Article

Zirconia-Doped Methylated Silica Membranes via Sol-Gel Process: Microstructure and Hydrogen Permselectivity

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Abstract: In order to obtain a steam-stable hydrogen permselectivity membrane, with tetraethyloorthosilicate (TEOS) as the silicon source, zirconium nitrate pentahydrate (Zr(NO$_3$)$_4$·5H$_2$O) as the zirconium source, and methyltriethoxysilane (MTES) as the hydrophobic modifier, the methyl-modified ZrO$_2$-SiO$_2$ (ZrO$_2$-MSiO$_2$) membranes were prepared via the sol-gel method. The microstructure and gas permeance of the ZrO$_2$-MSiO$_2$ membranes were studied. The physical-chemical properties of the membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM), and N$_2$ adsorption–desorption analysis. The hydrogen permselectivity of ZrO$_2$-MSiO$_2$ membranes was evaluated with Zr content, temperature, pressure difference, drying control chemical additive (glycerol) content, and hydrothermal stability as the inferred factors. XRD and pore structure analysis revealed that, as n$_{Zr}$ increased, the MSiO$_2$ peak gradually shifted to a higher 2θ value, and the intensity gradually decreased. The study found that the permeation mechanism of H$_2$ and other gases is mainly based on the activation–diffusion mechanism. The separation of H$_2$ is facilitated by an increase in temperature. The ZrO$_2$-MSiO$_2$ membrane with n$_{Zr}$ = 0.15 has a better pore structure and a suitable ratio of micropores to mesopores, which improved the gas permselectivities. At 200°C, the H$_2$ permeance of MSiO$_2$ and ZrO$_2$-MSiO$_2$ membranes was $3.66 \times 10^{-6}$ and $6.46 \times 10^{-6}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$, respectively. Compared with the MSiO$_2$ membrane, the H$_2$/CO$_2$ and H$_2$/N$_2$ permselectivities of the ZrO$_2$-MSiO$_2$ membrane were improved by 79.18% and 26.75%, respectively. The added amount of glycerol as the drying control chemical additive increased from 20% to 30%, the permeance of H$_2$ decreased by 11.55%, and the permselectivities of H$_2$/CO$_2$ and H$_2$/N$_2$ rose by 2.14% and 0.28%, respectively. The final results demonstrate that the ZrO$_2$-MSiO$_2$ membrane possesses excellent hydrothermal stability and regeneration capability.

Keywords: microporous membrane; H$_2$ permselectivity; zirconia-doped SiO$_2$ membrane; hydrothermal stability; regeneration

1. Introduction

It is well-known that hydrogen is a clean energy source [1]. At present, there are many ways to obtain H$_2$, but the biggest problem preventing its commercialization is the purification and separation of H$_2$. The purification of H$_2$ can be achieved in three main ways: pressure swing adsorption, cryogenic distillation, and membrane separation [2,3]. Although pressure swing adsorption and cryogenic distillation can be operated commercially, the economic benefits are low. The main commercial application of membranes in gas separation is the separation of hydrogen from nitrogen, methane, and argon in an ammonia sweep gas stream. In the past few years, hundreds of new polymer materials have been reported, and only eight or nine polymer materials have been used to make gas separation membrane bases. Surprisingly few of them were used to make industrial membranes [4]. Membrane separation technology is also one of the most promising hydrogen purification...
methods. At high temperatures, the H₂ separation membrane has attracted much attention in the application of membrane reactors, for example, in the steam reforming of natural gas. The characteristics of lower energy consumption and investment cost, as well as simple operation, have made the membrane separation method widely concerned. Compared to other techniques of hydrogen purification, the membrane separation method offers more energy efficiency and environmental friendliness. The quality of the separation membrane directly affects the separation performance. Therefore, it is very necessary to choose suitable materials to prepare efficient and stable membrane materials [5].

In recent years, research on hydrogen separation membranes has mainly focused on molecular sieves, alloys, and microporous silica [6–9]. Prominently, silica membranes have received extensive attention for H₂ separation due to their advantages such as high permselectivity and considerable thermal stability [10]. Amorphous silica membranes derived from sol-gel and chemical vapor deposition (CVD) methods received an enormous amount of attention [11,12]. They have a stable chemical structure and molecular sieve mechanism, which can separate hydrogen across a broad temperature range [13]. However, silica membranes have demonstrated poor steam and thermal stability. Due to the hydrophilic nature of silica membranes, if they are frequently exposed to humid, low-temperature atmospheres, the flux and permselectivity of H₂ will largely be reduced [14,15]. The study found that the addition of hydrophobic groups can reduce the affinity of silica for water and improve gas permselectivity [15]. At this stage, methyl, vinyl, perfluorodecyl, etc., are often used in the hydrophobic modification of gas permeation separation in silica membrane, and the effect of increasing the hydrothermal stability is obvious [16]. Wei et al. [17] prepared perfluorodecyl hydrophobically modified silica membranes. The results demonstrated that the addition of perfluorodecyl made the modified silica membrane change from hydrophilic to hydrophobic. The membrane exhibited excellent hydrothermal stability at 250 °C and a water vapor molar ratio of 5%. Debarati et al. [18] hydrophobically modified the surface of ceramic membranes with polydimethylsiloxane to achieve a contact angle of 141°. It shows that the surface of the ceramic membrane with the methyl group is highly hydrophobic. Somayeh et al. [19] also demonstrated that vinyl-modified silica particles can improve the hydrophobic properties of the membrane.

It is well-known that the addition of metal oxides (such as TiO₂ [20,21], Al₂O₃ [22,23], Fe₂O₃ [24], CoO [25], and ZrO₂ [26,27]) can not only enhance the hydrothermal stability of the membrane, but also further improve the antifouling ability and performance of the membrane. This indicates that the incorporation of metal oxides can form mixed oxide network structures that are more stable than amorphous silica materials [28,29]. In particular, ZrO₂ is an excellent transition metal oxide, which is often utilized in studies of gas membrane separation. Li et al. [30] prepared a zirconia membrane via the polymeric sol-gel method, which possessed H₂ permeance of about 5 × 10⁻⁸ mol·m⁻²·s⁻¹·Pa⁻¹, H₂/CO₂ permselectivity of 14, and outstanding hydrothermal stability under a steam pressure of 100 KPa. Gu et al. [31] used the sol-gel method to prepare the microporous zirconia membrane. After being treated with 0.50 mol·L⁻¹ of H₂SO₄, the hydrogen permeance was (2.8 to 3.0) × 10⁻⁶ mol·Pa⁻¹·m⁻²·s⁻¹. The H₂ permselectivities of the equimolar binary system were 6 and 9, respectively. Doping ZrO₂ in the SiO₂ matrix can improve the hydrophobicity and hydrothermal stability of the membrane matrix, and further enhance the gas permeability. Numerous studies have been carried out on ZrO₂-doped silica materials/membranes. According to mesoporous stabilized zirconia intermediate layers, Gestel et al. [32] revealed a much better membrane setup. For various CO₂/N₂ combinations, the as-prepared membrane demonstrated permselectivities of 20–30 and CO₂ permeances of 1.5 to 4 m³/(m²·h·bar). Ahn et al. [33] prepared a silica-zirconia membrane with hydrogen permselectivity on a porous alumina support using tetraethyl orthosilicate (TEOS) and tert-butanol zirconium (IV) under 923 K conditions by chemical vapor deposition. The H₂ permeance of the obtained membrane was 3.8 × 10⁻⁷ mol·m⁻²·s⁻¹·Pa⁻¹, and the permselectivities for CO₂ and N₂ were 1100 and 1400, respectively. Hove et al. [34] compared the gas permeation properties of a hybrid silica (BTESE) membrane, Zr-doped BTESE
membrane, and silica membrane before and after hydrothermal treatment under the same circumstances. At 100 °C, the hybrid silica membrane and Zr-doped BTESE membrane maintained good hydrothermal stability, while the silica membrane lost selectivity for all the studied gases. After hydrothermal treatment at 200 or 300 °C, the CO₂ permeance of the Zr-doped BTESE membrane decreased significantly, and the H₂/CO₂ permselectivity increased significantly, by 65.71%. So far, many scholars have demonstrated the effect of different conditions during preparation on the properties of zirconia-doped silica materials/membranes. The influence of the Zr/Si molar ratio on the microstructure of the membrane and the permeability of the gas is crucial. Unfortunately, there are few reports in this regard. Furthermore, the effects of methyl modification on the microstructure and steam stability of ZrO₂-SiO₂ membranes were rarely described in papers. Some scholars have found that adding a drying control chemical additive (DCCA) in the process of preparing the membrane via the sol-gel method can effectively reduce the uneven shrinkage of the membrane during the heating process and during the calcining process [35], and improve the gas permselectivity of the membrane.

