



Article

Hydrothermal Stability of Hydrogen-Selective Carbon–Ceramic Membranes Derived from Polybenzoxazine-Modified Silica–Zirconia

Sulaiman Oladipo Lawal, Hiroki Nagasawa, Toshinori Tsuru and Masakoto Kanezashi *

Chemical Engineering Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

* Correspondence: kanezashi@hiroshima-u.ac.jp

Abstract: This work investigated the long-term hydrothermal performance of composite carbon-SiO₂-ZrO₂ membranes. A carbon-SiO₂-ZrO₂ composite was formed from the inert pyrolysis of SiO₂-ZrO₂-polybenzoxazine resin. The carbon-SiO₂-ZrO₂ composites prepared at 550 and 750 °C had different surface and microstructural properties. A carbon-SiO₂-ZrO₂ membrane fabricated at 750 °C exhibited H₂ selectivity over CO₂, N₂, and CH₄ of 27, 139, and 1026, respectively, that were higher than those of a membrane fabricated at 550 °C (5, 12, and 11, respectively). In addition to maintaining high H₂ permeance and selectivity, the carbon-SiO₂-ZrO₂ membrane fabricated at 750 °C also showed better stability under hydrothermal conditions at steam partial pressures of 90 (30 mol%) and 150 kPa (50 mol%) compared with the membrane fabricated at 500 °C. This was attributed to the complete pyrolytic and ceramic transformation of the microstructure after pyrolysis at 750 °C. This work thus demonstrates the promise of carbon-SiO₂-ZrO₂ membranes for H₂ separation under severe hydrothermal conditions.

Keywords: benzoxazine; carbon–ceramic; pyrolysis; hydrothermal stability; silica–zirconia; hydrogen

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1. Introduction

Due to energy security and environmental concerns [1,2], hydrogen has been considered as both a clean and renewable source of energy to replace fossil fuels [3–5]. Hydrogen possesses a high energy density and the ability to form covalent bonds with other elements (such as nitrogen) for easy storage, transportation, and feedstock for other industrial chemical processes [5,6]. Hydrogen can electrochemically combine with oxygen from air in fuel cells to generate electricity with clean H₂O effluent [5,7]. Hydrogen can be generated from the chemical conversion of some hydrocarbon compounds. An advantage of this production route is the ability to produce hydrogen on a large scale and subsequently convert it to a transportable form in integrated chemical plants. Equations (1)–(4) show examples of important chemical reactions, which involve dehydrogenation and steam reforming of hydrocarbons.

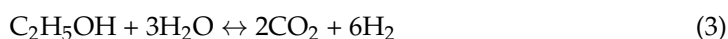
Dehydrogenation of propane



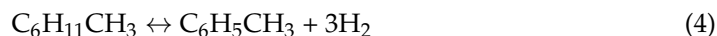
Methane steam reforming



Ethanol steam reforming



Dehydrogenation of methyl cyclohexane



Separation of hydrogen from other side product species, unreacted reactants, and intermediate reaction species is important. Table S1 presents a comparison of popular H_2 separation technologies, which include pressure swing adsorption (PSA), cryogenic distillation [8–10], and the recently developed inexpensive and energy-efficient membrane-separation processes [9,10]. Membranes for H_2 separation have been widely reviewed [9,11,12] and membranes with H_2 permeability of 1000 Barrer and H_2/X selectivity ≥ 100 are desired [12]. Studies on ceramic membranes derived from SiO_2 have highlighted their promise in this quest [9,11]. However, maintaining such high performance under hydrothermal conditions has been one of the major problems facing H_2 separation membranes [13–15]. For example, Lin et al. reported that SiO_2 membranes exposed to 50 mol% of steamed atmosphere at 600 °C for 30 h exhibited losses of 48 and 77% in specific surface area and pore volume, respectively [13]. Lin's group also reported similar effects on ZrO_2 , TiO_2 and Al_2O_3 -derived membranes [14]. These structural changes are deemed to be due to the rearrangement of networks initiated from hydrolysis by water vapor and from a subsequent recondensation of the formed -OH groups [16].

Carbonized ceramic membranes have been proposed as promising candidates that could perform long-term under hydrothermal conditions for hydrogen production. Duke and co-workers found that the carbonization of surfactant-templated silica (hexyl trimethyl ammonium bromide–silica) improved the hydrothermal stability of a silica membrane quite significantly [17,18]. The amorphous carbon nanoparticles that formed inhibited the silanol (-Si-OH) migration and condensation that results in closure of the microporous structure. In addition to this, the presence of the carbon nanoparticles also served to increase the pore volume required for enhanced H_2 permeability [17,19]. However, the surfactant carbonization route did not allow pore size tuning of the silica structure for targeted applications [17].

Another method for the carbonization of ceramic networks involves the use of organic coordination ligands to form coordinate complexes where the precursor to be modified is a transition metal ion compound [20–22]. Molecular sieving membranes were successfully fabricated by using an acetylacetone ligand to modify SiO_2 - ZrO_2 [23], and the fabrication of hydrogen-selective carbon- SiO_2 - ZrO_2 membranes was later studied by pyrolysis of the acetylacetone ligand at 550 °C [19,24]. Carbon- SiO_2 - ZrO_2 membranes have shown promise for high-temperature H_2/CO_2 separation performance [24], whereas the lower pyrolysis temperature of acetylacetone and its non-thermosetting properties prevents the formation of molecular sieving that is required in hydrothermal applications at much higher temperatures. Therefore, the fabrication of a hydrothermally stable and molecular sieving carbon- SiO_2 - ZrO_2 membrane required a better carbon precursor. In a more recent work, we studied the novel use of a traditional thermosetting group of organic compounds known as benzoxazines as the chelating ligand for the modification and carbonization of the SiO_2 - ZrO_2 network [25]. A carboxylic benzoxazine (3-(3-oxo-1,4-benzoxazin-4-yl) propanoic acid) possessing a hydroxylated nucleophilic carboxyl group was specifically chosen as the chelating ligand. This enabled the formation of a composite SiO_2 - ZrO_2 -polybenzoxazine resin material that was used to fabricate thin carbon- SiO_2 - ZrO_2 membranes with molecular sieving performances that could be tuned via pyrolysis temperature. H_2/SF_6 and H_2/CH_4 selectivity ranged from 10^2 to 10^4 and from 10 to 10^2 , respectively, depending on pyrolysis temperatures that ranged between 300 and 850 °C [25]. The wide range of the pyrolysis temperature for this SiO_2 - ZrO_2 -polybenzoxazine (SZ-PB) resin presented an opportunity for the fabrication of carbon–ceramic composite membranes at higher than the application temperatures that are usually required for a stable performance.

In this work, we therefore investigated the long-term hydrothermal applications of SiO_2 - ZrO_2 -polybenzoxazine-derived carbon- SiO_2 - ZrO_2 (C-SZ) membranes. First, we established an improved formation strategy for the preparation of SiO_2 - ZrO_2 -polybenzoxazine preceramic

resin. The effects of the pyrolysis temperature of $\text{SiO}_2\text{-ZrO}_2$ -polybenzoxazine at 550 and 750 °C on the resulting C-SZ surface properties and microstructure were studied and supported with various characterizations. Hydrothermal stability experiments were carried out to evaluate membrane properties at specific intervals. $\text{H}_2\text{O} + \text{N}_2$ mixtures (90 and 150 kPa partial pressure of steam) were fed to the membranes at 500 °C for several hours until steady permeance was observed. Membrane permeation properties before and after each steam treatment experiment were then compared to evaluate the progress of hydrothermal stability. Herein we propose mechanisms to explain the observed results.

2. Experimental Section

2.1. Materials

A precursor resin sol was prepared via a sol–gel process. Vinyltrimethoxysilane (VTMS; JNC Co. Ltd., Tokyo, Japan; 98% purity) was used as the silica precursor while zirconium n-butoxide (ZrTB; Sigma-Aldrich Japan, Tokyo, Japan; 80% in butanol) served as the zirconia precursor. 3-(3-oxo-1,4-benzoxazin-4-yl) propanoic acid (BZPA; Sigma-Aldrich Japan, Tokyo, Japan; 99%) was utilized as a chelating ligand for ZrTB modification. The solvent medium used to carry out the reactions was composed of a 50:50 mixture of dimethyl carbonate (DMC; Nacalai Tesque, Kyoto, Japan) and ethanol (EtOH; Sigma-Aldrich). In the sol–gel reactions, hydrochloric acid (HCl; Nacalai Tesque, Kyoto, Japan; 37% pure) served as the catalyst for hydrolysis. Dibenzoyl peroxide (BzO_2 ; Sigma-Aldrich Japan, Tokyo, Japan) was used as a radical initiator during thermal curing. All materials were used as received without further purification.

2.2. Preparation of $\text{SiO}_2\text{-ZrO}_2$ -Polybenzoxazine (SZ-PB) Precursor Resin Sol and of Carbon- $\text{SiO}_2\text{-ZrO}_2$ (C-SZ) Films, Powders, and Membranes

First, 2 wt% of SZ-PB was prepared in two stages. In the first stage, ZrTB dissolved in equal parts DMC and ethanol was modified via a reaction with BZPA (BZPA/ZrTB molar ratio 4:1) for one hour at room temperature. In the second stage, a solution of VTMS in equal parts DMC and ethanol was then co-hydrolyzed with the BZPA-modified ZrTB (Si/Zr molar ratio 9:1) using deionized water (H_2O /alkoxide molar ratio 4) and HCl as a catalyst (H^+ /alkoxide molar ratio, 1:4). To accomplish hydrolysis and poly-condensation, the mixture was stirred at 600 rpm for more than 12 h at room temperature.

After the hydrolysis and polycondensation reactions, dibenzoyl peroxide (BzO_2) was added (radical initiator/BZPA molar ratio 0.1) as a curing agent. The resulting sol was thermally cured dropwise in a platinum plate heated to 200 °C to obtain the SZ-PB preceramic resin gel. Carbon- $\text{SiO}_2\text{-ZrO}_2$ powders were then prepared from the SZ-PB preceramic resin gel by pyrolysis at 300 to 850 °C under a N_2 stream (600 mL min^{-1}) for 30 min.

Carbon- $\text{SiO}_2\text{-ZrO}_2$ (C-SZ) carbon–ceramic membranes were fabricated by hot-coating the SZ-PB resin sol diluted to 0.25 wt% onto a prefabricated substrate support (Figure S1) preheated to 200 °C followed by pyrolysis at the desired final temperature as shown by the sequence in Figure S2. Two kinds of membranes were fabricated for this work according to the final pyrolysis temperature: C-SZ550 and C-SZ750 with final pyrolysis temperatures of 550 and 750 °C, respectively.

