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Microstructure and Hydrothermal Stability of Microporous Niobia-Silica Membranes: Effect of Niobium Doping Contents

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Abstract: Methyl-modified niobium-doped silica (Nb/SiO₂) materials with various Nb/Si molar ratios (nNb) were fabricated using tetraethoxysilane and methyltriethoxysilane as the silica source and niobium pentachloride as the niobium source by the sol–gel method, and the Nb/SiO₂ membranes were prepared thereof by the dip-coating process under an N₂ calcining atmosphere. Their microstructures were characterized and gas permeances tested. The results showed that the niobium element existed in the formation of the Nb-O groups in the Nb/SiO₂ materials. When the niobium doping content and the calcining temperature were large enough, the Nb₂O₅ crystals could be formed in the SiO₂ frameworks. With the increase of nNb and calcination temperature, the formed particle sizes increased. The doping of Nb could enhance the H₂/CO₂ and H₂/N₂ permselectivities of SiO₂ membranes. When nNb was equal to 0.08, the Nb/SiO₂ membrane achieved a maximal H₂ permeance of 4.83 × 10⁻¹⁰ mol·m⁻²·Pa⁻¹·s⁻¹ and H₂/CO₂ permselectivity of 15.49 at 200 °C and 0.1 MPa, which also exhibited great hydrothermal stability and thermal reproducibility.

Keywords: niobium doping; calcination temperature; Nb/SiO₂ membrane; H₂ permselectivities; hydrothermal stability

1. Introduction

Environmental protection and resource shortage are nowadays issues that need to be faced in the process of world development. The continuous growth of the world’s population has led to the increasing consumption of the earth’s resources. Some experts have suggested hydrogen as an alternative fuel because of its zero pollution. Nowadays, hydrogen is primarily produced from fossil fuels, such as natural gas and coal through steam reforming/gasification and water gas shift reactions [1]. In order to obtain high purity hydrogen from either syngas or the products of the water-gas shift reaction, separation of H₂ from other gases such as CO₂, CO, or CH₄ is necessary. Consequently, hydrogen purification from the above CO₂-containing reaction gas mixture is becoming an important issue. After long-term research and efforts by scientists, a large number of experimental results have shown that the membrane separation technology has shown great potential in gas separation. An inorganic membrane has the advantages of good resistance to high temperature and pressure, high mechanical strength, good chemical stability, long service life, and resistance to halite, which make it attractive in the field of gas separation [2]. In the last two decades, H₂-separation membranes have been developed using various materials, such as palladium and its alloys, silica, alumina, etc. In the research to date, inorganic silica membranes, especially those derived from the sol-gel technique, are some of the best among the various inorganic materials for the separation of hydrogen-containing gas mixtures.

However, in high temperature and humid air, pure SiO₂ membranes showed poor hydrothermal stability. The Si-O-Si bonds were broken and Si-OH bonds were formed when inter-played with water, resulting in the densification of the silica structure [3,4]. Many scientists have carried out a lot of research work to improve the hydrothermal stability of silica...
membrane materials. In recent years, the two primary methods have been the introduction of groups such as F\(^{-}\), Cl\(^{-}\), -C\(_{2}\)H\(_{2n}\) or -C\(_{n}\)H\(_{2n+1}\), phenyl groups, etc. [5,6], and the doping of transition metals such as nickel [7–9], palladium [10,11], zirconium [12], niobium [13], magnesium [14], aluminum [15], cobalt [16,17], etc. Wei et al. [6] prepared a perfluorodecyl-modified silica membrane by the sol-gel method using tetraethyldimethoxosilicate (TEOS) and 1H, 1H, 2H, and 2H-perfluorodecyltriethoxysilane (PFDTES) as precursors. The H\(_{2}\) permeance of the as-prepared membrane was \(9.71 \times 10^{-7}\) mol m\(^{-2}\)s\(^{-1}\)Pa\(^{-1}\), and the H\(_{2}\)/CO\(_{2}\) permselectivity and binary gas separation factor were 7.19 and 12.11, respectively. Under humid conditions with a temperature of 250 °C and a water vapor molar ratio of 5%, the single H\(_{2}\) permeance and H\(_{2}\)/CO\(_{2}\) permselectivity remained almost constant for at least 200 h.

Among the transition metals, niobium doping has caught researchers’ eyes. Boffa et al. [18] prepared niobia-silica membranes using tetraethyl orthosilicate (TEOS) as the Si source and niobium pentoxide (n-butoxide) as the Nb source. Their research results showed that the hydrothermal stability of the microporous niobia-silica membranes was better than that of the pure SiO\(_{2}\) membrane because the incorporation of Nb ions into the silica matrix. Qi et al. [13] prepared a novel microporous hybrid silica membrane using 1,2-bis (triethoxysilyl) ethane (BTESE) and niobium penta (n-butoxide) as precursors for the permselectivity of CO\(_{2}\). The result showed that the permselectivity of H\(_{2}\)/CO\(_{2}\) for the Nb-BTESE membrane could be tuned by altering the calcination temperature. Lin et al. [19] investigated the influence of the sol particle size on the gas permselectivity of the niobium-doped hybrid silica membrane. The prepared Nb/SiO\(_{2}\) membrane had an H\(_{2}\) permeability of \(8.36 \times 10^{-8}\) mol m\(^{-2}\)s\(^{-1}\)Pa\(^{-1}\) with a mean particle size of 5 nm. However, there have been few studies focusing on the effects of niobium doping content on the microstructures and gas permeances of niobium-doped SiO\(_{2}\) membranes.