In this paper, methyl-modified ZrO₂-SiO₂ (ZrO₂-MSiO₂) materials/membranes with various Zr/Si molar ratios (n_Zr) were fabricated. Glycerol was chosen to be the DCCA. The impact of n_Zr on the microstructures and H₂ permselectivities of ZrO₂-MSiO₂ membranes was thoroughly addressed. The water vapor stability of ZrO₂-MSiO₂ membranes was investigated further by comparing the gas permeability characteristics of the ZrO₂-MSiO₂ membranes before and after steam treatment. The heat regeneration performance of ZrO₂-MSiO₂ membranes was also investigated.

2. Materials and Methods
2.1. Preparation of MSiO₂ Sols

The MSiO₂ sols were prepared by tetraethylorthosilicate (TEOS, purchased from Xi’an chemical reagent Co., Ltd., Xi’an, China) as a silica source, methyltriethoxysilane (MTES, purchased from Hangzhou Guibao Chemical Co., Ltd., Hangzhou, China) as a hydrophobic modified agent, anhydrous ethanol (EtOH, purchased from Tianjin Branch Micro-Europe Chemical Reagent Co., Ltd., Tianjin, China) as a solvent, and nitric acid (HNO₃, purchased from Sichuan Xilong Reagent Co., Ltd., Chengdu, China) as a catalyst. To begin, TEOS, MTES, and EtOH were completely combined in a three-necked flask using a magnetic stirrer. The flask was correctly immersed in an ice-water combination. The solution was then agitated for 50 min using a magnetic stirrer to ensure thorough mixing. The H₂O and HNO₃ combination was then dropped into the mixture while it was still being stirred. The reaction mixture was then agitated in a three-necked flask at a constant temperature of 60 °C for 3 h to yield the MSiO₂ sol.

2.2. Preparation of ZrO₂ Sols

In a three-necked flask, 0.6 M zirconium nitrate pentahydrate (Zr(NO₃)₄·5H₂O, purchased from Tianjin Fuchen Chemical Reagent Co., Ltd., Tianjin, China) and 0.2 M oxalic acid (C₂H₂O₄·2H₂O, purchased from Tianjin HedongHongyan Chemical Reagent Co., Ltd., Tianjin, China) solutions were combined at a molar ratio of 4.5:1.0 and agitated. The aforementioned mixture was then treated with 35% (v/v) glycerol (GL, purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China) as a catalyst. To begin, TEOS, MTES, and EtOH were completely combined in a three-necked flask using a magnetic stirrer. The flask was correctly immersed in an ice-water combination. The solution was then agitated for 50 min using a magnetic stirrer to ensure thorough mixing. The H₂O and HNO₃ combination was then dropped into the mixture while it was still being stirred. The reaction mixture was then agitated in a three-necked flask at a constant temperature of 60 °C for 3 h to yield the ZrO₂ sols.

2.3. Preparation of ZrO₂-MSiO₂ Sols

The ZrO₂ sols were aged for 12 h at 25 °C. The ZrO₂ sols and EtOH were then added to the MSiO₂ sols and stirred for 60 min to create the required ZrO₂-MSiO₂ sols. The n_Zr ratio was 0, 0.08, 0.15, 0.3, and 0.05. The ZrO₂-MSiO₂ sols were diluted three times with ethanol after 12 h. GL was used as a drying control agent at 0%, 10%, 20%, and 30% (DCCA). After 60 min of stirring, ZrO₂-MSiO₂ sols with varied GL contents were obtained.
2.4. Preparation of ZrO$_2$-MSiO$_2$ Materials

The ZrO$_2$-MSiO$_2$ sols were then placed individually in petri plates for gelation at 30 °C. The gel materials were ground and pulverized with a mortar, and then calcined at a heating rate of 0.5 °C·min$^{-1}$ at 400 °C for 2 h under nitrogen atmosphere protection, and then cooled down naturally. The ZrO$_2$-MSiO$_2$ materials with different n$_{Zr}$ were prepared. The ZrO$_2$-MSiO$_2$ materials with n$_{Zr}$=0 are also referred to as “MSiO$_2$” materials.

2.5. Preparation of ZrO$_2$-MSiO$_2$ Membranes

The ZrO$_2$-MSiO$_2$ membranes were coated on top of composite interlayers supported by porous α-alumina discs. The discs are 5 mm-thick and 30 mm in diameter, with a porosity of 40% and an average pore size of 100 nm. ZrO$_2$-MSiO$_2$ membranes were effectively prepared by dip-coating the substrates in three-fold ethanol-diluted silica sol for 7 s, then drying and calcining them. Each sample was dried at 30 °C for 3 h before being calcined at 400 °C in a temperature-controlled furnace in a N$_2$ environment with a ramping rate of 0.5 °C·min$^{-1}$ and a dwell period of 2 h. The dip-coating-drying-calcining process was repeated three times. Figure 1 demonstrates the preparation process of the ZrO$_2$-MSiO$_2$ materials/membranes. The ZrO$_2$-MSiO$_2$ membranes with n$_{Zr}$=0 are also referred to as “MSiO$_2$” membranes.

![Figure 1. Schematic diagram of the preparation of ZrO$_2$-MSiO$_2$ materials/membranes.](image)

2.6. Steam Treatment and Regeneration of ZrO$_2$-MSiO$_2$ Membranes

The ZrO$_2$-MSiO$_2$ membranes were subjected to a 7-day steam stability test in which they were placed into saturated steam at 25 °C. After steam treatment, for thermal regeneration of ZrO$_2$-MSiO$_2$ membranes, they were processed at a calcination temperature of 350 °C, with the same calcination technique as before. The gas permeances of ZrO$_2$-MSiO$_2$ membranes were investigated after steam treatment and regeneration, respectively.

2.7. Characterizations

Using Fourier transform infrared spectroscopy, the functional groups of ZrO$_2$-MSiO$_2$ materials were characterized (FTIR, Spotlight 400 and Frontier, PerkinElmer Corporation, Waltham, MA, USA), and the wavelength measuring range was 400 to 4000 cm$^{-1}$ using the KBr compression technique. Using a Rigaku D/max-2550pc X-ray diffractometer (XRD, Rigaku D/max-2550pc, Hitachi, Tokyo, Japan) with CuKα radiation at 40 kV and 40 mA, the ZrO$_2$-MSiO$_2$ materials’ phase structure was found. The X-ray photoelectron spectra (XPS) were acquired on a K-Alpha X-ray photoelectron spectroscope from Thermo Fisher Scientific with AlKα excitation and were calibrated regarding the signal of adventitious carbon (XPS, ESCALAB250xi, Thermo Scientific, Waltham, MA, USA). The binding energy estimates
were derived using the C (1s) line at 284.6 eV as the reference point. Transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan) was utilized to investigate the ZrO$_2$-MSiO$_2$ powders’ crystallization. Operating at 5 kV, scanning electron microscopy (SEM, JEM JSM-6300, Hitachi, Tokyo, Japan) was utilized to study the surface morphologies of the ZrO$_2$-MSiO$_2$ membranes. N$_2$ adsorption–desorption measurements were conducted using an automated Micromeritics, ASAP2020 analyzer (ASAP 2020, Micromeritics, Norcross, GA, USA). The ZrO$_2$-MSiO$_2$ materials’ BET surface area, pore volume, and pore size distribution were determined.

Figure 2 is a schematic of the experimental setup used to evaluate the performance of single gas permeation. Prior to the experiment, the pressure and temperature were set to the desired values for thirty minutes to allow the gas permeation to stabilize. The permeation properties of MSiO$_2$ and ZrO$_2$-MSiO$_2$ membranes were evaluated using H$_2$, CO$_2$, and N$_2$. The gas permeability was determined based on the outlet gas flow. The gas permeselectivity values (ideal permselectivities) were calculated by the permeance ratio between two gases.