2.3. Characterization of $\text{SiO}_2\text{-ZrO}_2$ -Polybenzoxazine-Derived and Carbon- $\text{SiO}_2\text{-ZrO}_2$ Films, Powders, and Membranes

The presence and transformation of structural moieties in thin films supported on UV-treated Si-wafers were monitored using Fourier Transform-Infrared spectroscopy (FT-IR, FTIR-4100, JASCO, Tokyo, Japan). Water contact angle measurements were carried out on films coated on Si-wafers and measured at room temperature with 0.1 μL drops (Dropmaster DM 300, Kyowa Interface Science Co. Ltd., Saitama, Japan). The decomposition properties of the SZ-PB resin gels and C-SZ powders were analyzed and monitored using thermogravimetry (DTG-60 Shimadzu Co., Kyoto, Japan) and mass spectroscopy-supported thermogravimetry (TG-MS, TGA-DTA-PIMS 410/S, Rigaku, Tokyo, Japan). The presence and the chemical states of constituent atoms were confirmed using X-ray photoelectron spectroscopy (XPS;

Shimadzu Co., Kyoto, Japan). The cross-section morphology and the elemental analysis of the carbon–ceramic membrane were examined via Field Emission-Scanning Electron Microscopy (FE-SEM, Hitachi S-4800, Tokyo, Japan). Prior to examination, carefully cut pieces of the membrane were attached to sample holders via carbon tape and vacuum-dried at 50 °C for 24 h. Furthermore, N₂ sorption of powders was analyzed at −196 °C using BELMAX sorption equipment (Microtrac Bell Co. Ltd., Osaka, Japan). Prior to this measurement, adsorbed gases and vapors were evacuated from the samples at 200 °C for at least 12 h.

2.4. Evaluation of Gas Permeance and Hydrothermal Stability

Figure 1 shows a flow diagram of the set-up for evaluating the membrane permeation characteristics and for hydrothermal stability testing. After fabrication, a C-SZ membrane was inserted into the membrane module in the permeation measurement rig at 300 °C under a moderate helium flow of 100 mL min^{−1} for about 12 h to remove the adsorbed vapor and for membrane post-treatment. Single-gas permeation tests of the membranes were carried out using high-purity gases (H₂, He, CO₂, N₂, CH₄, CF₄, and SF₆—in that order). Each gas was fed to the upstream of the membrane module at 200–500 kPa of absolute pressure under temperatures ranging from 50 to 500 °C. Permeate side pressure was kept at atmospheric pressure and the permeate gas flow was measured using a bubble film flow meter (HORIBA-STECH, Horiba Ltd., Kyoto, Japan). The gas permeance (mol m^{−2} s^{−1} Pa^{−1}) was then calculated by dividing the measured permeate flow rate by the product of the membrane effective surface area and the transmembrane pressure difference. It should be noted that the range of observed experimental error based on precision for the measured flow rates of gases was controlled to within ±5%.

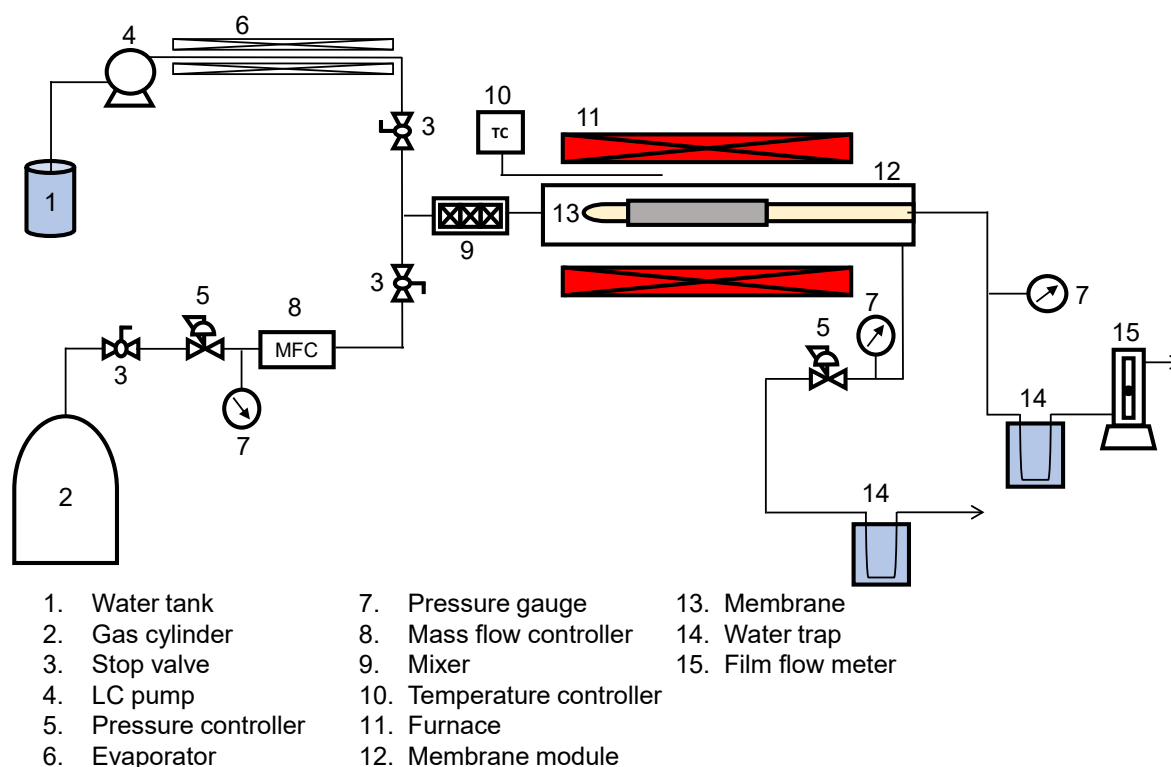


Figure 1. Schematic flow diagram of the membrane evaluation set-up.

Hydrothermal stability tests were carried out at 500 °C by feeding the H₂O + N₂ mixture to the membrane module such that the partial pressures of steam were 90 and 150 kPa making up 30 and 50 mol% of the mixtures, respectively. Water was pumped from a tank at a steady rate using a liquid chromatography pump and was then vaporized before mixing with N₂ in a mixer. A stage cut (ratio of the permeate flow rate to the feed flow rate) of lower than 0.167 was maintained. The compositions of the feed, retentate and

permeate streams were analyzed by employing the mass balance of the H₂O-N₂ binary system. To evaluate the transmembrane pressure-drop of each component, the logarithmic mean pressure difference ($\Delta P_{i,lm}$) was applied (Equation (5)).

$$\Delta P_{i,lm} = \frac{\Delta P_{i,in} - \Delta P_{i,out}}{\ln(\Delta P_{i,in} / \Delta P_{i,out})} \quad (5)$$

In Equation (5), $\Delta P_{i,in}$ and $\Delta P_{i,out}$ represent the difference in partial pressures of component *i* between the retentate side and the permeate side at the inlet and outlet of the module, respectively, that is $\Delta P_{i,in} = P_i$ (feed side inlet) – P_i (permeate side inlet) and $\Delta P_{i,out} = P_i$ (feed side outlet) – P_i (permeate side outlet).

3. Results and Discussion

3.1. Thermal Crosslinking of SiO₂-ZrO₂-Polybenzoxazine and Carbon-SiO₂-ZrO₂ Formation

In our previous work, the successful formation of a polybenzoxazine-modified SiO₂-ZrO₂ was established [25]. The resin of a SiO₂-ZrO₂ and polybenzoxazine inorganic-organic hybrid was formed from vinyl trimethoxysilane (VTMS), zirconium n-butoxide (ZrTB), and a benzoxazine compound 3-(3-oxo-1,4-benzoxazin-4-yl) propanoic acid (BZPA) precursors. The polymerization of benzoxazines is commonly accomplished by various methods including organic radical initiation, cationic radical initiation, and thermal polymerization [26]. The SiO₂-ZrO₂-polybenzoxazine hybrid was formed by curing at a relatively low temperature of 90 °C, which allowed the opening and propagation of an oxazine ring in the presence of a dibenzoyl peroxide organic radical initiator. However, the curing of benzoxazines is known to improve at temperatures well above 90 °C [27,28]. Hence, in the current work, a curing temperature of 200 °C was applied. Figure 2 shows a schematic representation of the idealized stages in the formation of a highly cured SiO₂-ZrO₂-polybenzoxazine. With the help of a radical initiator, the oxazine ring opens to form a tri-substituted benzene ring during stage 1 bonding to phenolic -OH and to a dangling -C-N-C- branch. Subsequent thermal application result in a curing process involving the crosslinking of the opened oxazine and the vinyl groups during stage 2.

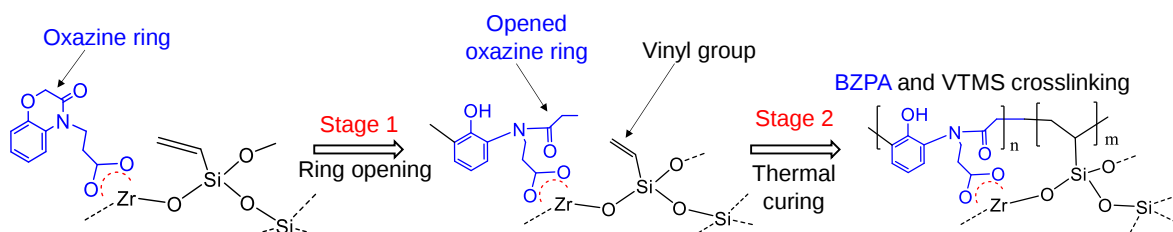


Figure 2. Schematic representation of the thermal crosslinking of the vinyl group of VTMS and of the oxazine ring of BZPA in a SiO₂-ZrO₂-polybenzoxazine hybrid.

This formation model was confirmed using ATR-assisted Fourier Transform Infrared Spectroscopy (FT-IR) to observe any appearance or disappearance of chemical moieties at each formation stage. Figure 3 shows the FTIR spectra of a SiO₂-ZrO₂-polybenzoxazine resin before and after thermal curing at 90 and 200 °C. At first, the spectrum of the fresh as-prepared film was measured as a control, as shown in Figure 3 (black line spectrum), and the peaks arising from the different moieties can be observed in the figure. After hydrolysis and condensation reactions, dibenzoyl peroxide (BzO₂) radical initiator was added to the prepared sol. Peaks representing the dibenzoyl peroxide appeared at 1766 and 1226 cm^{−1}. After curing the sol at 90 °C over a 4–5-day period, a gel-like resin formed and the FTIR spectra (red line) revealed that the 90 °C-cured resin showed a spectrum similar to that of the fresh as-prepared sample with the only difference being the disappearance of the BzO₂ peaks. This indicates that either the curing process did not proceed at 90 °C or it only occurred to a very minimal degree.

