

Inorganic Materials Science Group

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Master thesis

Influence of water vapor on silica membranes:

Effect of sorption and percolation



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Foreword

This final report for the assignment of Master Degree in Chemical Engineering at the University of Twente specialization in Materials Science is a part of the PhD project of Ms. Tijana Zivkovic in the Inorganic Materials Science Group of Professor Dave Blank.

During the one-year study at the University of Twente, I finished all of the required seven courses and this assignment. I sincerely thank Tijana for the full support, including the help with the literature and experiments.

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Abstract

Silica-based membranes are considered to be promising means of hydrogen separation at elevated temperatures due to their high H₂ permeance, very good selectivity and relative ease to scale up. This is especially relevant for their applications in coal gasification and steam reforming where water vapor is present. The membranes studied here are composed of three layers: macroporous α -Al₂O₃ as the support, mesoporous γ -Al₂O ₃ as the intermediate layer and microporous amorphous silica as the separation layer.

In this report, the influence of water vapor on He transport through silica membrane has been investigated in terms of adsorption and percolation effect at relatively low temperatures (i.e. 50 and 90°C). The selected temperatures maximize the difference of mobility between He and H₂O molecules and avoid the structural change. He is considered to be a mobile component, while H₂O is an immobile one when these two gases transported under the specified conditions.

Two main methods of characterization on the actual as-deposited membrane layers employed in this study are spectroscopic ellipsometry for water vapor adsorption and the gas permeation for He transport in presence of water vapor. The former is a versatile technique to record the water vapor adsorption *in situ*, while the later provides the information on the percolation effect.

The isotherms of water vapor adsorption in the silica layer obtained from the ellipsometry are of Type I according to the IUPAC classification, complying with the typical adsorption behavior in the microporous materials. This result is in accordance with the range of pore size of the studied silica membrane (~4 Å). The adsorption isotherms generally comply with the first-order Langmuir isotherm with a slight deviation probably caused by the heterogeneous adsorption of H₂O molecules at the different active sites on the silica surface.

He flux through the silica membrane decreases dramatically in presence of water vapor, even in the low p_{H2O} range due to the blocking effect by the strongly absorbed H₂O molecules. The transport of gas molecules through such small silica pores can be assumed not to be continuous any more, with the gas molecules hopping from one occupied site to another unoccupied one under the potential gradient. When the coverage of water vapor in the silica layer increases, the He permeance is affected by the percolation effect. The irregular lattice, heterogeneous sites and gas molecules hopping to the sites on the opposite wall of narrow pore may cause the transition of He flux to happen at the high coverage of immobile component. He flux does not vanish even when the coverage of immobile H₂O molecules is close to 100% likely due to the presence of big pores in the silica layer.

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Assignment description

Hydrogen is a high-value gas with versatile applications as a chemical feedstock or as an alternative fuel (e.g. for fuel cells). Currently, hydrogen is produced mainly from the processes in terms of coal gasification and steam reforming of methane. Both methods generate a mixture of H_2 , CO_2 , H_2O and other gases.

Microporous silica membrane is one of the feasible means for separating H_2 from this industrial gaseous mixture in an energy-efficient and cost-saving way, compared to the conventional separation methods (e.g. pressure swing adsorption and cryogenic separation).

At high temperatures and in the presence of water vapor, silica membrane can undergo the rehydration or viscous sintering, resulting in the change of pore structure. However, in this assignment, we have examined how the presence of water vapor can decrease significantly the permeance of an inert gas through the silica membranes at low temperatures, where no structural change is expected.

The objective of this assignment is to illustrate that the adsorption and blocking by the immobile component (e.g. H_2O at low temperature) present in the silica micropores may decrease the permeance of the mobile one (e.g. H_2 , He) in a binary mixture. In the case of the silica membrane exposed to the binary gas mixture (e.g. H_2 and H_2O) at low temperatures, H_2O is considered to be an immobile component, having a strong interaction with the silica surface. As a result, the permeance of mobile component is lowered due to the adsorption and blocking effect of water vapor being the most pronounced at the concentration near or above the percolation threshold, i.e. the point of no flux of the mobile component due to the absence of a connected path for the mobile component through the membrane.