![Image of experimental setup]

**Figure 2.** Single gas permeation experiment device diagram.

### 3. Results

#### 3.1. Chemical Structure Analysis

FTIR spectra were used to investigate the functional groups of ZrO$_2$-MSiO$_2$ materials. The FTIR spectra of ZrO$_2$-MSiO$_2$ materials containing various n$_{Zr}$ contents are displayed in Figure 3. The absorption peak at around 3448 cm$^{-1}$ was assigned to the stretching and bending vibration of the -OH group from the absorbed water. The absorption peak at 1630 cm$^{-1}$ corresponds to Si-OH and Zr-OH on the surface of ZrO$_2$-MSiO$_2$ materials [36]. The antisymmetric stretching vibration absorption peak -CH$_3$ at 2985 cm$^{-1}$ was mainly from unhydrolyzed TEOS and MTES. The absorption peak at 1278 cm$^{-1}$ was attributed to the Si-CH$_3$ group. It is also the main hydrophobic functional group of the membrane. The absorption peak observed at 1050 cm$^{-1}$ was attributed to the Si-O-Si bond [37]. Compared with the materials with n$_{Zr}$ = 0, the materials with n$_{Zr}$ = 0.08–0.5 all showed a new absorption peak at the wavenumber of 448 cm$^{-1}$. This was related to the formation of Zr-O bonds [38]. Meanwhile, with the increase of n$_{Zr}$, the peak at 1050 cm$^{-1}$ shifted to around 1100 cm$^{-1}$. This may be ascribed to the fact that partial substitution of Zr atoms for Si atoms in the Si-O-Si network to form Zr-O-Si bonds occurred [39], breaking the symmetry of SiO$_2$ and leading to the shift of peak positions. However, there was no obvious Zr-O-Si bond in the FTIR spectrum of ZrO$_2$-MSiO$_2$ materials due to the overlap of the Zr-O-Si bond with Si-O-Si bonds [40]. Furthermore, the decrease in the intensity of the silanol band at 779 and 835 cm$^{-1}$ with increasing n$_{Zr}$ could be attributed to the substitution of Si-OH bonds by Zr-O-Si bonds [41]. It demonstrates the formation of Zr-O-Si bonds in the produced materials.
The peaks corresponding to a crystalline tetragonal structure of zirconia are clearly apparent. The peaks of amorphous SiO$_2$ were concentrated at $2\theta = 23.1^\circ$ [42]. The SiO$_2$ peak moved progressively towards higher $2\theta$ values as $n_{Zr}$ rose, and it slowly dropped in intensity. This is attributable to the replacement of the portion of silicon atoms by the inserted Zr atoms, producing Zr-O-Si bonds, resulting in a drop in the SiO$_2$ concentration. The peaks corresponding to a crystalline tetragonal structure of zirconia are clearly apparent in the ZrO$_2$-MSiO$_2$ materials with $n_{Zr} = 0.15$–0.5. The (101), (112), and (202) reflection planes of the body-centered ZrO$_2$ (t-ZrO$_2$) tetragonal phase were ascribed to the large diffraction peaks occurring at 60.2°, 50.7°, and 30.2°, respectively (JCPDS No. 79-1771). XRD analysis demonstrated that with the growth of the Zr concentration, the peak intensity corresponding to t-ZrO$_2$ progressively increased. In other words, the content of t-ZrO$_2$ increased with the growth in Zr content. Combined with the FTIR analysis, the Zr element in ZrO$_2$-MSiO$_2$ materials may exist in the form of Zr-O-Si bonds and t-ZrO$_2$.

![Figure 3. FTIR spectra curves of ZrO$_2$-MSiO$_2$ materials with various $n_{Zr}$.](image)

3.2. Phase Structure Analysis

The XRD patterns of the ZrO$_2$-MSiO$_2$ materials with varied $n_{Zr}$ are presented in Figure 4. The peaks of amorphous SiO$_2$ were concentrated at $2\theta = 23.1^\circ$ [42]. The SiO$_2$ peak moved progressively towards higher $2\theta$ values as $n_{Zr}$ rose, and it slowly dropped in intensity. This is attributable to the replacement of the portion of silicon atoms by the inserted Zr atoms, producing Zr-O-Si bonds, resulting in a drop in the SiO$_2$ concentration. The peaks corresponding to a crystalline tetragonal structure of zirconia are clearly apparent in the ZrO$_2$-MSiO$_2$ materials with $n_{Zr} = 0.15$–0.5. The (101), (112), and (202) reflection planes of the body-centered ZrO$_2$ (t-ZrO$_2$) tetragonal phase were ascribed to the large diffraction peaks occurring at 60.2°, 50.7°, and 30.2°, respectively (JCPDS No. 79-1771). XRD analysis demonstrated that with the growth of the Zr concentration, the peak intensity corresponding to t-ZrO$_2$ progressively increased. In other words, the content of t-ZrO$_2$ increased with the growth in Zr content. Combined with the FTIR analysis, the Zr element in ZrO$_2$-MSiO$_2$ materials may exist in the form of Zr-O-Si bonds and t-ZrO$_2$.

![Figure 4. XRD patterns of ZrO$_2$-MSiO$_2$ materials with various $n_{Zr}$.](image)

To further investigate the presence of Zr and Si species in the ZrO$_2$-MSiO$_2$ materials, the XPS measurement was conducted. The survey XPS spectrum of ZrO$_2$-MSiO$_2$ material with $n_{Zr} = 0.15$ is shown in Figure 5. Figure 5 demonstrates that C, O, Si, and Zr elements are present in the ZrO$_2$-MSiO$_2$ material, which indicates the successful incorporation of Zr into the silica frameworks. Figure 6 presents the Si 2p and Zr 3d XPS spectra of the
ZrO$_2$-MSiO$_2$ sample with n$_{Zr}$ = 0.15. In Figure 6a, the peaks at the binding energies of 102.8 and 104.7 eV correspond to Si-C and Si-O bonds, respectively. In Figure 6b, the peaks at 186.6 and 183.3 eV correspond to the Zr-O 3d$_{3/2}$ and Zr-O 3d$_{5/2}$ peaks, respectively.

![Figure 5. The survey XPS spectrum of ZrO$_2$-MSiO$_2$ materials.](image)

![Figure 6. XPS peak decomposition for the (a) Si 2p and (b) Zr 3d photoelectron peaks of the ZrO$_2$-MSiO$_2$ materials.](image)

3.3. TEM Analysis

The TEM micrographs of the ZrO$_2$-MSiO$_2$ material with n$_{Zr}$ = 0 and 0.15 at 400 °C under nitrogen atmosphere are illustrated in Figure 7. Figure 7a depicts that the silica particles in MSiO$_2$ materials are amorphous, while in Figure 7b, a small amount of particles with darker color appear and are mixed in the silica skeleton, which may be due to the presence of t-ZrO$_2$. Overall, the ZrO$_2$-MSiO$_2$ materials with n$_{Zr}$ = 0.15 still maintained the amorphous state.