In this work, we prepared a kind of new niobium-doped SiO\(_{2}\) membrane using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as the Si sources and niobium pentachloride (NbCl\(_{5}\)) as the niobium source. Nb/SiO\(_{2}\) membranes with different Nb/Si molar ratios (n\(_{\text{Nb}}\)) were prepared. The effects of n\(_{\text{Nb}}\) and calcination temperature on the microstructures of Nb/SiO\(_{2}\) materials were studied in detail. Characterization and results were attained by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photo electron spectroscopy (XPS), N\(_{2}\) adsorption/desorption measurements, and scanning electron microscopy (SEM). The gas permeation tests and hydrothermal stability of the Nb/SiO\(_{2}\) membranes were performed and are discussed.

2. Experimental

2.1. Fabrication of Nb/SiO\(_{2}\) Sols

The Nb/SiO\(_{2}\) sols were prepared using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as the silica sources, niobium pentachloride (NbCl\(_{5}\)) as the niobium source, absolute ethanol (EtOH) as the solvent, and HCl as the catalyst. High purity solid NbCl\(_{5}\) powder was dissolved in absolute ethanol to obtain a 0.43 M NbCl\(_{5}\) solution. This process was carried out in a fume hood, stirred and stirring with a glass rod until the HCl gas was released. The reaction equation is as follows:

\[
\text{NbCl}_5 (s) + n\text{C}_2\text{H}_5\text{OH} (l) \rightarrow \text{NbCl}_5\cdot n(\text{OC}_2\text{H}_5)_n (l) + n\text{HCl} (g)
\]

According to the mol ratio of TEOS:MTES:EtOH:H\(_{2}\)O:HCl:NbCl\(_{5}\) = 1:0.8:16:7:0.085:n\(_{\text{Nb}}\), the EtOH, TEOS, and MTES were first mixed with the solution of NbCl\(_{5}\) solution in an ice bath and stirred magnetically for 40 min. After that, a mixture of HCl and water was carefully added drop-wise and then refluxed in a water bath at 60 °C for 3 h. In this way, the Nb-doped SiO\(_{2}\) sols were obtained. The n\(_{\text{Nb}}\) is the molar ratio of Nb/TEOS, which was 0, 0.08, 0.2, and 1, respectively. The Nb-doped SiO\(_{2}\) sol with n\(_{\text{Nb}}\) = 0 is also referred to as the SiO\(_{2}\) sol. The Nb-doped SiO\(_{2}\) sols were diluted three times using absolute ethanol to obtain the final Nb/SiO\(_{2}\) sols.
2.2. Fabrication of Nb/SiO2 Materials
The as-prepared Nb/SiO2 sols were dried in a vacuum oven to prepare the dry gels. The obtained dry gels were then ground into fine powders and calcined under N2 atmosphere in a temperature-controlled tubular furnace at various temperatures (200 °C, 400 °C, 600 °C, 800 °C) for 2 h with a ramping rate of 0.5 °C·min\(^{-1}\). The final niobium-doped silica (Nd/SiO\(_2\)) materials were produced. The Nb/SiO\(_2\) materials with \(n_{\text{Nb}} = 0\) were also referred to as the SiO\(_2\) materials.

2.3. Fabrication of Nb/SiO2 Membranes
To obtain the Nb/SiO2 membranes, part of the above Nb/SiO2 sols were applied to the surface of porous \(\alpha\)-Al\(_2\)O\(_3\) composite discs (Hefei Shijie Membrane Engineering Co., Ltd., Hefei, China) by the dip-coating method. The discs each had a thickness of 4 mm, a diameter of 30 mm, a mean pore diameter of 100 nm, and a porosity of 40%. The dipping time was 6 s. Four-layer Nb/SiO\(_2\) membranes were prepared, and each Nb/SiO\(_2\) layer was individually calcined under N\(_2\) atmospheres in a temperature-controlled furnace to 400 °C at a ramping rate of 0.5 °C·min\(^{-1}\) and with a dwell time of 2 h. The prepared Nb/SiO\(_2\) membranes were used to test the permeances of H\(_2\), CO\(_2\), and N\(_2\); the preparation process is shown in Figure 1.

![Figure 1. Schematic diagram of the fabrication of Nb/SiO\(_2\) membranes by the sol-gel process.](image)

2.4. Steam-Treatment and Regeneration of Nb/SiO2 Membranes
The steam stability of the membranes was tested by exposure to saturated steam at 25 °C for 10 d. The thermal regeneration of Nb/SiO\(_2\) membranes after steam treatment was carried out at a calcination temperature of 350 °C by the same calcining procedure as described above. After the steam-treatment and regeneration, the gas permeances of Nb/SiO\(_2\) membranes were tested, respectively.

2.5. Characterization
The sol densities were determined using a pycnometer. The solid contents of sols were determined by the weighing method. The particle size distributions of Nb/SiO\(_2\) sols were measured using a Malvern Nano ZS size analysis instrument (Malvern Instruments Ltd., Malvern, UK). The functional groups of samples were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, Thermo Nicolet Corporation, Fitchburg, WI, USA), and the wavelength measurement range was 400–4000 cm\(^{-1}\) as determined by the KBr compression method. The material phase structure was determined by a Rigaku D/max-
1.0, the mean particle size of Nb/SiO$_2$ were narrow, and their mean particle sizes were small. However, when $n_{Nb}$ increased, the mean size decreased, while the density and solid content increased. As seen in Figure 3, with the increase of $n_{Nb}$, the sol pH value decreased when two gases. The steam stability of the membranes was tested by exposure to saturated steam at 25 °C for 10 d. The thermal regeneration of Nb/SiO$_2$ membranes after steam stability testing was carried out at a calcination temperature of 350 °C by the same calcining procedure as described above. It should also be noted that permeate gas flow was only recorded after a steady state was attained. The gas permeation measurement was performed at 25 to 200 °C in a stainless-steel module with a cylindrical geometry and placed inside the furnace in the gas permeation measurement rig. The membranes were tested using single gases with different kinetic diameters (H$_2$, CO$_2$, and N$_2$), and permeance was measured by using a soap film flow meter. The gas permselectivities, also known as ideal selectivities, were calculated by the permeance ratio between two gases. The steam stability of the membranes was tested by exposure to saturated steam at 25 °C for 10 d. The thermal regeneration of Nb/SiO$_2$ membranes after steam stability testing was carried out at a calcination temperature of 350 °C by the same calcining procedure as described above. It should also be noted that permeate gas flow was only recorded after a steady state was attained.