In a word, this report focuses on the effect of water vapor on silica membranes in terms of sorption and percolation.

Chapter 1 Theory

1.1 Membranes for hydrogen separation

The need for hydrogen will increase greatly in the future as a raw material for the chemical industry and as clean fuels in cars and electric industry (e.g. fuel cells). Currently, hydrogen is produced mainly by the reforming of fossil fuels and coal gasification. However, hydrogen is there mixed with large quantities of non-desired components such as light hydrocarbons, CO and CO_2 from fossil fuels [1-2]. The purification or separation of hydrogen from these industrial gases by means of membrane has several advantages, including low energy consumption and cost saving.

In general, membranes can be classified as organic and inorganic based on their material composition, as porous and dense or as symmetric and asymmetric based on their structure etc. Flux, selectivity, chemical stability and mechanical strength are the important parameters for the membrane performance. Although organic membranes have an advantageously low price and good scalability, they cannot be used at high temperatures or in chemically aggressive environments containing e.g. HCl, SO_x, and their poor mechanical strength hinders their high-pressure application. Dense metal membranes, usually made of palladium or its alloys, have very high selectivity for hydrogen (~100%) based on the solution-diffusion mechanism, but a deadly sensitivity to CO and H₂S, in terms of coal gas application [3]. Proton conductors, such as doped BaCeO₃, have a very high selectivity in the water vapor atmosphere, because only protons can migrate through these materials. However, H₂ flux through the proton-conducting membranes is relatively low (~10⁻⁸ mol/cm²·s) [4], and their chemical stability in the presence of certain species (e.g. CO₂, H₂S) is another major concern. Furthermore, energy consumption is disadvantageous because they must be operated at high temperatures (e.g. 800-1000°C) in order to obtain high flux.

Inorganic porous membranes can be used in many industrial applications at high temperatures (>200°C), and they have high flux and very good selectivity. Two of the most promising porous materials for membrane are zeolite and silica: the pores in the zeolite membrane are a part of the crystal structure, and hence have uniform dimensions. Many zeolites are thermally stable above 500°C. Zeolite membranes are generally formed on porous supports by hydrothermal synthesis, and hence the membranes have a lot of defects, lowering the selectivity. The most critical barrier for zeolite applications is the difficulty in producing in a large scale. Microporous silica membranes have high hydrogen permeance and high selectivity and excellent capacity to scale up [5]. Hereby, silica-based membranes are

promising candidates for hydrogen separation at elevated temperatures, although the steam/water stability of these membranes may be an issue [2].

Generally, the porous ceramic membranes for gas separation consist of several layers (Fig. 1.1): macroporous ($d_p > 50$ nm) support is often several millimeters thick, giving the mechanical strength to the system; mesoporous (2 nm < d_p < 50 nm) intermediate layer of less than 100 µm thickness is the bridge of the gap between the large pores of the support and the small pores of the thin microporous layer ($d_p < 2$ nm); the top layer is the actual functional part for gas separation.



Fig. 1.1 Composite membranes

Ceramic top layer providing high hydrogen flux and selectivity is very suitable to hydrogen separation [6]. R. de Vos [7] reported about crack-free amorphous silica layers by dip-coating in a clean room, with high H₂ permeance $(2 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa} \text{ at } 200^\circ \text{C})$ and very low CO₂ and CH₄ permeance (10 and 50×lower, respectively, at 200°C), the details of each layer are listed in Table 1, and they correspond to the characteristics of the membranes described in this report.