3.4. Pore Structure Analysis

The N$_2$ adsorption-desorption isotherm of the ZrO$_2$-MSiO$_2$ materials with various n$_{Zr}$ are shown in Figure 8a. According to the Brunauer-Deming-Deming-Teller (BDDT) classification, the ZrO$_2$-MSiO$_2$ materials showed a type I adsorption isotherm, while n$_{Zr}$ = 0 indicated the formation of microporous structures. The isotherms for the four samples (n$_{Zr}$ = 0.08-0.5) all showed a similar trend, which could be categorized as type IV isotherms. However, the shapes of the hysteresis loops for the four samples were different, implying the variation of pore structures. A significant proportion of adsorption occurred in the range of low relative pressure, P/P$_0$ < 0.1, indicating that the materials contain a large quantity of micropores. The shape of the hysteresis loop of the ZrO$_2$-MSiO$_2$ materials
with $n_{Zr} = 0.5$ was altered, indicating the presence of larger mesopores or macropores. In addition, the distributions of pore size for all samples are depicted in Figure 8b. It is found that the samples with $n_{Zr} = 0.08-0.5$ showed a broader pore size distribution and a larger mean pore size than the samples with $n_{Zr} = 0$. The conclusion was also confirmed by the pore structure parameters of ZrO$_2$-MSiO$_2$ materials with various $n_{Zr}$ in Table 1. The average pore size, BET specific surface area, and total pore volume of the ZrO$_2$-MSiO$_2$ materials gradually increased with $n_{Zr} = 0.08$ and 0.15, and the pore size distribution became wider. However, the total pore volume of the ZrO$_2$-MSiO$_2$ materials with $n_{Zr} = 0.3$ and 0.5 decreased instead. The fact is that the bond length of Zr-O (1.78 Å) was slightly longer than that of Si-O (1.64 Å) [43]. Figure 9 shows the molecular structure models of MSiO$_2$, ZrO$_2$-MSiO$_2$, and t-ZrO$_2$ crystallites, respectively. Hence, the formation of Zr-O-Si bonds contributes to the formation of pores. With the increase of Zr content, more and more t-ZrO$_2$ crystallites were formed and distributed in the framework of MSiO$_2$ materials, and the internal pore structure of the ZrO$_2$-MSiO$_2$ materials was hindered from shrinking and pore collapse, resulting in the decrease of the BET surface area and pore volume. From Table 1, it can be seen that the ZrO$_2$-MSiO$_2$ materials with $n_{Zr} = 0.15$ had the maximal total pore volume (0.43 cm$^3$·g$^{-1}$), BET surface area (616.77 m$^2$·g$^{-1}$), and the minimum mean pore size (2.19 nm).

Figure 7. TEM images of ZrO$_2$-MSiO$_2$ materials with $n_{Zr} =$ (a) 0 and (b) 0.15.

Figure 8. (a) The nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution curves for the ZrO$_2$-MSiO$_2$ materials with various $n_{Zr}$. 

| $n_{Zr}$ | BET Surface Area (m$^2$·g$^{-1}$) | Average Pore Size (nm) | Pore Volume (cm$^3$·g$^{-1}$) | Vmicro/Vtotal (%) |
|----------|---------------------------------|------------------------|-------------------------------|-------------------|
| 0        | 616.77                          | 2.19                   | 0.43                          | 0.12              |
| 0.08     | 606.35                          | 2.35                   | 0.41                          | 0.08              |
| 0.15     | 545.32                          | 3.58                   | 0.38                          | 0.09              |
| 0.3      | 545.32                          | 3.58                   | 0.38                          | 0.09              |
| 0.5      | 545.32                          | 3.58                   | 0.38                          | 0.09              |
3.5. Gas Permselectivity Analysis

3.5.1. The Influence of $n_{Zr}$

Figure 10 depicts the influence of $n_{Zr}$ on the gas permeabilities and $H_2$ permselectivities of ZrO$_2$-MSiO$_2$ membranes with varying $n_{Zr}$ and 0% DCCA addition at 25 °C and 0.1 MPa. In Figure 10a, with the increase of $n_{Zr}$, the $H_2$, $CO_2$, and $N_2$ permeances of the samples increased until $n_{Zr} = 0.15$, and then decreased. Compared with the MSiO$_2$ membranes ($n_{Zr} = 0$), the $H_2$, $CO_2$, and $N_2$ permeance of the ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.15$ increased by 50.95%, 26.74%, and 36.36%, respectively. From the pore structure analysis (Table 1), the overall pore volumes of the ZrO$_2$-MSiO$_2$ membranes grew somewhat with increasing $n_{Zr}$ until $n_{Zr} = 0.15$, and then decreased, which can explain why the ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.15$ had the highest permeance to each gas. For the same membrane, the order of gas molecular permeance is $H_2 > CO_2 > N_2$. Gas permeance decreased with increasing $d_h$ (0.289, 0.33, and 0.364 nm, respectively), indicating that all membranes exhibited molecular sieve properties. However, when $n_{Zr} \geq 0.15$, the permeance of $CO_2$ decreased more closely to that of $N_2$. This behavior was related to the fact that following heat treatment at 400 °C, the Zr-O-Si bonds and t-ZrO$_2$ crystallites generated in the ZrO$_2$-SiO$_2$ membranes will generate a significant number of Bronsted acid sites. High acidity leads to a reduction in the affinity of the membranes for $CO_2$, hence lowering the $CO_2$ permeance [44].

It can be observed from Figure 10b that compared with MSiO$_2$ membranes, the $H_2/CO_2$ and $H_2/N_2$ permselectivities of ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.15$ increased by 22.93% and 33.04%, respectively. Combined with the previous characterization test, it was found that the ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.15$ had a good pore structure, which is beneficial to improve the permselectivity of gas. In addition, the acidic sites formed by the ZrO$_2$-MSiO$_2$ membranes reduced the affinity of the membranes for $CO_2$ and helped to separate it from $H_2$. However, the permselectivities of ZrO$_2$-MSiO$_2$ membranes after $n_{Zr} = 0.15$ showed a decreasing trend. Compared with the ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.15$, the $H_2/CO_2$ and $H_2/N_2$ permselectivities of the membranes with $n_{Zr} = 0.5$ decreased by 9.35% and 20.15%, respectively. As a result, just because the $n_{Zr}$ concentration is larger, it does not indicate that the separation effect is better. Since the Zr-O and Si-O

| $n_{Zr}$ | BET Surface Area (m$^2$·g$^{-1}$) | Average Pore Size (nm) | $V_{total}$ (STP) (cm$^3$·g$^{-1}$) | $V_{micro}$ (STP) (cm$^3$·g$^{-1}$) | $V_{micro}/V_{total}$ (%) |
|---------|-----------------|----------------|-------------------|----------------|------------------|
| 0       | 389.38          | 1.75           | 0.23              | 0.15           | 65.22            |
| 0.08    | 579.96          | 2.08           | 0.37              | 0.13           | 35.14            |
| 0.15    | 616.77          | 2.19           | 0.43              | 0.12           | 27.91            |
| 0.3     | 606.35          | 2.35           | 0.41              | 0.09           | 21.95            |
| 0.5     | 545.32          | 3.58           | 0.38              | 0.08           | 21.05            |

Figure 9. Molecular structural models of MSiO$_2$, ZrO$_2$-MSiO$_2$, and t-ZrO$_2$.

Table 1. Pore structure parameters of the ZrO$_2$-MSiO$_2$ materials with various $n_{Zr}$.
bonds in zirconium-substituted siloxane rings are longer than in pure siloxane rings, for the ZrO$_2$-MSiO$_2$ membranes with $n_{Zr} = 0.5$, the number of siloxane rings containing Zr increased, and the pore size of the membranes became larger. Meanwhile, a large number of t-ZrO$_2$ crystals were produced, which led to the shrinkage of the pore structure inside the membranes and the collapse of the pores, resulting in the decrease of the permselectivities of the membranes.

![Graph of permeance vs. $n_{Zr}$](image)

**Figure 10.** (a) Gas permeance and (b) H$_2$ permselectivities of ZrO$_2$-MSiO$_2$ membranes with various $n_{Zr}$ and 0% DCCA addition at a pressure difference of 0.1 MPa and 25 °C.

SEM images of surface topography for MSiO$_2$ and ZrO$_2$-MSiO$_2$ ($n_{Zr} = 0.15$) membranes calcined at 400 °C are shown in Figure 11. Compared to the MSiO$_2$ membranes, the particle size and distribution of the ZrO$_2$-MSiO$_2$ membranes were more uniform, the membranes’ surfaces had no obvious defects, and the surface was uniform and smooth. The particle size of MSiO$_2$ membranes was between 1.1 and 5.8 nm, while the particle size of ZrO$_2$-MSiO$_2$ membranes was between 1.3 and 8.9 nm. The formed ZrO$_2$-MSiO$_2$ membranes with a smooth surface and uniform membrane pores were more conducive to the gas permselectivity.

![SEM images](image)

**Figure 11.** SEM images of surface topography for (a) MSiO$_2$ and (b) ZrO$_2$-MSiO$_2$ ($n_{Zr} = 0.15$) membranes with 0% DCCA addition calcined at 400 °C.