![Figure 2. Schematic diagram of the experimental setup.](image)

3. Results and Discussion

3.1. Analysis of Nb/SiO$_2$ Sol Performance

The influence of $n_{Nb}$ on the pH value, density, and solid content of Nb/SiO$_2$ sol is shown in Table 1. The particle size distributions of Nb/SiO$_2$ sols with various $n_{Nb}$ are depicted in Figure 3. As seen in Table 1, with increasing $n_{Nb}$, the sol pH value decreased while the density and solid content increased. As seen in Figure 3, with the increase of $n_{Nb}$, the mean particle sizes of Nb/SiO$_2$ sols increased, and their particle size distributions became wider. The particle size distributions of Nb/SiO$_2$ sols with $n_{Nb}$ = 0, 0.08, and 0.2 were narrow, and their mean particle sizes were small. However, when $n_{Nb}$ was increased to 1.0, the mean particle size of Nb/SiO$_2$ sol increased greatly. In the experiment, the prepared

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2550 pc X-ray diffractometer (XRD, Rigaku D/max-2550, Hitachi, Tokyo, Japan) with CuK$_\alpha$ radiation under the conditions of 40 kV and 40 mA. The chemical components of Nb/SiO$_2$ samples were performed by an X-ray photoelectron spectrometer (XPS, ESCALAB250xi, Thermo Scientific, Waltham, MA, USA) with AlK$_\alpha$ excitation. The morphologies of surfaces and cross-sections for the membranes were observed by scanning electron microscopy (SEM, JEOL JSM-6300, Hitachi, Tokyo, Japan) under 5 kV acceleration voltage. Before the SEM tests, the samples were treated with gold spraying. The BET surface area and pore volume of the samples were measured by N$_2$ sorption/desorption isotherms with a specific surface area and pore and pore-size analyzer (ASAP 2020, Micromeritics, Norcross, GA, USA).

Single gas permeances of Nb/SiO$_2$ membranes were measured under a transmembrane pressure of 0.1-0.4 MPa using the schematic diagram of the experimental setup shown in Figure 2. Prior to the gas permeation measurement, the membranes were mounted in a stainless-steel module with a cylindrical geometry and placed inside the furnace in the gas permeation measurement rig at a temperature range of 25 to 200 °C. The membranes were tested using single gases with different kinetic diameters (H$_2$, CO$_2$, and N$_2$), and permeance was measured by using a soap film flow meter. The gas permselectivities, also known as ideal selectivities, were calculated by the permeance ratio between two gases.
The influence of $n_{\text{Nb}}$ in Nb/SiO$_2$ sol made the acidity of the sol increase, which sped up the hydrolysis–polycondensation reaction. As a result, the sol density, solid content, and particle size increased. On the other hand, with the occurrence of the hydrolysis-polycondensation reaction, Nb-O-Si bonds were formed gradually. The radius of the niobium atom (2.08 Å) is larger than that of the Si atom (1.46 Å), and the bond length of Nb-O is longer than that of Si-O (the bond lengths of Nb-O and Si-O are about 2.13 and 1.64 Å, respectively), which contributed to the increase of sol particles.

### Table 1. The influence of $n_{\text{Nb}}$ on the pH value, density, and solid content of Nb/SiO$_2$ sol.

| $n_{\text{Nb}}$ | pH     | Density/g cm$^{-3}$ | Solid Content/% |
|-----------------|--------|--------------------|-----------------|
| 0               | 3.41 ± 0.04 | 0.8418 ± 0.0007   | 22.31 ± 0.04   |
| 0.08            | 2.93 ± 0.03 | 0.8529 ± 0.0006   | 22.58 ± 0.05   |
| 0.2             | 2.64 ± 0.02 | 0.8710 ± 0.0008   | 22.80 ± 0.06   |
| 1               | 1.02 ± 0.02 | 0.9130 ± 0.0006   | 24.46 ± 0.07   |

\[ n_{\text{Nb}} = 0 \]
\[ n_{\text{Nb}} = 0.08 \]
\[ n_{\text{Nb}} = 0.2 \]
\[ n_{\text{Nb}} = 1.0 \]

Figure 3. The particle size distributions of Nb/SiO$_2$ sols with various $n_{\text{Nb}}$.