Layer	Component	Thickness	Sintering temperature	Pore size in diameter
Macroporous	α -Al ₂ O ₃	~2.00 millimeter	1100°C	80 nm
Mesoporous	γ-Al ₂ O ₃	~200 nm	650°C	2~3 nm
Microporous	Amorphous silica	~30 nm	400/600°C	~0.5 nm

Table 1.1 Layer properties of a typical silica membrane for hydrogen separation[7]

1.2 Gas transport in the porous materials

Gas transport in the porous materials largely depends on the properties of permeating gases (e.g. kinetic diameter, polarity), membrane characteristics (e.g. pore size, thickness and groups on the surface) and operating conditions (e.g. temperature, pressure). Single-component transport is easier to analyze than the multi-component one. For the single-component transport, Fick's first law can be applicable; while for the multi-component transport, even if the friction among components is neglected, Fick's first law must be modified. Maxell-Stefan equation is introduced to describe the multi-component transport when the friction between the component transport consisting of components greatly differing in mobility.

1.2.1 Single-component transport

1.2.1.1 Viscous flow

When the mean free path of gas molecule is smaller than the mean pore diameter, the collision of molecule-molecule is more frequent than that of molecule-wall, and viscous flow takes place.

It is assumed that molecules lose all their momentum at the pore wall, and the flux along a pressure gradient in the pore can be described by the modified Poisecuille equation to account for the contribution of the pore structure [9]:

$$N = -\frac{\varepsilon}{\tau} \frac{r^2}{8\eta} \frac{P}{RT} \frac{dP}{dz}$$
(1.2.1)

Where N is molar flux [mol/m²·s], ε is porosity, τ is tortuosity, r is pore radius, η is gas viscosity, P is pressure, R is gas constant, T is absolute temperature and dP/dz is pressure gradient.

1.2.1.2 Knudsen diffusion

When the mean free path of gas molecule is larger than the mean pore diameter, the collision of molecule-wall cannot be negligible compared to that of molecule-molecule, and Knudsen diffusion happens.

For Knudsen diffusion, the following expression is given [9]:

$$F = \frac{N}{\Delta P} = -\frac{2}{3} \frac{\varepsilon}{\tau} \frac{r}{L} \sqrt{\frac{8}{\pi M R T}}$$
(1.2.2)

Where F is permeance in $[mol/m^2 \cdot s \cdot Pa]$, M is molar mass of the gas and L is pore length.

1.2.1.3 Surface diffusion

Surface diffusion plays an important role when a significant number of gas molecules are absorbed on the pore surface by either physisorption or chemisorption, with relative strong affinity between the gases and surface, so that the gas molecules can transport along the surface concentration gradient. When the energy barrier between neighboring sites is smaller than the heat of adsorption, it is easier for the gas molecules to hop to the next sites than to desorb from the wall surface. Surface flux (J_s) can be described by the Fick's law [10]:

$$J_s = -\frac{1-\varepsilon}{\tau} \rho q^{sat} D_s \frac{\partial \theta}{\partial z}$$
(1.2.3)

Where ρ is density, q^{sat} is saturated amount of adsorbates, D_s is chemical surface diffusion coefficient and θ is coverage which indicates the covering extent.

There are two important factors: adsorption and mobility, both of which dominate the surface diffusion. When temperature increases, the mobility of adsorbed molecules also increases, while the amount of adsorbed molecules decreases. Therefore, the final surface diffusion rate depends on the dominant effect induced by the temperature increase. Furthermore, coverage θ can affect the value of D_s : at relative low θ , D_s is independent on the coverage; while D_s decreases when θ becomes higher.

1.2.2 Multi-component transport

1.2.2.1 Gaseous diffusion in the macroporous materials

If the pore size is much larger than the mean free path of the gas molecules and more than that of any type of species, momentum transfer from the light (fast) molecules to the heavy (slow) ones gives rise to a non-selective mass transport mechanism. This transport mechanism is referred to as gaseous diffusion with the binary diffusion coefficient D_{ij} showing a small variation with composition. For non-polar gases up to 10 bars, the binary diffusion coefficient can be estimated from [10]:

$$D_{ij} = 1.013 \times 10^{-2} \frac{T^{1.75}}{p(V_i^{1/3} + V_j^{1/3})^2} \sqrt{\frac{M_i + M_j}{M_i M_j}}$$
(1.2.4)

Where T is absolute temperature, p is pressure, V is diffusion volume of a species and M is molar mass.