### 3.5.2. The Influence of Temperature

The permeances and permselectivities of the MSiO$_2$ and ZrO$_2$-MSiO$_2$ ($n_{Zr} = 0.15$) membranes with 0% DCCA addition at a pressure difference of 0.1 MPa and temperature changing from 25 to 200 °C are shown in Figure 12. Obviously, with the increasing temperature, the permeance of H$_2$ of MSiO$_2$ and ZrO$_2$-MSiO$_2$ membranes increased gradually, as seen in Figure 12a. From 25 to 200 °C, the H$_2$ permeance of MSiO$_2$ and ZrO$_2$-MSiO$_2$ membranes rose by 19.66% and 7.12%, respectively, demonstrating that the H$_2$ permeation
behavior in the two membranes followed the activated diffusion transport mechanism. In contrast, the permeabilities of CO$_2$ and N$_2$ were similar to the Knudsen diffusion trend, whereby both slightly decreased. The CO$_2$ permeance of MSiO$_2$ and ZrO$_2$-MSiO$_2$ membranes decreased by 31.46% and 30.20% from 25 to 200 °C, respectively, and the N$_2$ permeance decreased by 18.60% and 29.98%, respectively. The major explanations for the decrease in CO$_2$ and N$_2$ permeance were the violent movement of molecules and the rise in the mean free path as temperature increased.

![Figure 12](image-url)

**Figure 12.** Influence of temperature on the (a) gas permeances and (b) H$_2$ permselectivities of MSiO$_2$ and ZrO$_2$-MSiO$_2$ (n$_{Zr}$ = 0.15) membranes with 0% DCCA addition at a pressure difference of 0.1 MPa.

In Figure 12b, it can be seen that the permselectivities in the membranes gradually increased with the increase of temperature. At 200 °C, compared with the MSiO$_2$ membranes, the H$_2$/CO$_2$ and H$_2$/N$_2$ permselectivities of the ZrO$_2$-MSiO$_2$ membranes increased by 21.11% and 23.34%, respectively. The above results show that the ZrO$_2$-MSiO$_2$ membranes had better permselectivity and permeance of H$_2$ than the MSiO$_2$ membranes under the same conditions.

Combined with the preceding studies, it was determined that a rise in temperature facilitated the separation of H$_2$ and that the separation process of H$_2$ from CO$_2$ and N$_2$ is dominated by activation diffusion, which is described by the Arrhenius equation [45]:

$$P = P_0 \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (1)

In Formula (1), $P$ is the permeation rate, $E_a$ is the apparent activation energy, and $P_0$ is a constant, which depends on the pore wall–gas molecule interaction, gas selective layer thickness, and pore shape and tortuosity [46]. For linear fitting, 1000/RT was used as the abscissa and lnP as the ordinate, and the slope of the fitting equation might be used to obtain the apparent activation energy. Figure 13 depicts the Arrhenius fitting diagrams for the three gases.

Figure 13 demonstrates that the apparent activation energy of H$_2$ is positive, while that of various other gases is negative. This is related to the gas-activated transport behavior, whereby there are two parallel transmission channels for gas through the membrane: one is through selective micropores, with gas transport processed by a thermally activated surface diffusion mechanism in the micropore state [47], and the other is through larger pores [48]. The activation energies for CO$_2$ and N$_2$ are negative, indicating that there are permeation pathways large enough in these types of membranes to allow the diffusion of these larger gases. It is generally believed that $E_a$ is composed of two parts [46], the adsorption heat, $Q_a$, of gas on the surface of the membrane and the activation energy, $E_m$, of gas flowing through the solid surface. The larger the $E_m$ is, the harder it is for the gas to diffuse, $E_a$.
Arrhenius equation parameter values are shown in Table 2. Table 2 shows that the $E_m$ values of the gases in the ZrO$_2$-MSiO$_2$ membrane are all less than those in the MSiO$_2$ membrane. It shows that the structure of ZrO$_2$-MSiO$_2$ membranes is not as dense as that of MSiO$_2$ membranes. This is in good accordance with the N$_2$ adsorption–desorption results. This finding also shows that ZrO$_2$ doping successfully diminishes the densification of the SiO$_2$ network. The higher porosity of the ZrO$_2$-MSiO$_2$ membranes allows the gas to cross the membrane pore barrier using their kinetic energy. Therefore, the gas (H$_2$, CO$_2$, and N$_2$) permeance of ZrO$_2$-MSiO$_2$ membranes is higher than that of MSiO$_2$ membranes.

![Figure 13](https://example.com/figure13.png)

**Figure 13.** Arrhenius plots of different gases of (a) MSiO$_2$ and (b) ZrO$_2$-MSiO$_2$ ($n_{Zr} = 0.15$) membranes.

| Membrane           | Gases   | $E_a$ (kJ mol$^{-1}$) | $Q_{st}$ (kJ mol$^{-1}$) | $E_m$ (kJ mol$^{-1}$) |
|--------------------|---------|----------------------|--------------------------|----------------------|
| MSiO$_2$           | H$_2$   | 2.32                 | 6.00                     | 8.32                 |
|                    | CO$_2$  | -1.53                | 24.00                    | 22.47                |
|                    | N$_2$   | -1.48                | 18.00                    | 16.52                |
| ZrO$_2$-MSiO$_2$   | CO$_2$  | -1.64                | 24.00                    | 22.36                |
|                    | N$_2$   | -1.94                | 18.00                    | 16.06                |

Table 3 displays the $E_a$ of H$_2$, pore diameter, H$_2$ permeance, and H$_2$ permselectivities for several membranes/films prepared by other researchers. It is challenging to concurrently enhance the membranes’ permselectivity and gas permeability, as seen in Table 3. Generally, the larger the average pore size of the membrane, the higher the permeance to H$_2$, which is accompanied by a smaller $E_a$. Meanwhile, the $E_a$ of H$_2$ is related to the interaction of H$_2$ with the membrane pore wall. It can be seen from Table 3 that the as-prepared ZrO$_2$-MSiO$_2$ membrane has a large H$_2$ permselectivity compared to other membranes.

| Type                   | Temperature/Pressure | $E_a$ of H$_2$ (kJ mol$^{-1}$) | Pore Diameter (nm) | $H_2$ Permeance (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) | H$_2$ Perme selectivities |
|------------------------|----------------------|--------------------------------|--------------------|-----------------------------------------------|--------------------------|
| SiO$_2$ [49]           | 200 °C, 2 bar        | -                              | 0.30-0.54          | 4.62 × 10$^{-7}$                              | 3.7                      | 10.5                     |
| ZIF-7-SiO$_2$ [50]     | 200 °C               | -                              | 5                  | 8 × 10$^{-7}$                                 | 8.78                     | 11.8                     |
| Pd-SiO$_2$ [51]        | 200 °C, 0.3 MPa      | -                              | 0.57               | 7.26 × 10$^{-7}$                              | 4.3                      | 14                       |
| ZrO$_2$ [52]           | 350 °C               | -                              | 4.95               | 5.3 × 10$^{-8}$                               | 14.3                     | 3.1                      |
| ZrO$_2$-SiO$_2$ [27]   | 550 °C               | 7.0                            | 0.165              | 1.8 × 10$^{-7}$                               | -                        | -                        |
| BTDA-DDS polyimide [53]| 30 °C, 5 MPa         | -                              | -                  | 2.52 × 10$^{-9}$                              | 5.16                     | 193.21                   |
| Cellulose acetate [54] | 25 °C, 1 bar         | -                              | -                  | 3.55 × 10$^{-9}$                              | -                        | 30.3                     |
| ZrO$_2$-MSiO$_2$ *     | 200 °C, 0.1 MPa      | 2.10                            | 2.19               | 6.46 × 10$^{-6}$                              | 11.64                    | 13.88                    |