### 3.2. Chemical Structure Analysis

The phase-chemical structure of Nb/SiO$_2$ materials may be influenced by the introduced Nb element, so that the effect may have been more evident in the samples containing higher Nb contents. In order to study the effect of calcination temperature on Nb/SiO$_2$ materials, the Nb/SiO$_2$ samples with $n_{\text{Nb}} = 1$ were used for the measurement analysis. Figure 4 shows the FTIR spectra of Nb/SiO$_2$ materials with $n_{\text{Nb}} = 1$ at different calcination temperatures. In Figure 4, the absorption peaks located at 1055 and 788 cm$^{-1}$ were associated with the Si-O-Si bonds. The peaks at 2985 cm$^{-1}$ and 1630 cm$^{-1}$ were assigned to the mode of -CH$_3$ groups and Si-OH bonds, respectively [11]. The band at 1278 cm$^{-1}$ was designated as Si-CH$_3$ groups. The intensity of the absorption peaks at 2985 cm$^{-1}$ and 1278 cm$^{-1}$ decreased obviously with increases in the calcination temperatures and disappeared as the calcination temperature reached 600 °C, indicating that the -CH$_3$ groups had been broken down at this temperature. The absorption peak observed at 619 cm$^{-1}$ corresponded to the Nb-O bonds, which enhanced in intensity with the increase of calcination temperatures.
The FTIR spectra of Nb/SiO$_2$ materials with various n$_{Nb}$ calcined at 400 °C are provided in Figure 5. It can be seen from Figure 5 that the hydrophobic Si-CH$_3$ groups located at 1278 cm$^{-1}$ were all involved in the Nb/SiO$_2$ materials with various n$_{Nb}$. The absorption peak locations of Nb/SiO$_2$ materials with n$_{Nb}$ = 0.08, 0.2, and 1 were roughly the same, but the intensities of individual peaks were different. The peak located at 619 cm$^{-1}$ corresponding to the Nb-O groups did not exist in the pure SiO$_2$ materials. This certified that the Nb had been successfully incorporated into the silica frameworks. At the same time, the peak intensity due to the Nb-O groups became strong continuously with the increase of niobium doping.

3.3. Phase Structure Analysis

The XRD patterns of Nb/SiO$_2$ materials with n$_{Nb}$ = 1 calcined at various temperatures are given in Figure 6. The broad diffraction peak at the range of about 2$\theta$ = 20–30° was assigned to the amorphous SiO$_2$. An obvious crystallization peak of Nb$_2$O$_5$ was detected when the calcination temperature was increased to 600 °C. According to the conclusion from Kosutova, there will be two new crystalline phases formed sequentially when the sample is heated up to 450 °C [20]. The first crystalline phase was identified as hexagonal TT-Nb$_2$O$_5$ (JCPDS No-400-028-0317) [21]. The TT notation comes from the German Tief-Tief
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(low–low), referring to the temperature at which the structure was observed in the sequence of niobium oxides obtained at elevated temperatures, first used in Ref [22]. In Figure 6, the diffraction peaks at 2θ = 22.6°, 28.6°, 36.8°, 46.2°, 50.8°, and 55.2° were assigned to the (001), (180), (201), (002), (380), and (182) crystal planes, respectively, of hexagonal TT-Nb$_2$O$_5$, which indicated the formation of hexagonal TT-Nb$_2$O$_5$ (JCPDS No.00-030-0873). In Figure 6, another phase transition was observed at 800 °C, which was associated with the transition from hexagonal TT-Nb$_2$O$_5$ to orthorhombic T-Nb$_2$O$_5$ (JCPDS No. 404-007-0752) [23]. The transformation caused the splitting of the diffraction peaks [24]. It is evident that a high calcining temperature can improve the crystallinity of Nb$_2$O$_5$ species.

![Figure 6. XRD patterns of Nb/SiO$_2$ materials with n$_{Nb}$ = 1 calcination at various temperatures.](image)

The XRD patterns of the Nb/SiO$_2$ materials with various n$_{Nb}$ calcined at 400 °C are provided in Figure 7. From Figure 7, it can be seen that as the n$_{Nb}$ ≤ 0.2, the XRD curves of the Nb/SiO$_2$ materials were similar, and only the diffraction peak between 20° and 30° corresponding to the amorphous SiO$_2$ could be observed. When the n$_{Nb}$ was increased to 1, a new diffraction peak assigned to the hexagonal TT-Nb$_2$O$_5$ appeared besides for the amorphous SiO$_2$. This means there was no crystalline form of hexagonal TT-Nb$_2$O$_5$ when the Nb-doped content was low. When the niobium doping content and the calcining temperature were large enough, the Nb$_2$O$_5$ crystals could be formed in the SiO$_2$ frameworks.

![Figure 7. XRD patterns of Nb/SiO$_2$ materials doped with various n$_{Nb}$ calcined at 400 °C.](image)
In order to explore the crystal form of niobium, the Nb/SiO₂ materials with \( n_{\text{Nb}} = 1 \) calcined at various temperatures were characterized by XPS, which are shown in Figure 8. In Figure 8, the Nb\(^{TT}\) 3d and Nb\(^{T}\) 3d mean the Nb-O of the hexagonal crystal system TT-Nb\(_2\)O\(_5\) and orthorhombic crystal system T-Nb\(_2\)O\(_5\), respectively. It can be seen that the Nb\(^{TT}\) 3d\(_{5/2}\) peak and the Nb\(^{T}\) 3d\(_{3/2}\) peak appeared at 206.4 eV and 209.1 eV, respectively, in the sample calcined at 400 °C. The data matched with the species of niobium oxide, which proved the formation of Nb\(_2\)O\(_5\) crystals. The temperature related to the formation of the TT-Nb\(_2\)O\(_5\) phase was reported to be approximately 500 °C or higher, according to the studies conducted on nanostructures or thin films [24,25]. Furthermore, the calcination temperature reached 600 °C, and the Nb\(^{T}\) 3d\(_{5/2}\) and Nb\(^{T}\) 3d\(_{3/2}\) peaks also appeared at 209.0 eV and 211.8 eV, respectively, which were the Nb 3d peaks of orthorhombic phase T-Nb\(_2\)O\(_5\). The conclusion was as same as that of XRD analysis.