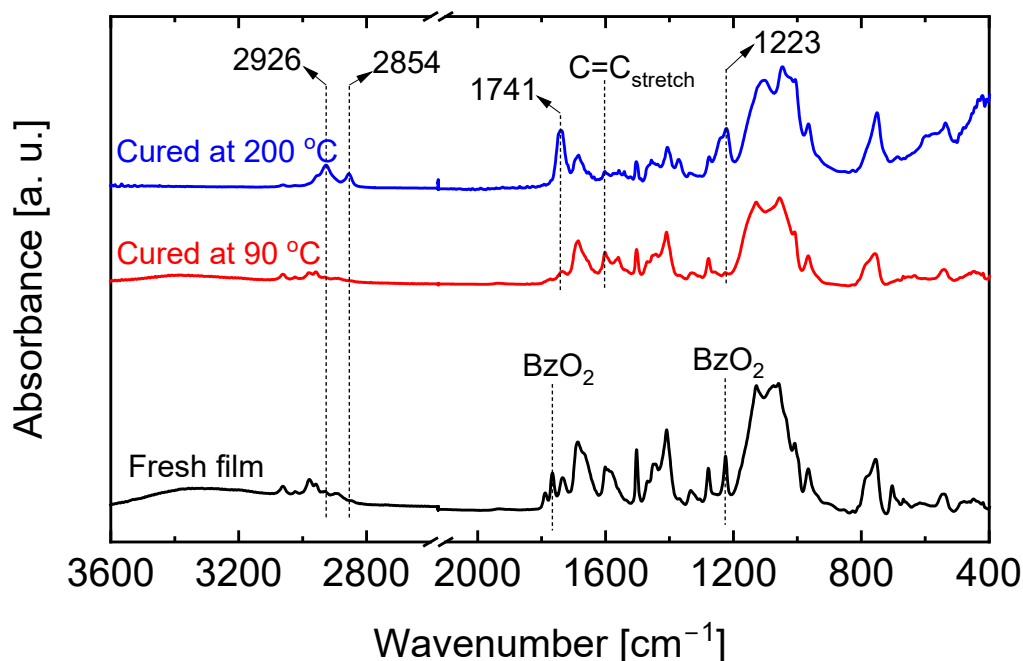


Figure 3. FTIR spectra of SiO₂-ZrO₂-polybenzoxazine before and after thermal curing at 90 (red line) and 200 °C (blue line).

Curing at a higher temperature was attempted by directly drying the as-prepared SiO₂-ZrO₂-benzoxazine sol at 200 °C. The FTIR profile of the resulting resin shown in Figure 3 (blue line spectrum) reveals the disappearance and appearance of certain peaks. The C=C peak at wavenumber 1603 cm⁻¹ was ascribed to the vinyl group of VTMS and was significantly reduced in intensity along with the peak belonging to the BZPA ligand at 1688 cm⁻¹. New peaks simultaneously appeared at several points indicating the formation of new moieties: 1223; 1741; 2854; and 2926 cm⁻¹ [28]. Both sets of observations may indicate the curing process involving a crosslinking of vinyl and opened oxazine rings since polymerizable moieties belonging to VTMS and BZPA were consumed simultaneously.

The SiO₂-ZrO₂-polybenzoxazine resin cured at 200 °C was pyrolyzed to form carbon-SiO₂-ZrO₂. The inert calcination of the SiO₂-ZrO₂-polybenzoxazine resin resulted in a decomposition of the polymer chain into a sp² type of carbon and the ceramic transformation of the -C-Si-O-Zr- phase to form a carbon-SiO₂-ZrO₂ composite [25]. Figure 4a shows the thermogravimetric (TG) profile of SiO₂-ZrO₂-polybenzoxazine decomposition under an inert atmosphere. There was an onset of decomposition at 200 °C, which continued with a sharp decline until about 500 °C indicating the breakdown of the organic polymer chain into volatile products. The rate of weight loss beyond 500 °C became slight until 1000 °C was reached. In this range of temperatures, weight loss could be attributed to the process of carbonization whereby carbon was converted into sp² from sp³ forms [25,29,30].

The non-volatile residue obtained at 1000 °C after the TG analysis was then subjected to further thermogravimetric analysis under an oxidative atmosphere (He + O₂ mixture; 20.2% O₂ by volume) accompanied by mass spectrometry, as shown in Figure 4b. This was performed to quantitatively prove the presence of free carbon in the carbon-SiO₂-ZrO₂ obtained after pyrolysis of the SiO₂-ZrO₂-polybenzoxazine hybrid. After exposure of the sample to the oxidative gas mixture, no weight loss was observed up to 500 °C. This suggests that below 500 °C the amount of free energy needed to initiate a spontaneous oxidative reaction was insufficient. Therefore, carbon-SiO₂-ZrO₂ should be oxidatively stable below 500 °C. However, the sample began to show a loss of weight beyond 500 °C and reached a stable value at around 700 °C. As mass spectrometry showed, the observed peak of *m/z* = 44 that aligned with the weight loss in the sample corresponded to the release

of CO₂ gas. This conclusively proves the presence of free reactive carbon that is released as CO₂ in a reaction such as $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$.

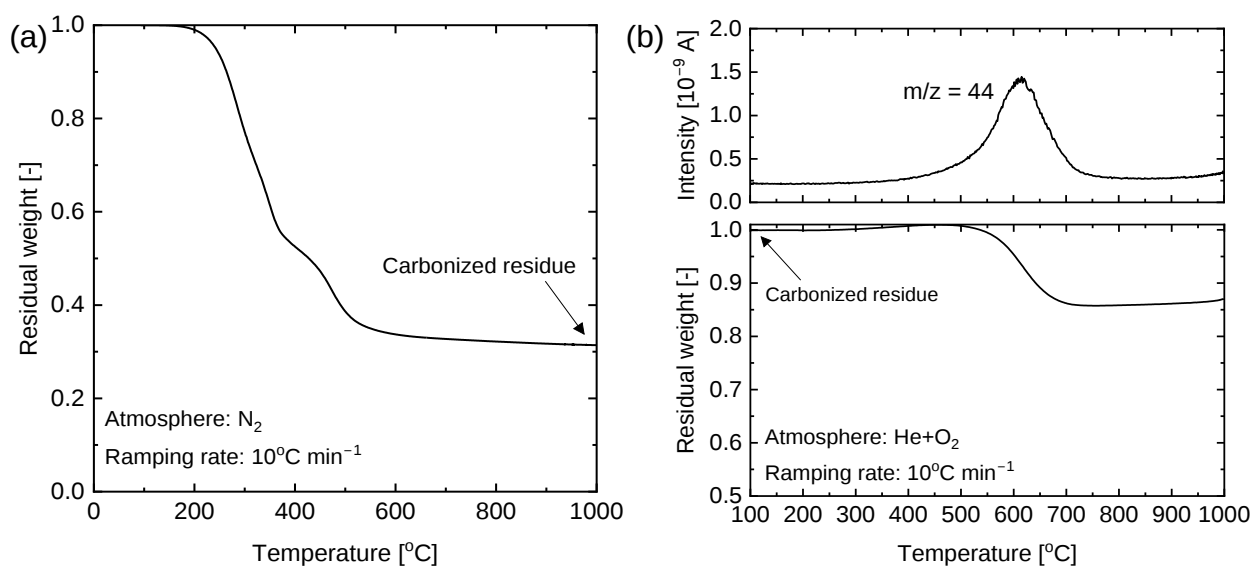


Figure 4. (a) Thermogravimetric analysis (TG) of the decomposition under a N₂ atmosphere of SiO₂-ZrO₂-polybenzoxazine resin cured at 200 °C. (b) Thermogravimetric analysis and mass spectrometry (TG-MS) of the decomposition under an oxidative atmosphere of the non-volatile residue derived following the TG procedure in (a).

3.2. The Effect of Pyrolysis Temperature on the Microstructural, Surface, and Membrane Permeation Properties of Carbon-SiO₂-ZrO₂

The conversion of carbon from the sp³ state to sp² during pyrolysis beyond 500 °C is usually accompanied by microstructural changes such as the rearrangement of graphitic sp² carbon strands into stacked sheets, which results in improved molecular sieving properties [31–33]. In the current study, the microstructural change occurring during the pyrolysis of SZ-PB between 550 and 750 °C was investigated despite the small weight loss observed between these two temperatures using nitrogen adsorption–desorption measurements. Figure 5 shows the nitrogen adsorption–desorption isotherms at 77 K of C-SZ powders derived from 200 °C-cured SZ-PB resin pyrolyzed at 550 and 750 °C, where both samples showed type I isotherms characteristic of microporous materials. Compared with the C-SZ750 sample, the C-SZ550 sample adsorbed a higher amount of nitrogen, which indicates that the higher pyrolysis temperature of 750 °C resulted in a densified structure with a smaller surface area and pore width (calculated from NLDFT with pore distribution shown in Figure S4). The shrinking of the pore size with increase in the pyrolysis temperature is a common feature of polymer-derived carbon molecular sieve membranes (CMSMs), and this allows them to finely separate gas species [34–36].

Examinations of the surface property differences between C-SZ550 and C-SZ750 revealed possible differences in the chemical states of the free carbon. The interaction of the surfaces with water at room temperature is a good indicator of completeness or otherwise of the pyrolysis transformation of carbon. Figure 6 shows the water adsorption isotherms of C-SZ550 and C-SZ750 powders measured at 25 °C. In carbon materials, the adsorption isotherms typically show negligible amounts of adsorbed water at low relative pressures (p/p_0 of 0–0.2 typically), but rapid uptakes thereafter [37–39]. On the other hand, water adsorption in hydroxylated silica-based materials usually follows a type II isotherm whereby a monolayer adsorption of water occurs at lower p/p_0 , and there is an onset of multilayer adsorption thereafter [40–42]. The C-SZ550 and C-SZ750 water adsorption isotherms in Figure 6 therefore seem to show an aggregate of water adsorption isotherms in silica and carbon-based materials, and despite a smaller surface area, C-SZ750 shows a higher amount of water adsorbed compared with that by C-SZ550 (Figure 5). Moreover, C-SZ750 powders show a Langmuir-type isotherm indicating a stronger interaction with water

compared with that of C-SZ550. Furthermore, in contrast to silica where hydrophobicity is achieved by removing surface silanol groups by calcination at higher temperatures [42,43], carbon-SiO₂-ZrO₂ materials showed an opposite trend.