1.2.2.2 Micropore diffusion

Micropore diffusion occurs in the micropores ($d_p < 2$ nm). With respect to the pore size, the following three cases are distinguished phenomenologically [7]:

A. When the pore size is close to the mesopore region: in the central region of the pore, the unabsorbed molecules can move freely (Knudsen diffusion), and the absorbed ones will diffuse along the surface (surface diffusion).

B. When the pore size is smaller than that in condition A, the molecules in the center of the pore still can move according to the Knudsen diffusion, but are not really free. The heat of sorption increases and the mobility of large molecules (compared to the pore size) decreases.

C. When the pore size is less than the summation of the diameters of gas X and Y, but more than the diameter of single gas X or Y, both gases can enter the pore but can not pass independently any more, i.e., the molecules may have a strong mutual influence on their permeance.

The following basic assumptions can be made when the pore size is so small that the movement of gas molecules is not continuous any longer [1]:

1. In the microporous materials, the gas molecules are surrounded by pore walls and shortrange interactions (e.g. Van der Waals forces and hydrogen bond) are considered to be important. Consequently, gas molecules vibrate around the positions where the potential energy is at a minimum; such a position is referred to as a vacancy. Jumps of the gas molecules from vacancy to vacancy are possible, and the time for a jump is short compared to the residence time of a molecule on a vacancy.

2. The microporous medium consists of a connected network of q^{sat} energetically independent vacancies, where only one molecule can be present at the same time. In other words, the sorption behavior of gas molecules obeys the ideal Langmuir isotherm.

3. Molecules diffuse from one of the adsorption sites to another one under the driving force of chemical potential only when that site is vacant, i.e. molecules cannot pass over each other. Furthermore, the interaction of molecules is assumed to be negligible and there are no external forces acting on the gas molecules.

When the friction between the components is negligible, the flux expression of a component *i* according to Onsager's theory of irreversible thermodynamics is given[1]:

$$J_i = c_i b_i \nabla \mu_i \tag{1.2.5}$$

Where J_i is flux, c_i is concentration, b_i is mobility, and $\nabla \mu_i$ is gradient in chemical potential. c_i can be expressed in terms of q^{sat} and θ .

$$c_i = q^{sat} \theta_i \tag{1.2.6}$$

When a vacancy diffusion mechanism operates, b_i is related with the probability of finding a neighboring vacancy.

$$b_i = b_i^0 (1 - \Sigma \theta_l) \tag{1.2.7}$$

Where b_i^0 is the mobility of component *i* in the limit of an infinitely low lattice occupancy. b_i can be related to the *component diffusion coefficient* D_i by using Nernst-Einstein equation.

$$D_j = b_j RT \tag{1.2.8}$$

For the single-component transport

$$\nabla \mu_i = RT \nabla \ln(\theta_i / (1 - \theta_i)) \tag{1.2.9}$$

Eq. (1.2.5) can now be rearranged into

$$J_i = -q^{sat} D_i \frac{\nabla \theta_i}{1 - \theta_i} = -q^{sat} \tilde{D}_i \nabla \theta_i$$
(1.2.10)

Where \tilde{D}_i is so-called *chemical diffusion coefficient*.

For the multi-component transport, the flux expression is changed into

$$J_{i} = -q^{sat} \tilde{D}_{i} \left((1 - \sum_{l \neq i} \theta_{l}) \nabla \theta_{i} + \theta_{i} \sum_{l \neq i} \nabla \theta_{l} \right)$$
(1.2.11)

1.2.2.3 Maxwell-Stefan equation

When the friction between the components is taken into consideration, Maxwell-Stefan equation is introduced [11].

There are two types of forces in the multi-component mixture:

- 1. Forces on the individual species
- 2. Forces due to the interactions between the species

The first forces are known as "driving forces"; the second forces are due to the differences in velocity between the diffusing species. The driving force on a species i in a mixture equals the sum of the friction forces between i and the other species j:

$$d_{i} = \sum_{j \neq i} \zeta_{ij} x_{j} (u_{i} - u_{j})$$
(1.2.12)

Where d_i is the driving force on *i*, $\zeta_{i,j}$ is the friction coefficient between *i* and *j*, x_j is the mole fraction of *j* and *u* is species velocity.

