawa, S. Uemiya and T. Kojima, *Catal. Today*, **56**, 75–81 (2000).
- 3) A. K. Prabhu and S. T. Oyama, *J. Membr. Sci.*, **176**, 233–248 (2000).
- 4) S. Kurungot, T. Yamaguchi and S. Nakao, *Cat. Lett.*, **86**, 273–278 (2003).
- 5) H. M. van Veen, M. Bracht, E. Hamoen, P. T., Alderliesten, A. J. Burgraaf and L. Cot, (Eds.), *Inorganic Membrane Science and Technology, Membrane Science and Technology Series, Vol. 4*, Elsevier, Amsterdam (1996) pp. 641–676.
- 6) Y. Yoshino, T. Suzuki, B. N. Nair, H. Taguchi and N. Itoh, *J. Membr. Sci.*, **267**, 8–17 (2005).
- 7) R. Kojima, K. Sato, T. Nagaono and Y. Iwamoto, *J. Ceram. Soc. Japan*, **114**, 929–933 (2006).
- 8) T. Nagano, K. Sato, T. Saito and Y. Iwamoto, *J. Ceram. Soc. Japan*, **114**, 533–538 (2006).
- 9) M. Knudsen, *Ann. Phys.*, **28**, 75–130 (1909).
- 10) D. Lee, L. Zhang, S. T. Oyama, S. Niu and R. F. Saraf, *J. Membr. Sci.*, **231**, 117–126 (2004).
- 11) T. Nagano, S. Fujisaki, K. Sato, K. Hataya, Y. Iwamoto, M. Nomura and S-I. Nakao, "Relationship between mesoporous intermediate layer structure and gas permeation property of amorphous silica membrane synthesized by counter diffusion chemical vapor deposition", *J. Am. Ceram. Soc.*, in press.
- 12) T. Inada, N. Uno, T. Kato and Y. Iwamoto, *J. Mater. Res.*, **20**, 114–120 (2005).
- 13) S. Yamazaki, N. Uno, Y. H. Ikuhara, H. Mori, Y. Iwamoto, T. Kato and T. Hirayama, *J. Mater. Sci.*, **41**, 2679–2683 (2006).
- 14) T. Nagano, N. Uno, T. Saito, S. Yamazaki and Y. Iwamoto, *Chem. Eng. Comm.*, **194**, 158–169 (2007).
- 15) D. W. Breck, "Zeolite Molecular Sieves", John Wiley & Sons, New York (1974) p. 636.
- 16) S. T. Oyama, D. Lee, P. Hacarlioglu and R. F. Saraf, *J. Membr. Sci.*, **244**, 45–53 (2004).
- 17) R. M. Barrer and D. E. W. Vaughan, *Trans. Faraday Soc.*, **63**, 2275–2282 (1967).
- 18) P. L. Studt, R. F. Shackelford and R. M. Fulrath, *J. Appl. Phys.*, **41**, 2777–2780 (1973).
- 19) R. F. Shackelford, P. L. Studt and R. M. Fulrath, *J. Appl. Phys.*, **43**, 1619–1626 (1972).
- 20) J. S. Masaryk and R. M. Fulrath, *J. Chem. Phys.*, **59**, 1198–1202 (1973).
- 21) G. R. Gavalas, C. E. Megiris and S. W. Nam, *Chem. Eng. Sci.*, **44**, 1829–1835 (1989).

- 22) M. Tsapatsis, S. Kim, S. W. Nam and G. Gavalas, *Ind. Eng. Chem. Res.*, **30**, 2152–2159 (1991).
- 23) C. E. Megiris and J. H. E. Glezer, *Chem. Eng. Sci.*, **147**, No. 15/16, 3925–3934 (1992).
- 24) H. Y. Ha, S. W. Nam, S. A. Hong and W. K. Lee, *J. Membr. Sci.*, **85**, 279–290 (1993).
- 25) J. C. S. Wu, H. Sabol, G. W. Smith, D. L. Flowers and P. K. T. Liu, *J. Membr. Sci.*, **96**, 275–287 (1994).
- 26) C. L. Lin, D. L. Flowers and P. K. T. Liu, *J. Membr. Sci.*, **92**, 45–58 (1994).
- 27) M. Tsapatsis and G. Gavalas, *J. Membr. Sci.*, **87**, 281–296 (1994).
- 28) S. Morooka, S. Yan, K. Kusakabe and Y. Akiyama, *J. Membr. Sci.*, **101**, 89–98 (1995).
- 29) S. Jiang, Y. Yan and G. R. Gavalas, *J. Membr. Sci.*, **103**, 211–218 (1995).
- 30) B. Sea, M. Watanabe, K. Kusakabe, S. Morooka and S. Kim, *Gas. Sep. Purif.*, **10**, 187–195 (1996).
- 31) H. A. Ha, J. S. Lee, S. W. Nam, I. W. Kim and S. A. Hong, *J. Mater. Sci.*, **16**, 1023–1026 (1997).