![Figure 8. The Nb 3d XPS patterns of Nb/SiO₂ materials with \( n_{\text{Nb}} = 1 \) calcined at various temperatures: (a) 400 °C, (b) 600 °C, and (c) 800 °C.](image)

3.4. SEM Analysis

Figure 9 shows the SEM images of Nb/SiO₂ materials with various \( n_{\text{Nb}} \) calcined at various temperatures. From Figure 9a–d, it can be seen that when calcined at 400 °C, the samples had the morphology of nanoparticles with dispersed amorphous structures, and the particle sizes increased with increasing \( n_{\text{Nb}} \).

![Figure 9. SEM image of Nb/SiO₂ materials with various \( n_{\text{Nb}} \) calcinations at various temperatures: (a) \( n_{\text{Nb}} = 0 \), 400 °C; (b) \( n_{\text{Nb}} = 0.08 \), 400 °C; (c) \( n_{\text{Nb}} = 0.2 \), 400 °C; (d) \( n_{\text{Nb}} = 1 \), 400 °C; (e) \( n_{\text{Nb}} = 1 \), 600 °C; (f) \( n_{\text{Nb}} = 1 \), 800 °C.](image)

Comparing Figure 9d with Figure 9e,f, it can be clearly observed that the morphology and particle size of Nb/SiO₂ material with \( n_{\text{Nb}} = 1 \) underwent a large change after being...
calcined at 600 °C, and the materials had a tendency to develop from an amorphous state to a spherical shape. It can be seen from Figure 9f that when the calcination temperature reached 800 °C, the materials exhibited a spherical structure, the particle size increased, and there were more small-sized spherical particles formed around the large particles. In summary, with the increase of calcination temperature and Nb-doping, the particle sizes increased.

Moreover, the SEM images of the pure SiO2 membrane and Nb/SiO2 with nNb = 0.08 calcined at 400 °C are depicted in Figure 10. From Figure 10 it can be observed that there were no visible cracks or pinholes on the membrane surfaces, indicating that the membranes were well coated. It could be seen that niobium doping could make particle sizes increase.

Figure 10. SEM image of Nb/SiO2 membranes with nNb = (a) 0 and (b) 0.08 calcined at 400 °C.

3.5. Pore Structure Analysis

The pore properties of the as-prepared Nb/SiO2 materials were investigated by N2 adsorption/desorption to characterize the surface area, pore volume, and porosity. Figure 11 shows the N2 adsorption/desorption isotherms of Nb/SiO2 materials with various nNb calcined at 400 °C under an N2 atmosphere. After calcining, all isotherms displayed similar tendencies, which were similar to a type I isotherm. It could be proved that the Nb/SiO2 materials all exhibited the adsorption isotherm characteristics of microporous materials. This material was subjected to a strong force due to the gas in the micropores, so it could quickly reach the absorption saturation state.

Figure 11. N2 adsorption-desorption isotherms of Nb/SiO2 materials doped with various nNb calcined at 400 °C.
Figure 12 manifests the pore size distribution of Nb/SiO$_2$ materials with various $n_{Nb}$ calcined at 400 °C. As shown in Figure 12, as $n_{Nb} \leq 0.2$, with the Nb doping, the pore size of Nb/SiO$_2$ materials were widened, and the microporous structure was maintained. When $n_{Nb} = 1$, the Nb/SiO$_2$ material became dense.

The pore structure parameters of Nb/SiO$_2$ materials with various $n_{Nb}$ calcined at 400 °C are shown in Table 2. It can be observed that with the increases of $n_{Nb}$, the mean pore size, BET surface area, and total pore volume increased until $n_{Nb} = 0.08$, and then they began to decrease. This is because the bond length of Nb-O is longer than that of Si-O (the bond lengths of Nb-O and Si-O are about 2.13 and 1.64 Å, respectively). The formation of the Nb-O bond helped the formation of larger particles. Thus, with the increase of the Nb doping amount, the particle size increased, and the formed pore grew gradually. However, when $n_{Nb}$ was >0.08, that changed. Some small hexagonal TT-Nb$_2$O$_5$ particles were formed and distributed in the SiO$_2$ network, which led to a decrease in the mean pore size, BET surface area, and total pore volume.

Table 2. Pore structure parameters of Nb/SiO$_2$ materials with various $n_{Nb}$ calcined at 400 °C.

| $n_{Nb}$ | BET/$m^2 \cdot g^{-1}$ | $V_t$/cm$^3 \cdot g^{-1}$ | $V_{mic}$/cm$^3 \cdot g^{-1}$ | Mean Pore Width/nm |
|----------|------------------------|--------------------------|-----------------------------|-------------------|
| 0        | 386.4545               | 0.1716                   | 0.1115                      | 1.8759            |
| 0.08     | 778.7121               | 0.4901                   | 0.0867                      | 2.4549            |
| 0.2      | 535.4072               | 0.4632                   | 0.0748                      | 2.2591            |
| 1        | 86.1599                | 0.0762                   | 0.0266                      | 1.2176            |

3.6. Gas Permeation and Separation Property Analysis

Based on all the results of the above, the Nb-doping content showed a significant impact on the microstructures of Nb/SiO$_2$ materials. Compared with the Nb/SiO$_2$ membrane with $n_{Nb} = 0.08$ and $n_{Nb} = 0.2$, the pore volume of the Nb/SiO$_2$ membrane with $n_{Nb} = 1$ was too small, which is bad for gas separation. Therefore, the Nb/SiO$_2$ membrane with $n_{Nb} = 1$ was not considered here.