The relation between flux J and u is

$$J = cu \tag{1.2.13}$$

Where *c* is concentration.

The Maxwell-Stefan diffusivity D^{ms} is defined as an inverse of the friction coefficient.

$$D_{ij}^{ms} = \frac{RT}{\zeta_{ij}} \tag{1.2.14}$$

For a proper description of the mass transport behavior of an *n*-component mixture in the microporous materials, the mechanical interactions between the mobile components and the solid matrix can be accounted by treating the q^{sat} vacancies as the $(n+1)^{th}$ component. The Maxwell-Stefan equation can be expressed as:

$$-d_{i} = \sum_{\substack{j=1\\j\neq i}}^{n} \theta_{i} \theta_{j} \frac{u_{i} - u_{j}}{D_{ij}^{ms}} + \theta_{i} \frac{u_{i} - u_{n+1}}{D_{i,n+1}^{ms}}$$
(1.2.15)

Where $D_{i,n+1}^{ms} = D_i^{ms}$ since $u_{n+1} = 0$

If there are no external forces acting on the mobile species, then d_i can be written as

$$d_{i} = \frac{q^{sat}\theta_{i}}{RT}\nabla\mu_{i} = q^{sat}\theta_{i}\nabla\ln(\frac{\theta_{i}}{1-\Sigma\theta_{l}})$$
(1.2.16)

Combining Equations (1.2.13, 1.2.15 and 1.2.16), the Maxwell-Stefan equation for multicomponent transport can be given [1]:

$$J_{i} = D_{i}^{ms} \sum_{j}^{n} \frac{\theta_{j} J_{i} - \theta_{i} J_{j}}{D_{ij}^{ms}} - \frac{q^{sat} D_{i}^{ms}}{(1 - \sum \theta_{l})} \left((1 - \sum_{l \neq i} \theta_{l}) \nabla \theta_{i} + \theta_{i} \sum_{l \neq i} \nabla \theta_{l} \right)$$
(1.2.17)

The first part of above equation on the right side is the contribution of the friction between the components.

1.2.3 Percolation effect

Imagine an infinite square lattice as shown in Fig 1.2, the *cluster* is defined as a group of neighboring sites connected by bonds. Each site (bond) of the lattice is occupied randomly with *probability* p, independent on its neighbors. Percolation theory deals with the formed clusters, in other words, with the groups of neighboring occupied sites (bonds)



Fig 1.2 Clusters in a 2-D square lattice

[12]. When the sites are considered, it's called *site percolation*, and its counterpart is called *bond percolation*. The former is more suitable to describe the behavior of the multicomponent transport in the porous materials, especially in case of a binary mixture of mobile and immobile components. When the pore size is so small that the continuity of gas transport does not exist any more, gas molecules are assumed to be transported by hopping from one site to another..

The *percolation threshold* p_c (Table 2) is that concentration p at and above which an infinite cluster of connected neighbors from one side of lattice to the other appears in an infinite lattice, whereas for $p < p_c$ no such infinite cluster exists [12].

Lattice	Site-percolation	Bond-percolation
Honeycomb	0.6962	0.6527
Square	0.5927	0.5000
Triangular	0.5000	0.3473
Diamond	0.4300	0.3880
Simple cubic	0.3116	0.2488
Body Centered Cubic	0.2460	0.1803
Face Centered Cubic	0.1980	0.1190

Table 1.2 Percolation thresholds for various lattices [12]

The percolation threshold can be theoretically predicted by many approaches, including Monte Carlo (MC) simulation and effective medium approximation (EMA) model. For a 3-dimensional single cubic lattice, the predicted threshold of site percolation is ~0.7 [12,13,14-16], for a 2-dimensional square lattice, it is 0.32-0.40 (0.40 [12], 0.37 [16], 0.33 [17], 0.38 [18] or 0.32 [19]).