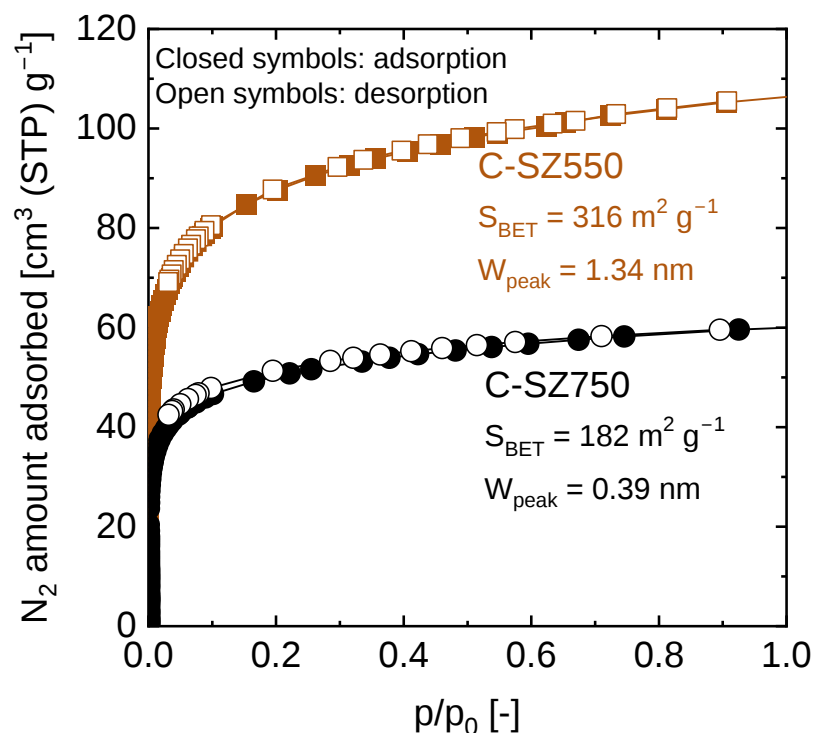


Figure 5. Nitrogen adsorption and desorption isotherms at 77 K of carbon-SiO₂-ZrO₂ (C-SZ) powders derived from 200 °C-cured SiO₂-ZrO₂-polybenzoxazine resins after pyrolysis at 550 and 750 °C (S_{BET} : Bruneuer–Emmett–Teller surface area; W_{peak} : peak pore width).

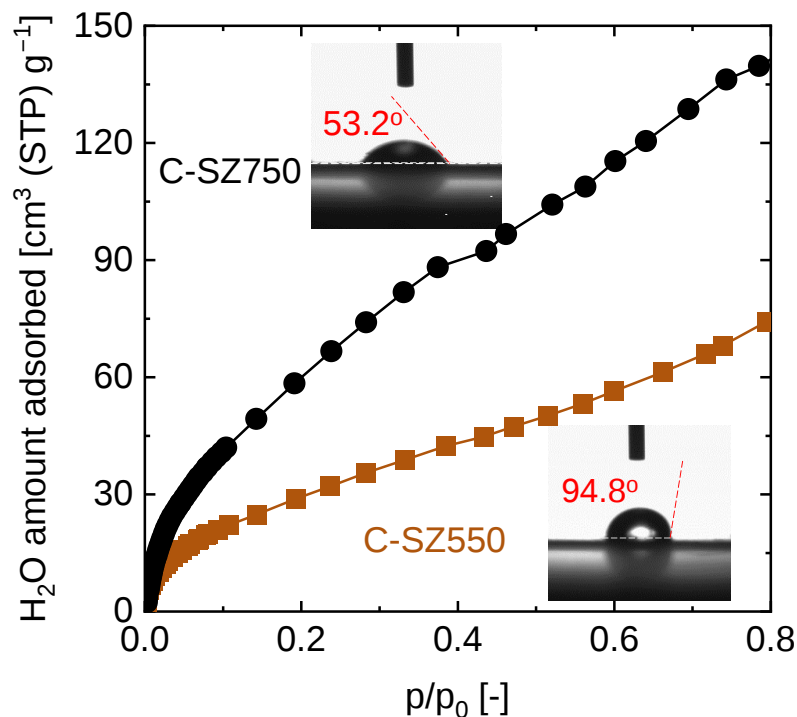


Figure 6. H₂O adsorption isotherms measured at 25 °C of carbon-SiO₂-ZrO₂ (C-SZ) powders derived after the pyrolysis of 200 °C-cured SiO₂-ZrO₂-polybenzoxazine resins at 550 and 750 °C (Inset: Water-contact angles of respective carbon-SiO₂-ZrO₂ films).

These observations were backed up by measurements of the water-contact angles of C-SZ550 and C-SZ750 films, as shown in the insets of Figure 6. The C-SZ550 film showed a higher contact angle of 94.8° compared with that of 53.2° for C-SZ750. Based on this result, it appears that C-SZ550 film retains some of the hydrophobic moieties present in the fresh and cured films (Figure S3) that also exhibited high water-contact angles. This shows that the pyrolysis transformation of carbon was not complete at 550°C . The reduction in the water-contact angle for C-SZ750 indicates the loss of the hydrophobic moieties, which gives rise to free stable carbon. Therefore, the choice of pyrolysis temperature in fabricated carbonized materials is important not only from the perspective of precursor weight loss, but also the chemical state of the non-volatile residue.

Thus, supported C-SZ membranes were fabricated from SZ-PB at 550°C and 750°C . The cross-sectional morphologies of the resulting supported membranes appear in Figure S5a,b, respectively, via FE-SEM. Continuous thin layers of C-SZ can be formed irrespective of the pyrolysis temperature. In addition, carbon-SiO₂-ZrO₂ exhibit homogeneous amorphous structures without crystalline phase segregations at both 550°C and 750°C [25]. Therefore, continuous, and uniform separation layers were formed. Figure 7 shows the kinetic diameter dependence of single-gas permeance measured at 300°C for C-SZ550 and C-SZ750 membranes. Gases with molecular diameters ranging from 0.26 to 0.55 nm were used to probe the molecular sieving properties of the membranes: He (0.26 nm), H₂ (0.289 nm), CO₂ (0.33 nm), N₂ (0.364 nm), CH₄ (0.38 nm), CF₄ (0.48 nm), and SF₆ (0.55 nm). In C-SZ550 membrane, these gases showed an order of permeance ($\text{H}_2 > \text{He} > \text{CO}_2 > \text{CH}_4 > \text{N}_2 > \text{CF}_4 > \text{SF}_6$) that does not conform to the order of their molecular diameters. The anomaly in this order is specific to the higher permeance of H₂ over He and CH₄ over N₂, respectively. This is a result of the loose pore size distribution of the C-SZ550, which allows Knudsen selectivity of H₂ (2 g mol^{-1}) over He (4 g mol^{-1}) and that of CH₄ (16 g mol^{-1}) over N₂ (28 g mol^{-1}), respectively, due to the preference of molecular mass over molecular size [44]. As a result, only low H₂ selectivity of 5, 12, and 11 were achieved over CO₂, N₂, and CH₄, respectively. Nonetheless, the C-SZ550 membrane still showed respectable H₂/CF₄ and H₂/SF₆ permeance ratios of 210 and 2800, respectively.

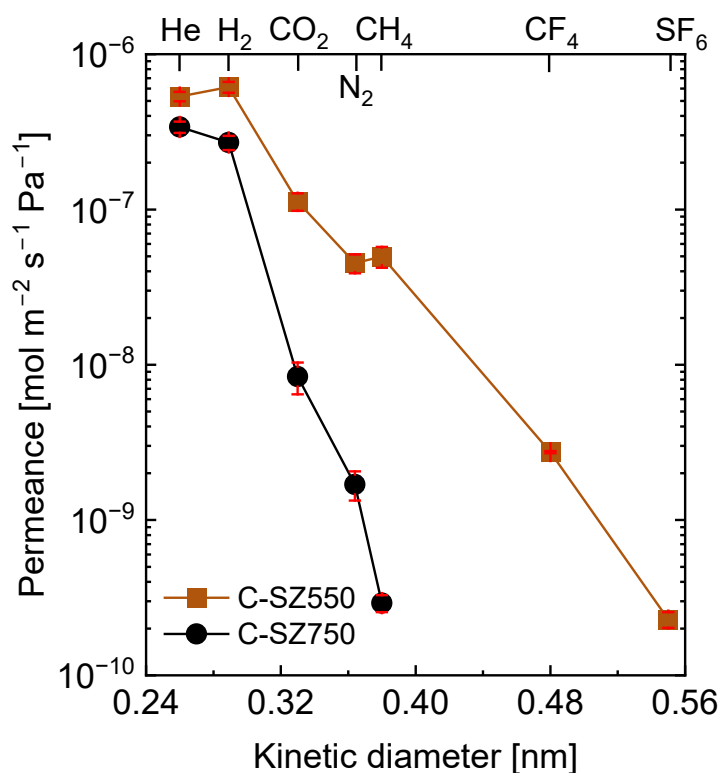


Figure 7. Single-gas permeance at 300°C as a function of kinetic diameter for carbon-SiO₂-ZrO₂ membranes prepared at 550°C and 750°C .

On the other hand, the C-SZ750 membrane showed a narrower pore size distribution, which was evident by the sharp order of gas permeance ($\text{He} > \text{H}_2 > \text{CO}_2 > \text{N}_2 > \text{CH}_4$) that followed the order of the molecular diameters. The narrower pore size distribution of C-SZ750 compared with that of the C-SZ550 membrane agrees with observations from the nitrogen-adsorption experiment. The sharp decline in gas permeance from H_2 to CO_2 indicates that the C-SZ750 membrane possesses a distribution of pore sizes with the highest probability of falling between the molecular diameters of H_2 and CO_2 . This can be attributed to the higher fabrication temperature allowing the complete pyrolytic and ceramic transformation of the carbon and -Si-O-Zr- phases to generate a narrower and denser pore structure. The result is high selectivity of H_2 over CO_2 , N_2 , and CH_4 of 27,139, and 1026, respectively, with H_2 permeance ($2.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) only slightly lower than that of the C-SZ550 membrane at $5.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (Table S2).