A transient test was conducted on the Nb/SiO$_2$ membranes with various $n_{Nb}$ at 25 °C and a differential pressure of around 0.1 MPa, and the gas permeances and H$_2$ permselectivities are shown in Figure 13. In Figure 13a, the H$_2$ and N$_2$ permeances of Nb/SiO$_2$ membranes with $n_{Nb} = 0.08$ and 0.2 were greater than those of the pure SiO$_2$ membrane, while the change trends of CO$_2$ permeances were the contrary. Compared with the pure SiO$_2$ membrane, the H$_2$ permeances of Nb/SiO$_2$ membranes with $n_{Nb} = 0.08$ and 0.2 in-

Figure 12. Pore size distribution of Nb/SiO$_2$ materials doped with various $n_{Nb}$ calcined at 400 °C.
creased by 39.0% and 8.9%, respectively. In Figure 13b, the permselectivities of H2/CO2 and H2/N2 for the pure SiO2 membrane were greater than the values based on Knudsen diffusion (4.69 and 3.74, respectively), which means the transport in pure SiO2 membrane is controlled by molecular sieving plus Knudsen diffusion. The H2/CO2 and H2/N2 permselectivities for the Nb/SiO2 membranes with nNb = 0.08 and 0.2, respectively, were obviously higher than those of the pure SiO2 membrane. Compared with the pure SiO2 membrane, the H2/CO2 permselectivity for the Nb/SiO2 membranes with nNb = 0.08 and 0.2 increased by 59.5% and 6.3%, respectively. The larger mean pore size and higher pore volume of Nb/SiO2 membranes with nNb = 0.08 and 0.2 than those of the SiO2 membrane can explain the increase of gas permeance. The larger mean pore size of Nb/SiO2 membrane indicated that the increase of H2/CO2 permselectivity was not due to molecular sieving. This suggests that the doping of Nb introduced another transport mechanism. Some researchers have proposed that doping transition metals into the microporous SiO2 network will generate Lewis acids on the surface of the membrane materials and ultimately endow the Nb/SiO2-derived microporous membrane with sufficiently high H2/CO2 permselectivity. The exceptionally low permeance of CO2 is explained as a consequence of strong chemical interactions between CO2 and the materials of the membrane pore surface, presumably Nb-bound hydroxy groups. The results indicate that the H2/CO2 separation was based on sorption rather than on the differences in molecular sizes [26]. In other words, the existence of acid sites on the surface of membranes may play a key role in reducing CO2 permeance. The H2/CO2 and H2/N2 permselectivities of the Nb/SiO2 membrane with nNb = 0.08 obtained the maximum. Furthermore, with the further increase of nNb, although there are still acid sites in the membrane materials, the formed Nb2O5 in the high-content Nb/SiO2 materials agglomerates to form a non-selective interfacial gap, which will lead to the densification of the membrane materials [13]. Thereby the average pore size will become smaller, resulting in the decrease of gas permeances and H2 permselectivities of the Nb/SiO2 membrane.

Figure 14 displays the influence of temperature differences on the gas permeance of the Nb/SiO2 membrane with various nNb at a pressure difference of 0.1 MPa and 25 °C. As shown in Figure 14, the H2 permeance and H2/CO2 permselectivities in the Nb/SiO2 membranes with different nNb revealed an upward trend with increasing temperature when maintaining a constant pressure difference of 0.1 MPa, which indicated that the transport of H2 molecules through the membranes was activated.

The permeance and permselectivity of the Nb/SiO2 membrane with nNb = 0.08 at a pressure difference of 0.1 MPa and temperature change from 25 °C to 200 °C are manifested in Figure 15. It can be clearly seen that H2 permeance was significantly enhanced with increasing temperature, and the other permeances of CO2 and N2 were reduced slightly. The results were the same as the temperature dependency of permeance of several gases in
the NS (Nb/SiO$_2$) membrane from Boffa [27]. Thus, this gives rise to the permselectivity of H$_2$/CO$_2$ and H$_2$/N$_2$ elevating with increasing temperature. With increasing temperatures, the H$_2$ permeance of the Nb/SiO$_2$ membrane increased gradually, which shows that the permeation behavior of H$_2$ in the membranes mainly follows an activation–diffusion mechanism. In the case of activated diffusion, molecules penetrate through the micropore while being subjected to a repulsive force from the pore walls, and the molecules with sufficient kinetic energy to overcome the repulsive force can penetrate the pores [16]. Conversely, the permeance of CO$_2$ and N$_2$ decreased slightly, similar to the trend of Knudsen diffusion, in which molecules collide with the pore walls more regularly than permeating molecules.

![Figure 14](image1.png)

**Figure 14.** Effect of temperature on (a) H$_2$ permeance and (b) H$_2$/CO$_2$ permselectivity of Nb/SiO$_2$ membranes with different n$_{Nb}$ at a pressure difference of 0.1 MPa.

![Figure 15](image2.png)

**Figure 15.** Effect of temperature on (a) gas permeance and (b) H$_2$ permselectivity of Nb/SiO$_2$ membrane with n$_{Nb}$ = 0.08 at a pressure difference of 0.1 MPa.