* In this work.
3.5.3. The Influence of Pressure Difference

Figure 14 illustrates the effect of pressure difference on the gas permeances and H₂ permselectivities of MSiO₂ and ZrO₂-MSiO₂ (nZr = 0.15) membranes at 200 °C with 0% DCCA addition. In Figure 14a, it can be observed that the H₂ permeance of the ZrO₂-MSiO₂ membranes with nZr = 0.15 improved with the increase of the pressure difference, and the pressure dependence increased. However, the H₂ permeance of MSiO₂ membranes remained basically unchanged. The MSiO₂ and ZrO₂-MSiO₂ membranes increased their H₂ permeance by 2.16% and 19.96%, respectively, when the pressure was increased from 0.10 to 0.40 MPa. In Figure 14b, the H₂ permselectivities of MSiO₂ membranes did not change significantly, and the H₂/CO₂ and H₂/N₂ permselectivities decreased by 5.27% and 1.12%, respectively. However, the H₂ permselectivities of the ZrO₂-MSiO₂ membranes with nZr = 0.15 changed greatly, where the H₂/CO₂ and H₂/N₂ permselectivities decreased by 22.04% and 21.12%, respectively. Clearly, it can be seen that the permselectivity of the ZrO₂-MSiO₂ membranes was reduced more than that of the MSiO₂ membranes, that is, the pressure had a relatively small effect on the gas permeation of the MSiO₂ membranes. This phenomenon is attributed to the relatively dense MSiO₂ membranes with micropores as the main component. With the increase of the pressure difference between the two sides of the membranes, the power of the gas passing through the ZrO₂-MSiO₂ membranes increased, making it easier for the gas to pass through the mesopores or even the macropores, which has a greater impact on the permeability of the membranes. At the same time, it is shown that the H₂ diffusion mechanism of ZrO₂-MSiO₂ membranes was different from that of MSiO₂ membranes due to the influence of doping ZrO₂. The gas transport in the ZrO₂-MSiO₂ membranes follows the surface diffusion mechanism. In addition, when the pressure difference increased to 0.4 MPa, the permselectivities of H₂/CO₂ and H₂/N₂ were still higher than their respective Knudsen diffusion (4.69 and 3.74, respectively), indicating that they still have good gas permeation performance under high pressure.

Figure 14. Influence of pressure difference on the (a) gas permeances and (b) H₂ permselectivities of MSiO₂ and ZrO₂-MSiO₂ (nZr = 0.15) membranes with 0% DCCA addition at 200 °C.

3.5.4. The Influence of the DCCA

Comparing and analyzing the previous results, it was found that the addition of DCCA (glycerol) by the sol-gel method can effectively reduce the uneven shrinkage of the membrane when it is heated during firing. The gas permeances and H₂ permselectivities of ZrO₂-MSiO₂ membranes (nZr = 0.15) with various DCCA additions at 200 °C and 0.1 MPa are shown in Figure 15.
Figure 15. H\textsubscript{2} permeances and permselectivities of ZrO\textsubscript{2}-MSiO\textsubscript{2} membranes (n\textsubscript{Zr} = 0.15) with various DCCA additions at 200 °C and 0.1 MPa.

Figure 15 demonstrates that the H\textsubscript{2} permeance of the ZrO\textsubscript{2}-MSiO\textsubscript{2} membranes reduced by 21.30% as the DCCA addition increased from 0 to 30%. The permselectivities of H\textsubscript{2}/CO\textsubscript{2} and H\textsubscript{2}/N\textsubscript{2} increased by 21.77% and 14.07%, respectively. However, compared with the 20% membranes, the H\textsubscript{2}/CO\textsubscript{2} and H\textsubscript{2}/N\textsubscript{2} permselectivities of the membranes with the addition of 30% only increased by 2.14% and 0.28%, respectively. Figure 16 shows the relationship between DCCA (GL) contents and F\textsubscript{H2} × α\textsubscript{H2} (F\textsubscript{H2} is the H\textsubscript{2} permeance, α\textsubscript{H2} is the permselective of H\textsubscript{2}). It was clearly observed that the addition of DCCA from 0 to 20% enhanced the F\textsubscript{H2} × α\textsubscript{H2} value, and after more than 20%, the F\textsubscript{H2} × α\textsubscript{H2} value showed a lower level. This is attributed to the fact that the addition of glycerol will gradually surround the sol particles, reduce the agglomeration caused by the collision of the colloid particles, accelerate the creation of the sol-gel network, and improve the stability of the sol structure [52]. In addition, the membrane layer collapsed and cracked easily during the drying and calcination processes, and the addition of glycerol can effectively reduce the liquid–gas surface tension to a certain extent, thereby protecting the gel skeleton from deformation [55]. However, the particles of the sol were surrounded by steric effects when too much GL was added, making the sol sticky and difficult to dry to form a membrane. The extension of the drying time makes the cross-linking of the sol more thorough and eventually leads to the densification of the membrane, which is not conducive to gas separation. From the above point of view, the membranes with 20% DCCA addition were the more worthy choice.
3.5.5. Steam Treatment and Regeneration Analysis

Figure 17 shows the effects of steam treatment and thermal regeneration on the gas permeances (H₂, CO₂, and N₂) and H₂ permselectivities of MSiO₂ and ZrO₂-MSiO₂ (n_{Zr} = 0.15) membranes with 0% DCCA addition at a pressure difference of 0.1 MPa and 25 °C. The permeances of H₂, CO₂, and N₂ for MSiO₂ and ZrO₂-MSiO₂ membranes appear to have reduced after steam treatment. After steam aging for 7 days, the permeance of H₂ for MSiO₂ and ZrO₂-MSiO₂ membranes dropped by 20.63% and 3.70%, respectively, as compared to untreated fresh samples, and the permselectivities of H₂/CO₂ and H₂/N₂ for MSiO₂ membranes decreased by 1.59% and 1.04%, respectively, whereas those of ZrO₂-MSiO₂ membranes increased by 0.09% and 0.43%, respectively.

The gas permeances (H₂, CO₂, and N₂), as well as the permselectivities of H₂/CO₂ and H₂/N₂ for two membranes, all exhibit an increased trend after regeneration by calcination at 350 °C. However, as compared to untreated fresh samples, the H₂ permeances of MSiO₂ and ZrO₂-MSiO₂ membranes after regeneration dropped by 9.96% and 1.65%, respectively, whereas the permselectivities of H₂/CO₂ and H₂/N₂ for MSiO₂ membranes improved by 1.12% and 4.71%, respectively, and those for ZrO₂-MSiO₂ membranes increased by 0.08% and 1.21%, respectively. The decrease in gas permeances in both membranes suggests that membrane pore shrinking occurs after calcination at 350 °C. Lower permeance and greater permselectivities are produced as a result of the smaller pores. This is attributed to the partial Zr atoms replacing the Si atoms in Si-O-Si to form more stable Zr-O-Si bonds, which further improves the hydrothermal stability of the membrane material. Therefore, the above results indicated that the ZrO₂-MSiO₂ membranes had a better hydrothermal stability and reproducibility than MSiO₂ membranes.

4. Conclusions

The ZrO₂-MSiO₂ membranes were manufactured to enhance the steam stability and H₂ permselectivity of SiO₂ membranes. It was found that with the increase of ZrO₂ content, the pore size distribution of the materials became wider and the average pore size increased, indicating that the doping of ZrO₂ had the effect of expanding the pores. The ZrO₂-MSiO₂ membranes with n_{Zr} = 0.15 had a good pore structure and suitable micropore/mesoporous ratio, which is beneficial to improve the permeance of natural gas. At 200 °C, the H₂/CO₂ and H₂/N₂ permselectivities of ZrO₂-MSiO₂ membranes were 79.18% and 26.75% greater than those of MSiO₂ membranes, respectively. Furthermore, when the pressure was increased to 0.4 MPa, the permselectivities were still higher than their respective Knudsen...
diffusion, indicating that they still had good gas permeance at high pressure. With the addition of DCCA from 20% to 30%, the $\text{H}_2/\text{CO}_2$ and $\text{H}_2/N_2$ permselectivities of $\text{ZrO}_2$-$\text{MSiO}_2$ membranes only increased by 2.14% and 0.28%, respectively, and the $P_{\text{H}_2} \alpha_{\text{H}_2}$ value with 20% addition was the highest. In conclusion, it is worthwhile to choose 20% GL as the DCCA addition for $\text{ZrO}_2$-$\text{MSiO}_2$ membranes. Compared with the untreated fresh sample, after 7 days of water vapor aging, the permeance of $\text{ZrO}_2$-$\text{MSiO}_2$ membranes to $\text{H}_2$ decreased by only 3.70%, and the permselectivities of $\text{H}_2/\text{CO}_2$ and $\text{H}_2/N_2$ increased by only 0.09% and 0.43%, respectively. After regeneration at 350 °C, the $\text{H}_2$ permeance of the $\text{ZrO}_2$-$\text{MSiO}_2$ membranes decreased by 1.65%, and the permselectivities of $\text{H}_2/\text{CO}_2$ and $\text{H}_2/N_2$ increased by 0.08% and 1.21%. It is enough to show that the prepared $\text{ZrO}_2$-$\text{MSiO}_2$ membranes had a good hydrothermal stability and certain regeneration performance. In the future, the influence of high temperature (for example, ≥300 °C) and mixed gases on the gas permeances and permselectivities of $\text{ZrO}_2$-$\text{MSiO}_2$ membranes should be explored, which is important to the practical engineering applications.