Figure 8a,b show the plots of He , H_2 and N_2 permeance for the C-SZ550 and C-SZ750 membranes, respectively, as a function of inverse temperature. The average pore sizes of C-SZ550 and C-SZ750 membranes were obtained using the modified-gas translational model (m-GT) proposed by Lee et al. [45], the values of which appear in Table 1 while the pore-size distributions are shown in Figure S6. The values of the apparent activation energies of He , H_2 , and N_2 permeation were calculated using Equation (6) [46].

$$P_i = \frac{k_{0,i}}{\sqrt{M_i RT}} \exp\left(-\frac{E_{p,i}}{RT}\right) \quad (6)$$

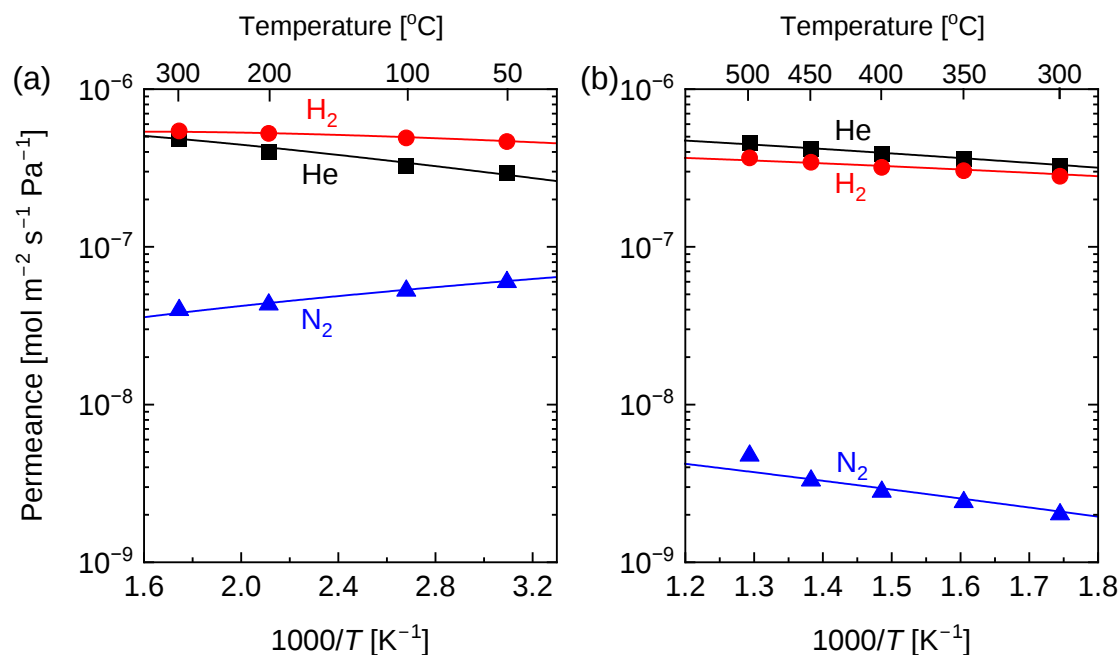


Figure 8. Temperature dependence of the He , H_2 and N_2 permeance of carbon- SiO_2 - ZrO_2 membranes prepared at (a) 550 and (b) 750 °C.

Table 1. Carbon- SiO_2 - ZrO_2 membrane properties determined from the temperature dependence of He , H_2 , and N_2 permeance values.

Fabrication Temperature [°C]	Average Pore Size ^a [nm]	Activation Energies [kJ mol ⁻¹]		
		He	H ₂	N ₂
550	0.56	5.0	2.6	−1.1
750	0.40	7.5	6.5	13.5

^a Determined by the modified gas-translational model.

In Equation (6), the pre-exponential factor $k_{0,i}$ expresses the combination of configurational factors of the membrane and the permeating molecule, $E_{p,i}$ is the apparent activation energy of permeation for a gas species, i , while M_i is the molecular weight of the gas species, R is the universal gas constant, and T is the permeation temperature. The obtained values indicate that at 0.56 nm, the average pore size of the C-SZ550 membrane is larger than the molecular diameter of SF₆. Thus, in Figure 8a, N₂ shows a Knudsen type of permeation mechanism whereby the gas permeance reduces as permeation temperature increases, giving the apparent activation energy of -1.1 kJ mol^{-1} , which is typical of membranes with a loose pore-size distribution. On the other hand, the permeance of both He and H₂ was increased with temperature showing positive activation energies of 5.0 and 2.6 kJ mol^{-1} , respectively (Table 1), which is indicative of activated diffusion.

The permeation of He, H₂, and N₂ through the C-SZ750 membrane showed an activated diffusion mechanism. The activation energies of these gases (He: 7.5 kJ mol^{-1} , H₂: 6.5 kJ mol^{-1} , N₂: 13.5 kJ mol^{-1}) are much higher than in the C-SZ550 membrane, which supports calculations for the pore size of the C-SZ750 membrane at 0.4 nm, because a higher amount of energy is required to permeate the smaller pores of the C-SZ750 membrane. It should also be noted that the activation energy of N₂ was much higher than those of He and H₂ because gases with larger molecular diameters require higher amounts of energy to permeate smaller pores.

3.3. Hydrothermal Stability of Carbon-SiO₂-ZrO₂ Membranes

Having examined the different permeation properties of C-SZ550 and C-SZ750 membranes, hydrothermal stability tests were carried out to investigate the roles that the different microstructural and surface properties of both membranes played in their durability under steamed conditions. Figure 9 shows the time courses at 500 °C for He and N₂ permeance under dry and hydrothermal conditions of 90 and 150 kPa of steam partial pressure (30 and 50 mol% steam, respectively) for the C-SZ550 membrane. After steady states of He and N₂ permeance (5.4×10^{-7} and $2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively) were established at 500 °C, a mixture composed of 30 mol% of steam and 70 mol% of N₂ was fed to the membrane until steady-state fluxes of both N₂ and trapped H₂O were achieved. At a steam partial pressure of 90 kPa, the steady value of N₂ permeance was significantly lower than that for a dry state. This reduction in N₂ permeance could have been due to the blocking effect of water molecules as both water and N₂ molecules permeated the micropores. After 90 kPa of steam treatment for 23 h and complete drying of the membrane, the steady-state N₂ permeance of $3.8 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was higher than the starting permeance of $2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ before hydrothermal treatment, while He permeance was only marginally increased. Therefore, an enlargement of the pores had occurred during the hydrothermal treatment. Further hydrothermal testing at 150 kPa for 9 h revealed a similar trend of reduced N₂ permeance under hydrothermal conditions. However, after stable N₂ and H₂O permeance were achieved and the membrane was returned to the dry state, He and N₂ permeance were permanently reduced to 3.8×10^{-7} and $9.8 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively, from the initial dry state values. This indicates a densification of the C-SZ structure upon exposure to more severe hydrothermal conditions. Thus, it is evident that the C-SZ550 membrane was unstable during long-term hydrothermal testing.

The procedure carried out for the C-SZ550 membrane was repeated for the C-SZ750 membrane. Figure 10 shows the time course at 500 °C for He and N₂ permeance under dry conditions and for N₂ permeance under hydrothermal conditions for the C-SZ750 membrane. As with the C-SZ550 membrane, in the C-SZ750, N₂ also showed a reduced permeance in the presence of steam compared with that of the dry-state. Following the removal of steam and drying for several hours, the permeance values for He and N₂ (5.2×10^{-7} and $6.6 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively) were unchanged compared with that before hydrothermal stability testing. After further exposure at 150 kPa steam partial pressure, the permeance values for He and N₂ (5.7×10^{-7} and $7.5 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively) were only slightly increased after drying and reaching a confirmed steady state. This shows

a substantially more stable performance under hydrothermal conditions for the carbon-SiO₂-ZrO₂ membrane fabricated at 750 °C.

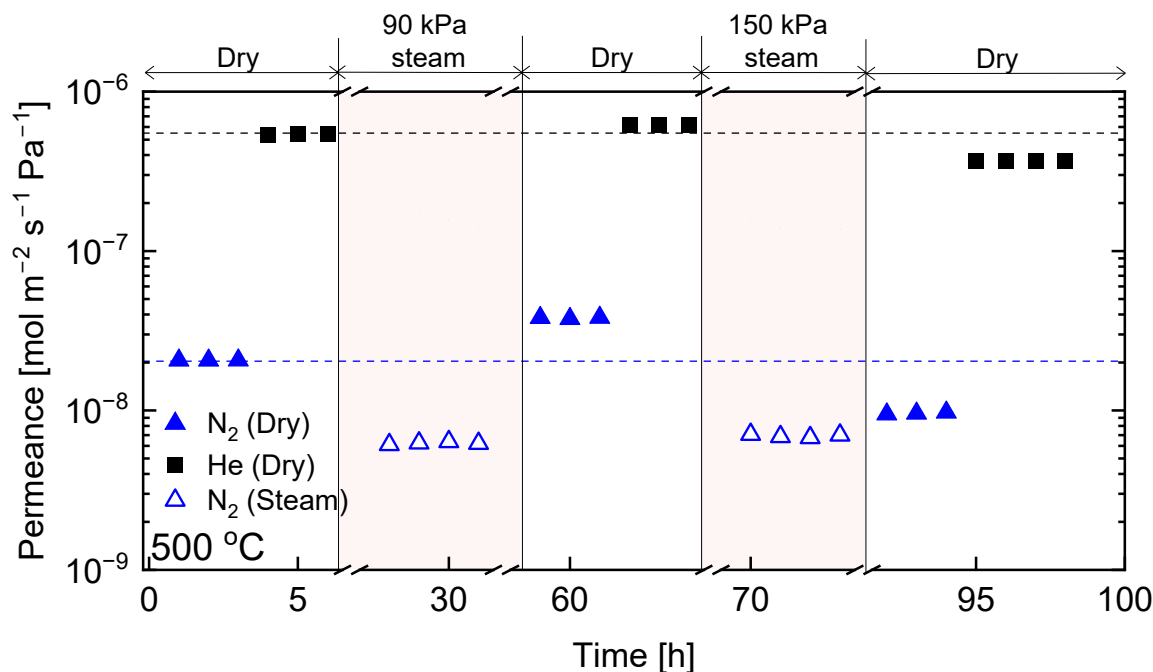


Figure 9. Time courses of hydrothermal stability tests at 500 °C in a mixture of H₂O + N₂ (90 and 150 kPa of steam partial pressure; total pressure of 300 kPa) for carbon-SiO₂-ZrO₂ membranes prepared at 550 °C.