After the previous discussion, we believe that the permselectivity of Nb/SiO$_2$ membranes has a sorption separation mechanism. High temperature is conducive to the permselectivity of H$_2$, indicating that the permselectivity mechanism of H$_2$ to other gases is mainly dominated by activation diffusion, which follows the Arrhenius equation.

$$F = A_0 \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (1)

In the formula, F means permeance, $A_0$ means former factor, $E_a$ means apparent activation energy, R means the ideal gas constant, T means the temperature, and Equation (1) can be described in another form:

$$\ln F = \ln A_0 - \frac{E_a}{RT} = A - \frac{E_a}{RT}$$  \hspace{1cm} (2)
The 1/T is used as the abscissa and lnF as the ordinate to draw the graph. It can be seen from the above formula that it is a straight line in theory. The apparent activation energy can be calculated from the slope of the straight line. Then the Arrhenius curves of the three gases are shown in Figure 16. Moreover, from the slope of the straight-line fitting in Figure 16, the apparent activation energy of the three gases can be obtained: 

\[ E_a = E_m + Q_{st} \] [28]. The results are shown in Table 4.

![Figure 16. Arrhenius plots of gas (H₂, CO₂, and N₂) permeances in Nb/SiO₂ membrane with n_{Nb} = 0.08 at a pressure difference of 0.1 MPa.](image)

From Table 3, Q_{st} means isosteric heat of adsorption, CO₂ exhibits a greater adsorption heat, and the gas with the lowest adsorption heat is H₂. The apparent activation energy \( E_a \) can be positive or negative, depending on their relative magnitudes. A negative value of \( E_a \) is generally interpreted as being caused by strong sorption of the molecule on the pore surface. Such a negative value suggests a high enthalpy of sorption [26]. The mobility energy \( E_m \) of gas molecules moving on the surface of the Nb/SiO₂ membrane was \( E_m (CO_2) > E_m (N_2) > E_m (H_2) \). The permselectivity of the Nb/SiO₂ membrane towards H₂/CO₂ increased rapidly as a function of temperature. This was probably a result of the high activation energy of the mobility of hydrogen and the high heat of sorption of carbon dioxide. This result has never been reported for pure silica [29–32]. Thus, the strong heat of adsorption should be related to the presence of Nb ions in the microporous framework. Table 4 shows the \( E_a \) value of H₂, H₂ permeance, H₂ permselectivities, and mean pore diameter of silica membranes by the sol–gel method from other researchers. From Table 4, it can be observed that it is difficult to improve the H₂ permeance and permselectivity at the same time. In addition, a higher \( E_a \) always corresponds to a smaller mean pore diameter and lower H₂ permeance. This means that the \( E_a \) value maybe have a link with the mean pore diameter and the interplay between the molecules of H₂ and the pore walls of the membrane. Therefore, compared with other research groups, the Nb-doping in this work may be the reason for the lower \( E_a \) value of H₂.

| Gases  | \( E_a \) [kJ·mol⁻¹] | \( Q_{st} \) [kJ·mol⁻¹] [28] | \( E_m \) [kJ·mol⁻¹] |
|--------|------------------|------------------------|------------------|
| H₂     | 2.53             | 6                      | 8.53             |
| CO₂    | -4.28            | 24                     | 19.72            |
| N₂     | -4.07            | 18                     | 13.93            |
The pressure dependence of various gas permeances and $\text{H}_2/\text{CO}_2$ permselectivities in the pure $\text{SiO}_2$ membrane and $\text{Nb}/\text{SiO}_2$ membrane with various $n_{\text{Nb}}$ at 200 °C were further investigated in the pressure difference range from 0.10 MPa to 0.40 MPa, which is shown in Figure 17. It could be observed that $\text{H}_2$ permeance with various $n_{\text{Nb}}$, increased with the pressure-dependence increase. This is because the pressure difference elevated, and the gas force increased, resulting in an elevation in the gas concentration in the membrane, and then leading to higher $\text{H}_2$ permeance. As seen in Figure 17b, the permselectivity of $\text{H}_2/\text{CO}_2$ changed slightly with increases in the pressure difference.

Figure 18 demonstrates the effect of pressure differences on the permeance and permselectivity of different gases for the $\text{Nb}/\text{SiO}_2$ membrane with $n_{\text{Nb}} = 0.08$ and a temperature at 200 °C. As seen in Figure 18a, as the pressure difference increased from 0.10 to 0.40 MPa, all of the gas permeances increased. The reason is that the increases in intake pressure resulted in an elevation of the gas concentration, thus yielding a higher permeance. Furthermore, the relationship between permselectivity and pressure differences is shown in Figure 18b. For example, with the pressure increasing from 0.10 MPa to 0.40 MPa, the permeance of $\text{N}_2$ and $\text{CO}_2$ slightly increased. This was due to the small influence of pressure on Knudsen diffusion, as previously reported in the literature [30]. Hence, no matter how high the pressure was, the change in permselectivity would not increase significantly.

Traditional $\text{SiO}_2$ membranes have poor hydrothermal stability due to a large amount of Si-OH groups on their surfaces, which easily absorb water vapor in the air. In the $\text{Nb}/\text{SiO}_2$ membrane, not only the Nb-doping but also the introduced hydrophobic groups can improve the vapor stability, which can reduce the hydroxyl groups on the pore surface and enhance the hydrophobicity. In order to test the hydrothermal stability of membranes, the $\text{Nb}/\text{SiO}_2$ membranes with $n_{\text{Nb}} = 0$ and 0.08 were chosen to investigate the gas permeance before and after steam treatment.