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**References**

1. Nazir, H.; Louis, C.; Jose, S.; Prakash, J.; Muthuswamy, N.; Buan, M.E.; Flox, C.; Chavan, S.; Shi, X.; Kauranen, P.; et al. Is the $\text{H}_2$ economy realizable in the foreseeable future? Part I: $\text{H}_2$ production methods. *Int. J. Hydrogen Energy* 2020, 45, 13777–13788. [CrossRef]

2. Nordio, M.; Wassie, S.A.; Van Sint Annaland, M.; Tanaka, D.A.P.; Sole, J.L.V.; Gallucci, F. Techno-economic evaluation on a hybrid technology for low hydrogen concentration separation and purification from natural gas grid. *Int. J. Hydrogen Energy* 2020, 46, 23417–23435. [CrossRef]

3. Cai, L.; Cao, Z.; Zhu, X.; Yang, W. Improved hydrogen separation performance of asymmetric oxygen transport membranes by grooving in the porous support layer. *Green Chem. Eng.* 2020, 2, 96–103. [CrossRef]

4. Lv, B.; Luo, Z.; Deng, X.; Chen, J.; Fang, C.; Zhu, X. Study on dry separation technology of a continuous gas-solid separation fluidized bed with a moving scraper (H)-Separation performance. *Powder Technol.* 2021, 377, 565–574. [CrossRef]

5. Koutsonikolas, D.E.; Pantoleontos, G.; Karagiannakis, G.; Konstandopoulos, A.G. Development of $\text{H}_2$ selective silica membranes: Performance evaluation through single gas permeation and gas separation tests. *Sep. Purif. Technol.* 2021, 264, 118432. [CrossRef]

6. Wu, R.; Yue, W.; Li, Y.; Huang, A. Ultra-thin and high hydrogen permeable carbon molecular sieve membrane prepared by using polydopamine as carbon precursor. *Mater. Lett.* 2021, 295, 129863. [CrossRef]

7. Singla, S.; Shetti, N.P.; Basu, S.; Mondal, K.; Aminabhavi, T.M. Hydrogen production technologies—Membrane based separation, storage and challenges. *J. Environ. Manag.* 2022, 302, 113963. [CrossRef]

8. Yan, E.; Huang, H.; Sun, S.; Zou, Y.; Chu, H.; Sun, L. Development of Nb-Ti-Co alloy for high-performance hydrogen separating membrane. *J. Membr. Sci.* 2018, 565, 411–424. [CrossRef]

9. Farina, L.; Santucci, A.; Tosti, S. Plasma Enhancement Gases separation via ceramic porous membranes for plasma exhaust processing system of DEMO. *Fusion Eng. Des.* 2021, 169, 112484. [CrossRef]

10. Zhang, D.; Zhang, X.; Zhou, Y.; Song, Y.; Jiang, Y.; Lin, B. Phase stability and hydrogen permeation performance of $\text{BaCo}_0.4\text{Fe}_0.4\text{Zr}_0.1\text{Y}_0.1\text{O}_3$-5 ceramic membranes. *Ceram. Int.* 2021, 48, 9946–9954. [CrossRef]

11. Bakoglidis, K.D.; Palisaitis, J.; Dos Santos, R.B.; Rivelino, R.; Persson, P.O.; Gueorguieva, G.K.; Hultman, L. Self-Healing in Carbon Nitride Evidenced As Material Inflation and Superlubric Behavior. *ACS Appl. Mater. Interfaces* 2018, 10, 16238–16243. [CrossRef]

12. Kakanakova-Georgieva, A.; Gueorguieva, G.; Sangiovanni, D.G.; Suwannaharn, N.; Ivanov, I.G.; Cora, I.; Pécz, B.; Nicotra, G.; Giannazzo, F. Nanoscale phenomena ruling deposition and intercalation of AlN at the graphene/SiC interface. *Nanoscale* 2020, 12, 19470–19476. [CrossRef] [PubMed]
13. Thirumal, V.; Yuvarkkumar, R.; Kumar, P.S.; Ravi, G.; Keerthana, S.P.; Velauthapillai, D. Facile single-step synthesis of [email-protected] hybrid nanocomposite by CVD method to remove hazardous pollutants. Chemosphere 2021, 286, 131733. [CrossRef] [PubMed]

14. Kanzezashi, M.; Asaeda, M. Hydrogen permeation characteristics and stability of Ni-doped silica membranes in steam at high temperature. J. Membr. Sci. 2006, 271, 86–93. [CrossRef]

15. Rosli, A.; Ahmad, A.L.; Low, S.C. Anti-wetting polyvinylidene fluoride membrane incorporated with hydrophobic polyethylene-functionalized-silica to improve CO₂ removal in membrane gas absorption. Sep. Purif. Technol. 2019, 221, 275–285. [CrossRef]

16. Yang, J.; Chen, J. Hydrophobic modification and silver doping of silica membranes for H₂/CO₂ separation. J. CO2 Util. 2013, 3–4, 21–29. [CrossRef]

17. Wei, Q.; Ding, Y.L.; Nie, Z.R.; Liu, X.G.; Li, Q.Y. Wettability, pore structure and performance of perfluorodecyl-modified silica membranes. J. Membr. Sci. 2014, 466, 114–122. [CrossRef]

18. Mukherjee, D.; Kar, S.; Mandal, A.; Ghosh, S.; Majumdar, S. Immobilization of tannery industrial sludge in ceramic membrane preparation and hydrophobic surface modification for application in atrazine remediation from water. J. Eur. Ceram. Soc. 2019, 39, 3235–3246. [CrossRef]

19. Karimiab, S.; Mortazavia, Y.; Khodadadia, A.A.; Holmgrenb, A.; Korelskiyc, D.; Hedlund, J. Functionalization of silica membranes. Sep. Purif. Technol. 2020, 235, 116207. [CrossRef]

20. Khan, A.A.; Maitlo, H.A.; Khan, I.A.; Lim, D.; Zhang, M.; Kim, K.-H.; Lee, J.; Kim, J.-O. Metal oxide and carbon nanomaterial based membranes for reverse osmosis and membrane distillation: A comparative review. Environ. Res. 2021, 202, 117176. [CrossRef]

21. Kurt, T.; Topuz, B. Sol-gel Control on Mixed Network Silica Membranes for Gas Separation. Sep. Purif. Technol. 2020, 255, 117654. [CrossRef]

22. Zhang, Y.; Huang, B.; Mardkhe, M.K.; Woodfield, B.F. Thermal and hydrothermal stability of pure and silica-doped mesoporous aluminas. Microporous Mesoporous Mater. 2019, 284, 60–68. [CrossRef]

23. Gu, Y.; Hacarlioglu, P.; Oyama, S.T. Hydrothermally stable silica-alumina composite membranes for hydrogen separation. J. Membr. Sci. 2008, 310, 28–37. [CrossRef]

24. Teo, H.T.; Siah, W.R.; Yuliati, L. Enhanced adsorption of acetylsalicylic acid over hydrothermally synthesized iron oxide-mesoporous silica MCM-41 composites. J. Chem. Eng. Jpn. 2016, 65, 591–598. [CrossRef]