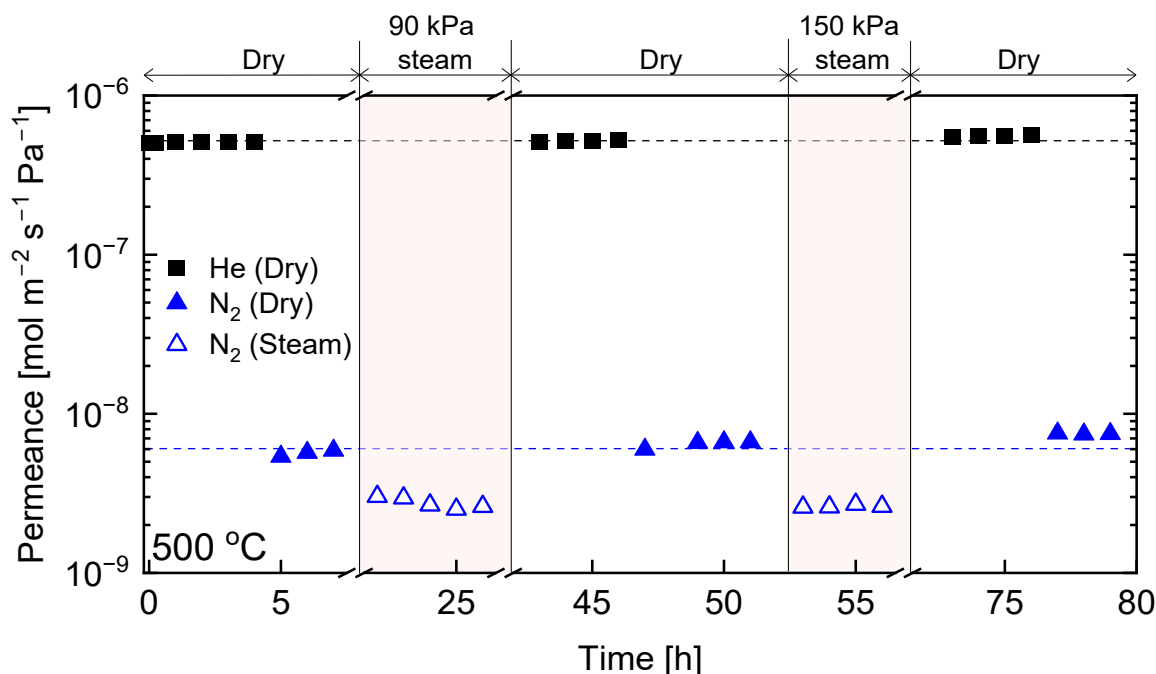


Figure 10. Time courses for hydrothermal stability tests at 500 °C in a mixture of H₂O + N₂ (90 and 150 kPa of steam partial pressure; total pressure of 300 kPa) for carbon-SiO₂-ZrO₂ membranes prepared at 750 °C.

Figure 11a,b show the plots of single-gas permeance at 300 °C as a function of kinetic diameter for C-SZ550 and C-SZ750 membranes, respectively, before and after the hydrothermal stability tests under steam with partial pressures of 90 and 150 kPa. As noted from

the discussion on the time course of hydrothermal stability for the C-SZ550 membrane, the permeance of N_2 increased after the hydrothermal stability test at 90 kPa steam partial pressure. Figure 11a shows that the permeance values for CH_4 , CF_4 , and SF_6 also increased significantly after the hydrothermal test, but the membrane continued to retain a molecular sieving property. The selectivity of H_2 over N_2 and CH_4 was reduced from 21 to 17 and 35 to 19, respectively (Table S2). This suggests the formation of a looser pore size distribution, which allowed the permeance of large gases to increase. The permeance values for He and H_2 remained largely the same as they were permeating the smaller micropores yet unaffected by the steam permeation. After the hydrothermal stability test at 150 kPa partial pressure of steam, the pore size distribution was significantly changed. The permeance values for He, H_2 , CO_2 , N_2 , and CH_4 were reduced quite considerably while those for CF_4 and SF_6 were increased. The ratios of the permeance of H_2 over those of N_2 and CH_4 were both increased to 23, due to the densification of the micropores (Table 1). However, the ratios of N_2 and CH_4 permeance values to those of CF_4 and SF_6 then approached Knudsen selectivity. This type of property is characteristic of a bimodal pore size distribution and suggests a loss of molecular sieving ability by the membrane.

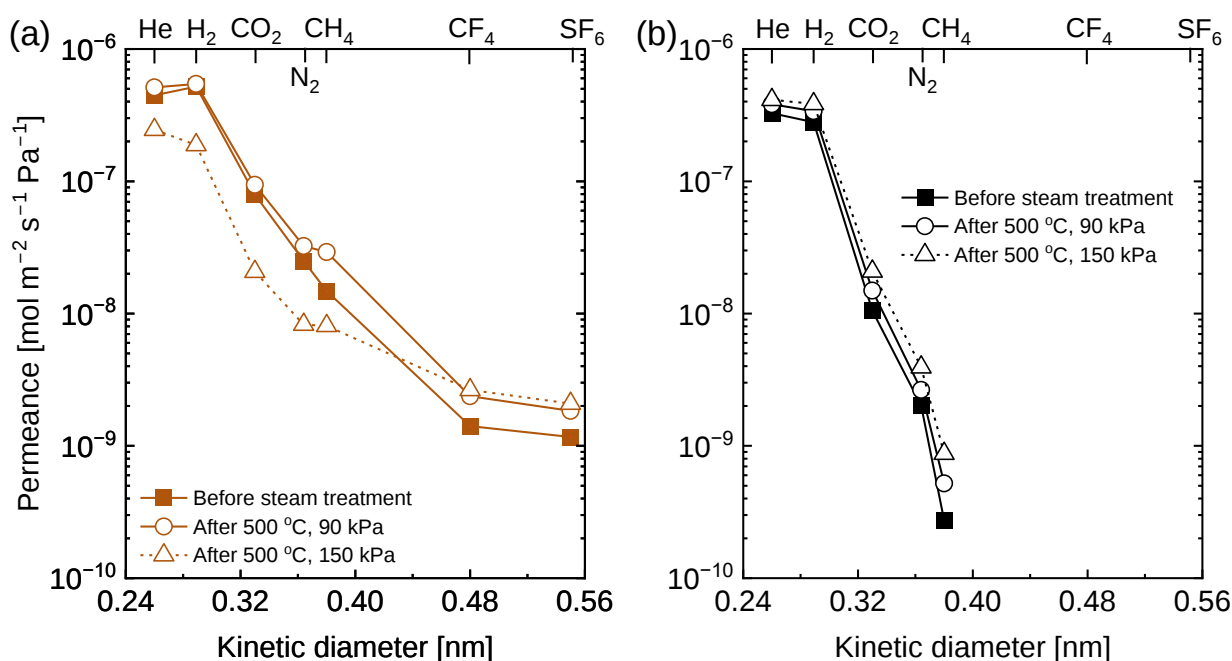


Figure 11. Single-gas permeance as a function of kinetic diameter measured at 300 °C of carbon-SiO₂-ZrO₂ membranes fabricated at (a) 550 and (b) 750 °C before and after hydrothermal stability tests at 500 °C with steam partial pressures of 90 and 150 kPa.

In Figure 11b, the kinetic diameter dependence of single-gas permeance in the C-SZ750 membrane before and after hydrothermal stability tests tell a different story. An ideal membrane for application in alcohol steam reforming reactions to produce CH_4 -free H_2 must be able to maintain a H_2/CH_4 selectivity equal to or greater than 100 [12]. The C-SZ750 membrane not only maintained the integrity of the pore structure, but also maintained a high H_2 permeance and H_2/CH_4 selectivity of $3.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and 439, respectively, after exposure to hydrothermal conditions of 150 kPa of steam partial pressure at 500 °C.

The observations during the hydrothermal stability tests of C-SZ550 and C-SZ750 membranes were confirmed via X-ray photoelectron spectroscopic (XPS) examinations of C-SZ550 and C-SZ750 films supported on Si wafers before and after exposure to steam. Figure 12a,b show the narrow C 1s XPS spectra of C-SZ550 and C-SZ750 films, respectively, before and after steam treatment conditions of 90 kPa steam partial pressure at 500 °C for 3 h. In Figure 12a, the observed C 1s spectra (black line) of C-SZ550 before and after steam

treatment can be deconvoluted into four constituent peaks each representing the status of carbon bonds. Before steam treatment, the more prominent peak at 60.5% represents the existence of sp^3 hybridized carbon with only 5.5% of sp^2 hybridized carbon formed. This supports the idea that pyrolytic transformation was yet to be complete at 550 °C. Following steam exposure, the proportion of sp^3 to sp^2 carbon changed considerably. Sp^3 carbon then made up 33.2% while sp^2 carbon made up 30.3%. It could thus be concluded that steam had a deleterious effect on the carbon atoms still bonded in the sp^3 state.

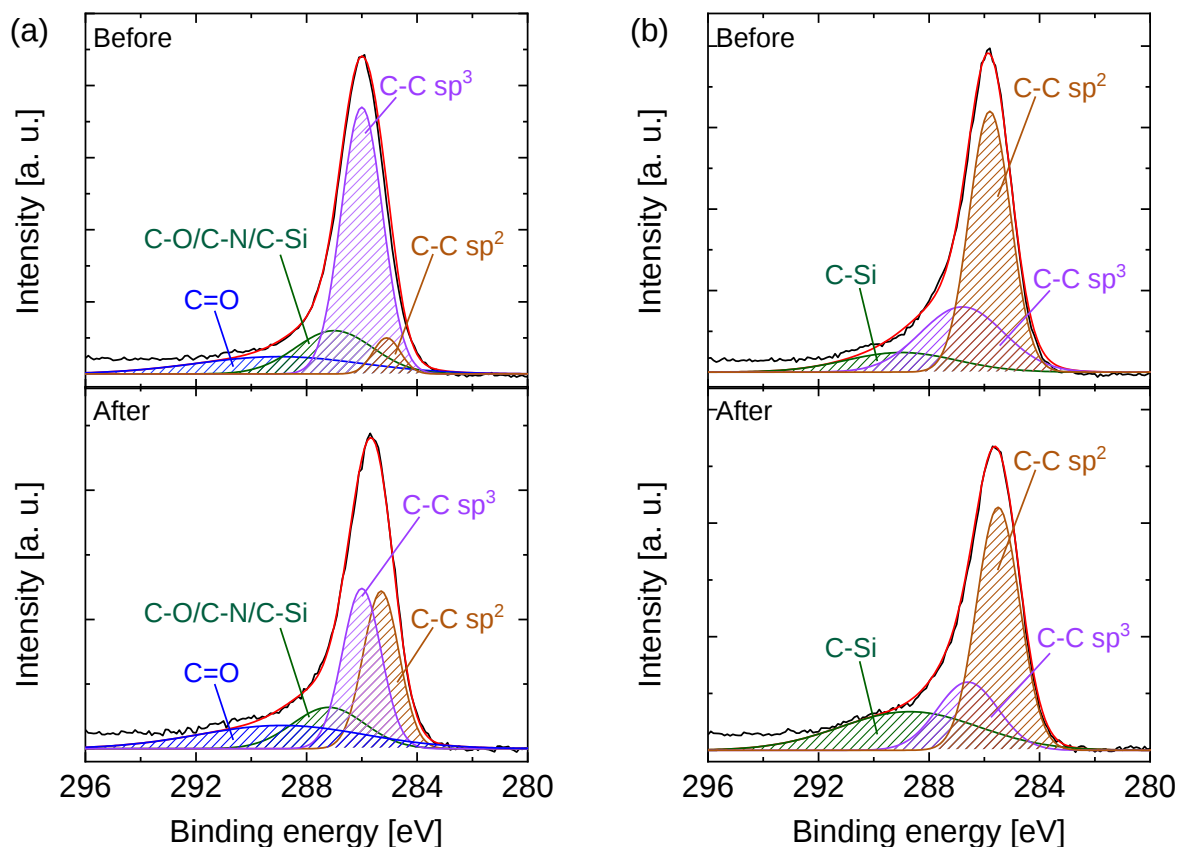


Figure 12. C 1s X-ray photoelectron spectroscopy of carbon-SiO₂-ZrO₂ films prepared at (a) 550 and (b) 750 °C before and after 3 h of steam treatment at 500 °C, 90 kPa steam partial pressure.