Table 4. $E_a$ of $\text{H}_2$, $\text{H}_2$ permeances, $\text{H}_2$ permselectivities, and mean pore diameter for various $\text{SiO}_2$ membranes prepared by other researchers using the sol–gel process.

| Membrane Type | Temperature and Pressure | $E_a$ of $\text{H}_2$ (kJ·mol$^{-1}$) | $\text{H}_2$ Permeance (mol m$^{-2}$·Pa·s$^{-1}$) | $\text{H}_2$ Permeances | Mean Pore Diameter (nm) | Ref. |
|---------------|--------------------------|---------------------------------|----------------------------------|--------------------------|-------------------------|-----|
| $\text{SiO}_2$ | 200 °C, 2 bar             | 8.0                            | $4.62 \times 10^{-7}$            | 7.3                      | 0.30–0.54               | [33]|
| $\text{SiO}_2$(400) | 200 °C, 1 bar             | 8.6                            | $17.4 \times 10^{-7}$            | 7.5                      | 0.38–0.55               | [28]|
| $\text{SiO}_2$(600) | 200 °C, 2 bar             | 7.6                            | $4.03 \times 10^{-7}$            | 66.0                     | 0.36–0.38               | [28]|
| $\text{Pd}/\text{SiO}_2$ | 200 °C, 0.3 MPa           | 2.0                            | $7.26 \times 10^{-7}$            | 4.3                      | 14.0                    | [34]|
| $\text{Co}/\text{SiO}_2$ | 200 °C, 0.2 MPa           | 1.98                           | $1.97 \times 10^{-5}$            | 10.48                    | 13.08                   | [35]|
| $\text{Nb}/\text{SiO}_2$ * | 200 °C, 0.1 MPa           | 2.53                           | $4.83 \times 10^{-6}$            | 15.49                    | 9.54                    | 2.4549|

* In this work.

Figure 17. Effect of pressure difference on (a) $\text{H}_2$ permeance and (b) $\text{H}_2/\text{CO}_2$ permselectivity of $\text{Nb}/\text{SiO}_2$ membranes with different $n_{\text{Nb}}$, at 200 °C.
Figure 18. Effect of pressure difference on (a) gas permeances and (b) H₂ permselectivities of Nb/SiO₂ membrane at 200 °C.

Figure 19 shows the permeances of various gases (H₂, CO₂, and N₂) and H₂ permselectivities of Nb/SiO₂ membranes with n_{Nb} = 0 and 0.08 at 25 °C and a pressure difference of 0.1 MPa before and after steam treatment and regeneration. As shown in Figure 19, compared with the fresh membranes, the H₂ permeances of SiO₂ and Nb/SiO₂ membranes after steam treatment decreased by 17.90% and 6.68%, respectively, while their H₂/CO₂ permselectivities decreased by 3.2% and increased by 1.6%, respectively. After regeneration by calcination at 350 °C, the gas permeances and the permselectivities of H₂/CO₂ and H₂/N₂ for the two membranes showed an upward trend. Compared with the fresh membranes, the H₂ permeances of SiO₂ and Nb/SiO₂ membranes after regeneration decreased by 10.95% and 3.21%, respectively, while their H₂/CO₂ permselectivities increased by 2.8% and 2.1%, respectively. The above results indicate that niobium doping improves the hydrothermal stability of SiO₂ membranes.

Figure 19. (a) Gas permeance and H₂ permselectivities and (b) H₂ permselectivities of Nb/SiO₂ membranes with n_{Nb} = 0 and 0.08 at a pressure difference of 0.1 MPa before and after steam treatment and regeneration.

4. Conclusions

To sum up, using the sol-gel technique, Nb/SiO₂ materials and membranes with various n_{Nb} were successfully synthesized. Their microstructures and gas permeances were investigated. The results showed that the niobium element existed in the formation of the Nb-O groups in the Nb/SiO₂ materials. As the niobium doping content and the calcining temperature were high enough, the Nb₂O₅ crystals could be formed in the SiO₂ frameworks. With the increase of n_{Nb}, the formed particle sizes increased, and the mean...
pore size, BET surface area, and total pore volume also increased until \( n_{\text{Nb}} = 0.08 \), and then they began to decrease. The doping of Nb could enhance the \( \text{H}_2 / \text{CO}_2 \) and \( \text{H}_2 / \text{N}_2 \) permselectivities of the SiO\textsubscript{2} membrane. When \( n_{\text{Nb}} \) was equal to 0.08, the Nb/SiO\textsubscript{2} membrane achieved a maximal \( \text{H}_2 \) permeance of \( 4.83 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \) and \( \text{H}_2 / \text{CO}_2 \) permselectivity of 15.49 at 200 °C and 0.1MPa, which increased by 36.7% and 155.47%, respectively, compared with that of the pure SiO\textsubscript{2} membrane. Compared with the fresh membranes, the \( \text{H}_2 \) permeances of SiO\textsubscript{2} and Nb/SiO\textsubscript{2} membranes after steam treatment decreased by 17.90% and 6.68%, respectively, while their \( \text{H}_2 / \text{CO}_2 \) permselectivities decreased by 3.2% and increased by 1.6%, respectively. After regeneration, the gas permeances and the permselectivities of \( \text{H}_2 / \text{CO}_2 \) and \( \text{H}_2 / \text{N}_2 \) for the two membranes showed an upward trend. Compared with the fresh membrane, the \( \text{H}_2 \) permeances of SiO\textsubscript{2} and Nb/SiO\textsubscript{2} membranes after regeneration decreased by 10.95% and 3.21%, respectively, while their \( \text{H}_2 / \text{CO}_2 \) permselectivities increased by 2.8% and 2.1%, respectively. Niobium doping improved the hydrothermal stability of the SiO\textsubscript{2} membrane. The Nb/SiO\textsubscript{2} membranes also exhibited great thermal reproducibility.

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