25. Uhlmann, D.; Smart, S.; da Costa, J.C.D. H₂S stability and separation performance of cobalt oxide silica membranes. J. Membr. Sci. 2011, 380, 48–54. [CrossRef]

26. 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]

27. Yoshida, K.; Hirano, Y.; Fuji, H.; Tsuru, T.; Asaeda, M. Hydrothermal stability of silica magnetron sputtered films on hydrographite for hydrogen separation in hydrothermal conditions. J. Chem. Eng. Jpn. 2001, 34, 523–530. [CrossRef]

28. Diez, B.; Roldán, N.; Martin, A.; Sotto, A.; Perdigón-Melón, J.; Arsuaga, J.; Rosal, R. Fouling and biofouling resistance of metal-doped mesostructured silica/polyethersulfone ultrafiltration membranes. J. Membr. Sci. 2017, 526, 252–263. [CrossRef]

29. Wang, L.; Yang, J.; Mu, R.; Guo, Y.; Hou, H. Sol-Gel Processed Cobalt-Doped Methylated Silica Membranes Calcined under N₂ Atmosphere: Microstructure and Hydrogen Perm-Selectivity. Materials 2021, 14, 4188. [CrossRef]

30. Li, L.; Hong, Q. Gas separation using sol-gel derived microporous zirconia membranes with high hydrothermal stability. Chin. J. Chem. Eng. 2015, 23, 1300–1306. [CrossRef]

31. Gu, Y.; Kusakabe, K.; Morooka, S. Sulfuric acid-modified zirconia membrane for use in hydrogen separation. Sep. Purif. Technol. 2001, 24, 489–495. [CrossRef]

32. Van Gestel, T.; Velterop, F.; Meulenber, W.A. Zirconia-supported hybrid organosilica microporous membranes for CO₂ separation and pervaporation. Sep. Purif. Technol. 2007, 59, 243–250. [CrossRef]

33. Diez, B.; Roldán, N.; Martin, A.; Sotto, A.; Perdigón-Melón, J.; Arsuaga, J.; Rosal, R. Fouling and biofouling resistance of metal-doped mesostructured silica/polyethersulfone ultrafiltration membranes. J. Membr. Sci. 2017, 526, 252–263. [CrossRef]

34. Wang, L.; Yang, J.; Mu, R.; Guo, Y.; Hou, H. Sol-Gel Processed Cobalt-Doped Methylated Silica Membranes Calcined under N₂ Atmosphere: Microstructure and Hydrogen Perm-Selectivity. Materials 2021, 14, 4188. [CrossRef]

35. Li, L.; Hong, Q. Gas separation using sol-gel derived microporous zirconia membranes with high hydrothermal stability. Chin. J. Chem. Eng. 2015, 23, 1300–1306. [CrossRef]

36. Gu, Y.; Kusakabe, K.; Morooka, S. Sulfuric acid-modified zirconia membrane for use in hydrogen separation. Sep. Purif. Technol. 2001, 24, 489–495. [CrossRef]

37. Van Gestel, T.; Velterop, F.; Meulenber, W.A. Zirconia-supported hybrid organosilica microporous membranes for CO₂ separation and pervaporation. Sep. Purif. Technol. 2007, 59, 243–250. [CrossRef]

38. Diez, B.; Roldán, N.; Martin, A.; Sotto, A.; Perdigón-Melón, J.; Arsuaga, J.; Rosal, R. Fouling and biofouling resistance of metal-doped mesostructured silica/polyethersulfone ultrafiltration membranes. J. Membr. Sci. 2017, 526, 252–263. [CrossRef]

39. Wang, L.; Yang, J.; Mu, R.; Guo, Y.; Hou, H. Sol-Gel Processed Cobalt-Doped Methylated Silica Membranes Calcined under N₂ Atmosphere: Microstructure and Hydrogen Perm-Selectivity. Materials 2021, 14, 4188. [CrossRef]

40. Del Monte, F.; Larsen, W.; Mackenzie, J.D. Chemical Interactions Promoting the ZrO₂ Tetragonal Stabilization in ZrO₂–SiO₂ Binary Oxides. J. Am. Ceram. Soc. 2010, 83, 1506–1512. [CrossRef]
41. Wang, W.; Zhou, J.; Wei, D.; Wan, H.; Zheng, S.; Xu, Z.; Zhu, D. ZrO$_2$-functionalized magnetic mesoporous SiO$_2$ as effective phosphate adsorbent. *J. Colloid Interface Sci.* 2013, 407, 442–449. [CrossRef] [PubMed]

42. Musić, S.; Filipović-Vinceković, N.; Sekovanić, L. Precipitation of amorphous SiO$_2$ particles and their properties. *Braz. J. Chem. Eng.* 2011, 28, 89–94. [CrossRef]

43. Zheng, W.; Bowen, K.H.; Li, J.; Dabkowska, I.; Gutowski, M. Electronic structure differences in ZrO$_2$ vs. HfO$_2$. *J. Phys. Chem. A* 2005, 109, 11521–11525. [CrossRef] [PubMed]

44. Kazunari, K.; Jyunichi, I.; Hideaki, M.; Satoshi, F. Evaluation of hydrogen permeation rate through zirconium pipe. *Nucl. Mater. Energy* 2018, 16, 12–18.

45. Lin, R.B.; Xiang, S.; Xing, H.; Zhou, W.; Chen, B. Exploration of porous metal–organic frameworks for gas separation and purification. *Coord. Chem. Rev.* 2017, 378, 87–103. [CrossRef]

46. Hong, Q.; Chen, H.; Li, L.; Zhu, G.; Xu, N. Effect of Nb content on hydrothermal stability of a novel ethylene-bridged silsesquioxane molecular sieving membrane for H$_2$/CO$_2$ separation. *J. Membr. Sci.* 2012, 5421–5422, 190–200.

47. Boffa, V.; Blank, D.; Elshof, J. Hydrothermal stability of microporous silica and niobia–silica membranes. *J. Membr. Sci.* 2008, 319, 256–263. [CrossRef]

48. Liu, L.; Wang, D.K.; Martens, D.L.; Smart, S.; da Costa, J.C.D. Binary gas mixture and hydrothermal stability investigation of cobalt silica membranes. *J. Membr. Sci.* 2015, 493, 470–477. [CrossRef]

49. Qureshi, H.F.; Nijmeijer, A.; Winnubst, L. Influence of sol–gel process parameters on the micro-structure and performance of hybrid silica membranes. *J. Membr. Sci.* 2013, 446, 19–25. [CrossRef]

50. He, D.; Zhang, H.; Ren, Y.; Qi, H. Fabrication of a novel microporous membrane based on ZIF-7 doped 1,2-bis(triethoxysilyl)ethane for H$_2$/CO$_2$ separation. *Microporous Mesoporous Mater.* 2022, 331, 111674. [CrossRef]

51. Song, H.; Zhao, S.; Lei, J.; Wang, C.; Qi, H. Pd-doped organosilica membrane with enhanced gas permeability and hydrothermal stability for gas separation. *J. Mater. Sci.* 2016, 51, 6275–6286. [CrossRef]

52. Beyler, A.P.; Boye, D.M.; Hoffman, K.R.; Silversmith, A.J. Fluorescence enhancement in rare earth doped sol-gel glass by N,N-dimethylformamide as a drying control chemical additive. *Phys. Procedia* 2011, 13, 4–8. [CrossRef]

53. Garcia, M.G.; Marchese, J.; Ochoa, N.A. Aliphatic-aromatic polyimide blends for H$_2$ separation. *Int. J. Hydrogen Energy* 2010, 35, 8983–8992. [CrossRef]

54. Nikolaeva, D.; Azcune, I.; Tanczyk, M.; Warmuzinski, K.; Jaschik, M.; Sandru, M.; Dahl, P.I.; Genua, A.; Lois, S.; Sheridan, E.; et al. The performance of affordable and stable cellulose-based poly-ionic membranes in CO$_2$/N$_2$ and CO$_2$/CH$_4$ gas separation. *J. Membr. Sci.* 2018, 564, 552–561. [CrossRef]

55. Chen, F.; Ji, Z.; Qi, Q. Effect of liquid surface tension on the filtration performance of coalescing filters. *Sep. Purif. Technol.* 2019, 209, 881–891. [CrossRef]