In Figure 12b, sp^2 carbon was the more prominent peak for C-SZ750 before steam treatment with a proportion of 58.8% compared with 29.4% for sp^3 carbon. This shows a more complete pyrolytic transformation of SiO₂-ZrO₂-polybenzoxazine at 750 °C. After the exposure to steam, C-SZ750 retained similar proportions of sp^2 and sp^3 carbon at 52.5 and 20.8%, respectively, compared with those before steam treatment. This, therefore, indicates that C-SZ750 is more stable than C-SZ550 in the presence of steam. The prior conversion of more sp^3 -type carbon to sp^2 at a higher pyrolysis temperature provided greater resistance to adverse hydrothermal conditions.

Figure 13a,b present a schematic summary of the observations on the hydrothermal stability performances of C-SZ550 and C-SZ750 membranes, respectively. XPS examination has shown that there is a large proportion of sp^3 hybridized carbon in C-SZ550, as discussed above. A detailed discussion on the effects of pyrolysis temperature on the pyrolysis mechanism and the nature of residual carbon can be found in a previous work [25]. These sp^3 carbons may represent incompletely pyrolyzed carbon chains due to low pyrolysis temperature. From the observations in Figure 9 for the C-SZ550 membrane, it appears that the initial exposure to steam at 90 kPa partial pressure caused a gasification of incompletely carbonized organic moieties leaving larger pores and exposing the decarbonized -Si-O-Zr- linkages. This phenomenon was also reported by Duke et al. [18]. A more severe

steam exposure at 150 kPa partial pressure then resulted in hydrolysis of the exposed -Si-O-Zr- linkages forming -Si-OH and -Zr-OH groups and to migration and subsequent recondensing under dry conditions [16], as illustrated in Figure 13a. This recondensation leads to a densification of the C-SZ550 membrane and a resultant reduction in permeance. For a C-SZ750 membrane, Figure 13b illustrates a structure with a complete ceramic and carbonized form. Upon exposure to steam atmosphere, free sp^2 carbon, being stable, shields most of the -Si-O-Zr- linkages from H_2O attack. Some outlying -Si-O-Zr- bonds could be hydrolyzed but the resulting -Si-OH and -Zr-OH groups are prevented from migration and thus recondensation by the free carbon, as suggested by Duke et al. [18].

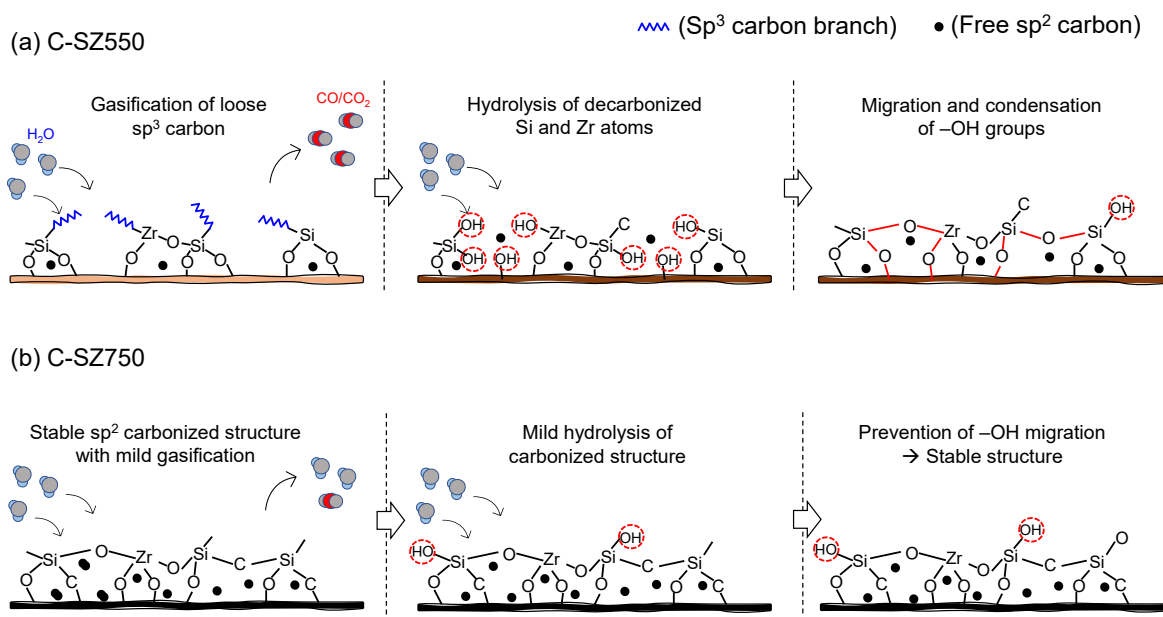


Figure 13. Schematic illustration of the role of fabrication temperature in the microstructural stability of carbon-SiO₂-ZrO₂ membranes fabricated at (a) 550 and (b) 750 °C upon exposure to steam.

Yoshida et al. [47] investigated the hydrothermal stability of several unmodified SiO₂-ZrO₂ membranes. While a SiO₂-ZrO₂ membrane with a silica-to-zirconia ratio of 9/1 showed the best balance of hydrothermal stability and H₂/N₂ selectivity at 500 °C and 100 kPa partial pressure of steam, the pore size distribution of the membrane changed considerably as hydrothermal exposure increased. The selectivity of H₂ over N₂ increased but the permeance of all gases reduced considerably and the membrane assumed a bimodal pore size distribution. Ahn et al. [48] also tested the hydrothermal stability of an unmodified SiO₂-ZrO₂ membrane (10% ZrO₂) at 650 °C under a steam partial pressure of 101 kPa. After the steady state of the membrane was established at the testing conditions, H₂ permeance was found to have reduced by 56%, although with a corresponding increase in H₂ selectivity over N₂. These two studies have shown that a trend of reduced H₂ permeance with a corresponding selectivity increase is to be expected after pure SiO₂-ZrO₂ membranes are exposed to high-temperature hydrothermal conditions. However, a sustained high permeance of H₂ is important in membrane reactor applications. This work has thus shown that the modification of SiO₂-ZrO₂ via carbonization can be utilized in achieving hydrothermally robust membranes with sustained levels of H₂ permeance and selectivity.

4. Conclusions

Carbon-SiO₂-ZrO₂ was formed from the pyrolysis of polybenzoxazine-modified SiO₂-ZrO₂ under an inert atmosphere. The chosen pyrolysis temperature determined the surface and microstructural properties of the resulting carbon-SiO₂-ZrO₂ composite. Pyrolysis of the cured SiO₂-ZrO₂-polybenzoxazine membrane at 750 °C resulted in a sharp pore size distribution compared with pyrolysis at 550 °C, which also resulted in higher H₂

selectivity over CO₂, N₂, and CH₄. After conducting hydrothermal stability tests at 500 °C under steam partial pressures of 90 and 150 kPa, a carbon-SiO₂-ZrO₂ membrane fabricated at 750 °C showed stable performance under the hydrothermal conditions applied with sustained levels of H₂ permeance and H₂ selectivity attributed to the complete pyrolytic formation of free carbon which prevented structural changes in the ceramic membrane backbone during hydrothermal exposure.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/membranes13010030/s1>, Figure S1: Flow of membrane support fabrication; Figure S2: C-SZ membrane pyrolysis sequence; Figure S3: Water-contact angles of (a) fresh and (b) 90 °C-cured SiO₂-ZrO₂-polybenzoxazine films; Figure S4: Non-local density functional theory (NLDFT)-derived pore size distribution for carbon-SiO₂-ZrO₂ powders prepared at 550 (C-SZ550) and 750 °C (C-SZ750); Figure S5: Scanning electron microscopy images of the cross-sections of carbon-SiO₂-ZrO₂ membranes prepared at (a) 550 and (b) 750 °C; Figure S6: Pore size distributions of C-SZ550 and C-SZ750 membranes determined by normalized Knudsen permeance as a function of kinetic diameter of gases; Table S1: A comparison of popular H₂ separation technologies; Table S2: Membrane performance characteristic values measured at 300 °C before (0 kPa) and after (90 and 150 kPa) steam treatment at 500 °C. Refs. [49,50] are cited in Supplementary materials.

Author Contributions: S.O.L.—conceptualization, investigation, data curation, writing (original draft preparation); H.N.—supervision, writing (editing and revision); T.T.—supervision, validation, writing (editing and revision); M.K.—conceptualization, methodology, writing (original draft preparation and revision), funding acquisition. All authors have read and agreed to the published version of the manuscript.