Furthermore, percolation threshold largely depends on the connectivity of lattices, i.e. the coordination number N [20]. The percolation threshold increases with increasing the connectivity [21].

When the gas transport in the micropores is dominated by the basic assumptions in Section 1.2.2.2 in the case of a binary mixture of components that greatly defer in mobility, percolation behavior may occur if the motion of the mobile component is suppressed. The minimum value of coverage of the immobile component, above which the transport of the mobile molecules through the pores is blocked, is also referred to as the *percolation threshold* [13], with a reverse value of the ones in Table 2, i.e. 1- p_c , represented by p_c^{im} in this report.

The transport behavior of a binary mixture through a zeolite membrane was investigated where the studied gas mixture consisted of fast and weakly adsorbing hydrogen and slow and strongly adsorbing n-butane [22-23]. The flux of weakly adsorbing H_2 is reduced significantly

compared to its single-component flux below 100°C; while the flux of strong adsorbing nbutane is hardly changed due to the presence of weakly adsorbing component. However, the authors did not attribute these changes to the percolation effects.

N.E. Benes *et al* [13] studied multi-component lattice gas diffusion, predicting the effect of percolation (Fig 1.3). The onset of percolation behavior was investigated by simulating the transport of mobile component *i* under a fixed gradient, while slowly increasing the occupancy of the immobile component *j* (i.e. with no gradient). The larger the difference of jump frequencies between two components, the smaller the value of percolation threshold p_c^{im} . In principle, Maxwell-Stefan (MS) theory only predicts a linear relationship on the coverage of the immobile component and the diffusivity of the mobile component, shown in Fig. 1.3 for $v_i/v_j=1$, and thus MS theory does not incorporate the percolation effect. Consequently, the standard mass transport descriptions used in the field of membrane separation (e.g. Maxwell-Stefan theory) should be used with caution due to the fact that they do not incorporate the percolation effect.



Fig 1.3 The dependence of diffusivity on coverage for a binary mixture of mobile components [13], Where v_i / v_j is the ratio of jump frequencies between the component *i* and the component *j* θ_j is the coverage of immobile component *j*, $\sigma \tilde{D}_i^{app}$ is the normalized diffusivity of *i*

In this study, the percolation phenomenon is investigated by employing microporous silica membrane in the case of a binary mixture containing He and water vapor at low temperature where water molecules tend to be absorbed on the silica surface. The low mobility of H₂O molecules, compared to that of He, may induce the percolation behavior.

1.3. Silica membrane

1.3.1 Synthesis of the silica membrane

The sol-gel process is one of the most widely used methods for the preparation of very thin inorganic membranes [24]. Other approaches include Chemical Vapor Deposition, Chemical Vapor Infiltration and Pulse Laser Deposition. The two main sol-gel routes are colloidal and polymeric one. Colloidal system is a dispersion of small particles whose diameter is below 1000 nm in a liquid medium so that the effect of gravitational force is negligible and dispersion is maintained by mutual repulsion forces between the particles. Colloidal particles can be obtained from hydrolysis and condensation of metal salts or metal alkoxides in water. The polymeric system is the only gel system where a true oxide network is formed by chemical polymerization in the liquid near room temperature. Hydrolysis of the alkoxide groups forms hydroxyl groups; condensation of the hydroxyls forms inorganic polymers and the polymers are linked to obtain the gel. In the polymerization : acid-catalyzed and base-catalyzed polymerization [25].

In general, the pore size of the materials obtained by the colloidal route is of the order of nanometer, whereas the pores of several angstroms can be obtained by the polymeric route. For silica synthesis, Tetra-Ethyl-Ortho-Silicate (TEOS) is one of the most widely used precursors. State-of-the-art silica membranes with very narrow pore size and a low number of defects can be prepared by sol-gel approach in the clean room [7].