- 32) B. Sea, E. Soewito, M. Watanabe, K. Kusakabe, S. Morooka and S. Kim, *Ind. Eng. Chem. Res.*, **37**, 2502–2508 (1998).
- 33) G. Hwang, K. Onuki, S. Shimizu and H. Ohya, *J. Membr. Sci.*, **162**, 83–90 (1999).
- 34) D. Lee and S. T. Oyama, *J. Membr. Sci.*, **210**, 291–306 (2002).
- 35) M. Asaeda, Y. Oki and T. Manabe, "Preparation of Porous Silica Membranes for Separation of Inorganic Gaseous Mixtures at High Temperature," in "Energy Conversion Utilization with High efficiency, Subarea C: Science and Technology for Energy Conversion, September (1993) pp. 253–258.
- 36) M. Asaeda and M. Kashimoto, "Sol-Gel Derived Silica Membranes for Separation of Hydrogen at High Temperature-Separation Performance and Stability against Steam", in the Proceedings of 5th ICM (1998) pp. 172–175.
- 37) R. M. de Vos, W. F. Maier and H. Verweij, *J. Membr. Sci.*, **158**, 277–288 (1999).
- 38) Y. Iwamoto, K. Sato, T. Kato, T. Inada and Y. Kubo, *J. Eur. Ceram. Soc.*, **25**, 257–264 (2005).
- 39) M. Kanezashi and M. Asaeda, *J. Membr. Sci.*, **271**, 86–93 (2006).
- 40) K. Yoshida, Y. Hirano, H. Fuji, T. Tsuru and M. Asaeda, *J. Chem. Eng. Jpn.*, **34**, 523–530 (2001).
- 41) M. Nomura, K. Ono, S. Gopalakrishnan, T. Sugawara and S-I. Nakao, *J. Membr. Sci.*, **251**, 151–158 (2005).
- 42) M. Nomura, H. Aida, S. Gopalakrishnan, T. Sugawara, S-I. Nakao, S. Yamazaki, T. Inada and Y. Iwamoto, *Desalination*, **193**, 1–7 (2006).
- 43) Y. Iwamoto, *Membrane*, **29**, 258–264 (2004).
- 44) Y. Iwamoto, *Materia*, **44**, 220–225 (2005) [in Japanese].
- 45) Y. H. Ikuhara, H. Mori, T. Saito and Y. Iwamoto, *J. Am. Ceram. Soc.*, **90**, 546–552 (2007).
- 46) E. Kroke, Y-L. Li, C. Konetschny, E. Lecomte, C. Fasel and R. Riedel, *Mater. Sci. Eng.*, **R26**, 97–199 (2000).
- 47) Y. Iwamoto, W. Völger, E. Kroke, R. Riedel, T. Saitou and K. Matsunaga, *J. Am. Ceram. Soc.*, **84**, 2170–2178 (2001).
- 48) R. Riedel, H.-J. Kleebe, H. Schönfelder and F. Aldinger, *Nature (London)*, **374**, 526–528 (1995).
- 49) L. An, R. Riedel, C. Konetschny, H.-J. Kleebe and R. Raj, *J. Am. Ceram. Soc.*, **81**, 1349–1352 (1998).
- 50) R. Riedel, A. Kienzle, W. Dressler, L. Ruwisch, J. Bill and F. Aldinger, *Nature (London)*, **382**, 796–798 (1996).
- 51) L. Ruwisch, "Synthese und Hochtemperaturverhalten borhaltiger Silicium-carbonitride", PhD. Thesis, Technische Universität Darmstadt, Darmstadt, Germany, July 17, 1998.
- 52) H.-P. Baldus, M. Jansen and O. Wagner, "New Materials in the system Si-(N,C)-B and their characterization", 75–80 in Silicon Nitride '93, Key Engineering Materials Vol. 89–91, Edited by M. J. Hoffmann, P. F. Becher and G. Petzow, Trans Tech Publications, Aedermannsdorf, Switzerland (1994).
- 53) K. W. Völger, R. Hauser, E. Kroke, R. Riedel, Y. H. Ikuhara and Y. Iwamoto, *J. Ceram. Soc. Japan*, **114**, 576–560 (2006).
- 54) A. O. Gabriel and R. Riedel, *Angew. Chem., Int. Ed. Engl.*, **36**, 384–386 (1997).
- 55) A. O. Gabriel, R. Riedel, S. Storck and W. F. Maier, *Appl. Organomet. Chem.*, **11**, 833–841 (1997).
- 56) R. Hauser, S. Nahar-Borchard, R. Riedel, Y. H. Ikuhara and Y. Iwamoto, *J. Ceram. Soc. Japan*, **114**, 524–528 (2006).
- 57) R. Riedel, G. Mera, R. Hauser and A. Klönczynski, *J. Ceram. Soc. Japan*, **114**, 425–444 (2006).



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