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References

- Chang, Y.; Lee, J.; Yoon, H. Alternative projection of the world energy consumption-in comparison with the 2010 international energy outlook. *Energy Policy* **2012**, *50*, 154–160. [\[CrossRef\]](#)
- Abas, N.; Kalair, A.; Khan, N. Review of fossil fuels and future energy technologies. *Futures* **2015**, *69*, 31–49. [\[CrossRef\]](#)
- Johnston, B.; Mayo, M.C.; Khare, A. Hydrogen: The energy source for the 21st century. *Technovation* **2005**, *25*, 569–585. [\[CrossRef\]](#)
- Nicoletti, G.; Arcuri, N.; Nicoletti, G.; Bruno, R. A technical and environmental comparison between hydrogen and some fossil fuels. *Energy Convers. Manag.* **2015**, *89*, 205–213. [\[CrossRef\]](#)
- Edwards, P.P.; Kuznetsov, V.L.; David, W.I.F.; Brandon, N.P. Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy* **2008**, *36*, 4356. [\[CrossRef\]](#)
- Pivovar, B.; Rustagi, N.; Satyapal, S. Hydrogen at scale (H₂@Scale): Key to a clean, economic, and sustainable energy system. *Electrochem. Soc. Interface* **2018**, *27*, 47. [\[CrossRef\]](#)
- Carrette, L.; Friedrich, K.A.; Stimming, U. Fuel cells: Principles, types, fuels, and applications. *ChemPhysChem* **2000**, *1*, 162–193. [\[CrossRef\]](#)
- Rousseau, R.W. *Handbook of Separation Process Technology*; John Wiley and Sons: New York, NY, USA, 1987.
- Ockwig, N.W.; Nenoff, T.M. Membranes for hydrogen separation. *Chem. Rev.* **2007**, *107*, 4078–4110. [\[CrossRef\]](#)
- Simpson, A.P.; Lutz, A.E. Exergy analysis of hydrogen production via steam methane reforming. *Int. J. Hydrogen Energy* **2017**, *32*, 4811–4820. [\[CrossRef\]](#)
- Adhikari, S.; Fernando, S. Hydrogen membrane separation techniques. *Ind. Eng. Chem. Res.* **2006**, *45*, 875. [\[CrossRef\]](#)
- Bernardo, G.; Araujo, T.; da Silva Lopes, T.; Sousa, J.; Mendes, A. Recent advances in membrane technologies for hydrogen purification. *Int. J. Hydrogen Energy* **2020**, *45*, 7313–7338. [\[CrossRef\]](#)
- Fotou, G.P.; Lin, Y.S.; Pratsinis, S.E. Hydrothermal stability of pure and modified microporous silica membranes. *J. Mater. Sci.* **1995**, *30*, 2803–2808. [\[CrossRef\]](#)
- Chang, C.-H.; Gopalan, R.; Lin, Y.S. A comparative study on thermal and hydrothermal stability of alumina, titania and zirconia membranes. *J. Membr. Sci.* **1994**, *91*, 27–45. [\[CrossRef\]](#)
- Boffa, V.; Blank, D.H.A.; ten Elshof, J.E. Hydrothermal stability of microporous silica and niobia-silica membranes. *J. Membr. Sci.* **2008**, *319*, 256–263. [\[CrossRef\]](#)

16. Imai, H.; Morimoto, H.; Tominaga, A.; Hirashima, H. Structural changes in sol-gel derived SiO₂ and TiO₂ films by exposure to water vapor. *J. Sol-Gel Sci. Technol.* **1997**, *10*, 45–54. [\[CrossRef\]](#)
17. Duke, M.C.; da Costa, J.C.D.; Lu, G.Q.; Petch, M.; Gray, P. Carbonized template molecular sieve silica membranes in fuel processing systems: Permeation, hydrostability and regeneration. *J. Membr. Sci.* **2004**, *241*, 325–333. [\[CrossRef\]](#)
18. Duke, M.C.; da Costa, J.C.D.; Do, D.D.; Petch, M.; Gray, P.G.; Lu, G.Q. Hydrothermally robust molecular sieve silica for wet gas separation. *Adv. Funct. Mater.* **2006**, *16*, 1215–1220. [\[CrossRef\]](#)
19. Lawal, S.; Nagasawa, H.; Tsuru, T.; Kanezashi, M. Enhancement of the H₂-permselectivity of a silica-zirconia composite membrane enabled by ligand-ceramic to carbon-ceramic transformation. *J. Membr. Sci.* **2022**, *642*, 119948. [\[CrossRef\]](#)
20. Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. Chemical modification of alkoxide precursors. *J. Non-Cryst. Solids* **1988**, *100*, 65–76. [\[CrossRef\]](#)
21. Livage, J.; Sanchez, C. Sol-gel chemistry. *J. Non-Cryst. Solids* **1992**, *145*, 11–19. [\[CrossRef\]](#)
22. Livage, J.; Henry, M.; Sanchez, C. Sol-gel chemistry of transition metal oxides. *Prog. Solid St. Chem.* **1988**, *18*, 25–341. [\[CrossRef\]](#)
23. Lawal, S.; Kanezashi, M.; Nagasawa, H.; Tsuru, T. Development of an acetylacetonate-modified silica-zirconia membrane applicable to gas separation. *J. Membr. Sci.* **2020**, *599*, 117844. [\[CrossRef\]](#)
24. Lawal, S.; Yu, L.; Nagasawa, H.; Tsuru, T.; Kanezashi, M. A carbon-silica-zirconia membrane with CO₂ flow-switching behavior promising high-temperature H₂/CO₂ separation. *J. Mater. Chem. A* **2020**, *8*, 23563. [\[CrossRef\]](#)
25. Lawal, S.O.; Nagasawa, H.; Tsuru, T.; Kanezashi, M. Design of carbon-ceramic composite membranes with tunable molecular cut-offs from a carboxylic benzoxazine ligand chelated to silica-zirconia. *Mol. Syst. Des. Eng.* **2022**, *7*, 1030–1038. [\[CrossRef\]](#)
26. Shaer, C.; Oppenheimer, L.; Lin, A.; Ishida, H. Advanced Carbon Materials Derived from Polybenzoxazines: A Review. *Polymers* **2021**, *13*, 3775. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Agag, T.; Jin, L.; Ishida, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4'-diaminodiphenyl sulfone-based benzoxazine monomer. *Polymer* **2009**, *50*, 5940–5944. [\[CrossRef\]](#)
28. Andreu, R.; Reina, J.A.; Ronda, J.C. Carboxylic acid-containing benzoxazines as efficient catalysts in the thermal polymerization of benzoxazines. *J. Polym. Sci. Pol. Chem.* **2008**, *46*, 6091–6101. [\[CrossRef\]](#)
29. Lei, L.; Pan, F.; Lindbråthen, A.; Zhang, X.; Hillestad, M.; Nie, Y.; Bai, L.; He, X.; Guiver, M.D. Carbon hollow fiber membranes for a molecular sieve with precise-cut-off ultramicropores for superior hydrogen separation. *Nat. Commun.* **2021**, *12*, 268. [\[CrossRef\]](#)
30. Richter, H.; Voss, H.; Kaltenborn, N.; Kamnitz, S.; Wollbrink, A.; Feldhoff, A.; Caro, J.; Roitsch, S.; Voigt, I. High-flux carbon molecular sieve membranes for gas separation. *Angew. Chem. Int. Ed.* **2017**, *56*, 7760–7763. [\[CrossRef\]](#)
31. Steel, K.M.; Koros, W.J. Investigation of porosity of carbon materials and related effects on gas separation properties. *Carbon* **2003**, *41*, 253–266. [\[CrossRef\]](#)
32. Rungta, M.; Wenz, G.B.; Zhang, C.; Xu, L.; Qiu, W.; Adams, J.S.; Koros, W. Carbon molecular sieve structure development and membrane performance relationships. *Carbon* **2017**, *115*, 237–248. [\[CrossRef\]](#)
33. Sazali, N. A comprehensive review of carbon molecular sieve membranes for hydrogen production and purification. *Int. J. Adv. Manuf. Technol.* **2020**, *107*, 2465–2483. [\[CrossRef\]](#)
34. Hou, M.; Li, L.; Song, J.; Xu, R.; He, Z.; Lu, Y.; Pan, Z.; Song, C.; Wang, T. Polyimide-derived carbon molecular sieve membranes for high-efficient hydrogen purification: The development of a novel phthalide-containing polyimide precursor. *Sep. Purif. Technol.* **2022**, *301*, 121982. [\[CrossRef\]](#)
35. Ning, X.; Koros, W.J. Carbon molecular sieve membranes derived from Matrimid® polyimide for nitrogen/methane separation. *Carbon* **2014**, *66*, 511–522. [\[CrossRef\]](#)
36. Qiu, W.; Li, F.S.; Fu, S.; Koros, W.J. Isomer-tailored carbon molecular sieve membranes with high gas separation performance. *ChemSusChem* **2020**, *13*, 5318–5328. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Alcaniz-Monge, J.; Lozano-Castello, D. Assessment of Ultramicroporosity on Carbon Molecular Sieves by Water Adsorption. *Adsorpt. Sci. Technol.* **2003**, *21*, 841–848. [\[CrossRef\]](#)
38. Do, D.D.; Junpirom, S.; Do, H.D. A new adsorption-desorption model for water adsorption in activated carbon. *Carbon* **2009**, *47*, 1466–1473. [\[CrossRef\]](#)
39. Yoon, Y.H.; Lively, R.P. Co-transport of water and p-xylene through carbon molecular sieve membranes. *J. Membr. Sci.* **2022**, *654*, 120495. [\[CrossRef\]](#)
40. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [\[CrossRef\]](#)
41. Pires, J.; Pinto, M.L.; Carvalho, A.; de Carvalho, M.B. Assessment of hydrophobic-hydrophilic properties of microporous materials from water adsorption isotherms. *Adsorption* **2003**, *9*, 303–309. [\[CrossRef\]](#)
42. Baker, F.S.; Sing, K.S.W. Specificity in adsorption of nitrogen and water on hydroxylated and dehydroxylated silicas. *J. Colloid Interf. Sci.* **1976**, *55*, 605–613. [\[CrossRef\]](#)
43. Matsuda, A.; Matsuno, Y.; Tatsumisago, M.; Minami, T. Changes in porosity and amounts of adsorbed water in sol-gel derived porous silica films with heat treatment. *J. Sol-Gel Sci. Technol.* **2001**, *20*, 129–134. [\[CrossRef\]](#)
44. Oyama, S.T.; Yamada, M.; Sugawara, T.; Takagaki, A.; Kikuchi, R. Review on mechanisms of gas permeation through inorganic membranes. *J. Jpn. Petrol. Inst.* **2011**, *54*, 298–309. [\[CrossRef\]](#)

45. Lee, H.R.; Kanezashi, M.; Shimomura, Y.; Yoshioka, T.; Tsuru, T. Evaluation and fabrication of pore-size-tuned silica membranes with tetramethoxydimethyl disiloxane for gas separation. *AIChE J.* **2011**, *57*, 2755–2765. [[CrossRef](#)]
46. Nagasawa, H.; Niimi, T.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Modified gas-translation model for the prediction of gas permeation through microporous organosilica membranes. *AIChE J.* **2014**, *60*, 4199–4210. [[CrossRef](#)]
47. Yoshida, K.; Hirano, Y.; Fujii, H.; Tsuru, T.; Asaeda, M. Hydrothermal stability and performance of silica-zirconia membranes for hydrogen separation in hydrothermal conditions. *J. Chem. Eng. Jpn.* **2001**, *34*, 523–530. [[CrossRef](#)]
48. Ahn, S.-J.; Takagaki, A.; Sugawara, T.; Kikuchi, R.; Oyama, S.T. Permeation properties of silica-zirconia composite membranes supported on porous alumina substrates. *J. Membr. Sci.* **2017**, *526*, 409–416. [[CrossRef](#)]
49. Sircar, S. Pressure swing adsorption. *Ind. Eng. Chem. Res.* **2002**, *41*, 1389–1392. [[CrossRef](#)]
50. Hinchliffe, A.B.; Porter, K.E. A comparison of membrane separation and distillation. *Trans. IChemE* **2000**, *78*, 255–268. [[CrossRef](#)]

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