1.3.2 Influence of water vapor on the gas permeance through silica membrane

A good H₂-separation membrane should have high hydrogen flux, high H₂/CO₂ selectivity, high mechanical strength and good resistance to CO₂ & CO and water vapor, necessary for the application in coal gasification and steam reforming. The kinetic diameters of H₂, CO₂, and H₂O are 2.89 Å, 3.3 Å and 2.65 Å, respectively. Generally speaking, the greater the difference between the kinetic diameters of two gas molecules, the higher the membrane selectivity, and thus the separation of H₂ and CO₂ is easier than that of H₂ and H₂O. However, the separation of gases from a gaseous mixture also depends on the nature of the gas-gas and gas-surface interaction.

On the silica surface, there are three different groups: siloxane bridges (\equiv Si-O-Si \equiv), hydroxyl groups (-OH) and unsaturated Si atoms. The siloxane bridges are somewhat hydrophobic, while hydroxyl groups (-OH) and unsaturated Si atoms are absolutely hydrophilic. At low temperature, water vapor is absorbed on the silica surface by physisorption; at high temperature, it becomes chemisorbed by reacting with the siloxanes. Currently there is a high interest in understanding how the permeance of H₂ through silica membrane is affected in the presence of water vapor.

Since the hydrophobicity of silica surface increases with the decreasing of the amount of hydroxyl groups, the hydrothermal stability of silica can be improved by increasing the sintering temperature [7] or by modifying with some organic [26-28] or inorganic [29] groups to substitute the hydroxyl groups. However, the organic groups on the silica surface themselves are not very stable at elevated temperatures.

Some general conclusions about the thermal and hydrothermal stability of silica membrane were represented by R. de Vos [7]:

Thermal stability:

- 1. The thermal stability up to 300°C is higher for membranes calcined at higher temperature.
- 2. Exposure of silica membrane calcined at 400°C to a dry atmosphere at 350°C for 200 hours results in a slight densification of the porous structure

Hydrothermal stability:

- 1. The influence of water vapor pressure on the membrane deterioration is larger than that of temperature.
- For silica membranes calcined at 600°C, hydrothermal exposure at 350°C and 475°C causes the formation of 200-300 μm holes

3. Although silica membrane calcined at higher temperatures has less hydroxyl groups, the decrease of hydroxyl group concentration does not increase the hydrothermal stability due to the fact that the pore size is reduced with high calcining temperature.

Q. Wei *et al* [30-31] studied the effect of a low water vapor pressure (p_{H20} =3.6× 10³ Pa) on the hydrogen permeance at 200°C for 120 hours in the case of Silica (400) and methylmodified Silica (400) membranes made by sol-gel approach. The H₂ permeance of pure Silica (400) is continually decreasing during 120 hours; however, that of methyl-modified Silica (400) becomes stable after 50 hours, only dropping about 6% compared with the initial permeance without the existence of water vapor (Fig. 1.4). This phenomenon indicates that methyl-modified Silica (400) membrane is more stable than the pure Silica (400). The initial permeance of modified Silica (400) is higher than that of Silica (400), implying the pore size of modified Silica (400) is larger, probably due to the addition of methyl groups in the original sol.

It can be concluded that the permeance through the silica membrane, even the organicmodified one, is decreased in presence of water vapor. At high temperatures, the interaction between water vapor and silica surface causes the densification or damage of pore structure, while at low temperatures, the permeance decreases significantly due to the presence of water vapor, even without destroying the pore structure [30-31]. The decrease in H₂ permeance could be attributed to the adsorption of water vapor and blocking of silica micropores. This phenomenon should be more significant at lower temperature where the mobility of H₂O molecules decrease, while the amount of adsorbed H₂O molecules increase due to the stronger interaction.







Fig. 1.4 H₂ permeance during the water vapor exposure
(a) Pure Silica (400) membrane
(b) Methyl modified Silica (400) membrane
The number in the bracket is the calcining temperature in [°C].

1.4 Gas sorption

1.4.1 Introduction

When gas molecules meet a solid surface, it is adsorbed onto the solid surface, (the gas and solid are called *adsorbate* and *adsorbent*, respectively) in the process called *adsorption*, while the reverse process is called *desorption*.

Based on the interaction of adsorbate and adsorbent, adsorption can be divided into following types:

(1) Physisorption.

Physical adsorption is caused mainly by Van der Waals force and electrostatic force between adsorbate molecules and adsorbent surface. As an important parameter for physisorption, *surface polarity* governs the affinity of adsorbent and adsorbate. Polar adsorbents are thus called "*hydrophilic*" (e.g. zeolites, porous silica and alumina), while nonpolar adsorbents are generally "*hydrophobic*" (e.g. carbon, polymer). The heat of physisorption is low (less negative than –25kJ/mol).

(2) Chemisorption

During chemisorption, the adsorbate molecules react with the adsorbent surface by forming chemical bonds. Generally, the heat of chemisorption is larger than that of physisorption, more negative than -40 kJ/mol.

Based on the number of layers of the adsorbed molecules, adsorption can be divided into:

(1) Monolayer adsorption

There is only one layer of adsorbate molecules that is formed on the adsorbent surface. A typical example is chemisorption.

(2) Multilayer adsorption

More than one adsorbate layer are formed due to the interaction of adsorbates or adsorbates/adsorbents.

1.4.2 Adsorption isotherm

An adsorption isotherm for a single gaseous adsorbate on a solid is the function that relates the amount of adsorbate adsorbed at the equilibrium to the pressure (or concentration) of the adsorbate in the gas phase at a constant temperature.

The IUPAC classification of adsorption isotherms is illustrated in Fig. 1.5 [32]



Fig. 1.5 IUPAC classification of adsorption isotherms [32].

Six types of isotherm are the characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III, and VI) or mesoporous (types IV and V). The differences between types II and III isotherms and between types IV and V isotherms arise from the relative strengths of the adsorbate-adsorbent and adsorbate-adsorbate attractive interactions: types II and IV are associated with stronger adsorbate-adsorbent interactions and types III and V are associated with weaker adsorbate-adsorbent interactions. The hysteresis loops usually exhibited by types IV and V isotherms are associated with the capillary condensation in the mesopores. Type VI isotherm represents adsorption on nonporous or macroporous solids where stepwise multilayer adsorption occurs.

1.4.3 Langmuir isotherm

The extent to which adsorption has taken place on the adsorbent surface is indicated by the *coverage* θ :

$$\theta = \frac{n_a}{n_{sat}} \tag{1.4.1}$$

Where n_a is the number of occupied adsorption sites and n_{sat} is the number of total adsorption sites.

The ratio of partial vapor pressure of the adsorptive (p) and adsorptive vapor pressure at which the adsorbent is saturated (p_{sat}) is indicated by *relative pressure* p_r :

$$p_r = \frac{p}{p_{sat}} \tag{1.4.2}$$

Langmuir adsorption is based on the following assumptions:

- (1) All adsorption sites are energetically equivalent
- (2) Each adsorption site can only host one adsorbate particle (1-to-1 adsorption)
- (3) No interaction between adsorbates exists
- (4) Coverage is independent on binding energy
- (5) Maximum monolayer coverage is 1 ($\theta = 1$)

The rate of adsorption (the change in surface coverage) is proportional to the partial vapor pressure p of the adsorbate and the amount of free adsorption sites (1- θ). This leads to the following expression by assuming first order kinetics:

$$r_a = \frac{d\theta}{dt} = k_a p(1-\theta) \tag{1.4.3}$$

Where r_a is the adsorption rate, k_a is the adsorption rate constant.

The desorption rate is

$$r_d = \frac{d\theta}{dt} = k_d \theta \tag{1.4.4}$$

Where r_d is the desorption rate, k_d is the desorption rate constant.

Then the equilibration of adsorption rate and desorption rate gives the equilibrium relations:

$$\theta = Kp/(1+Kp) \tag{1.4.5}$$

$$p = \frac{1}{K} \left(\frac{\theta}{1-\theta}\right) \tag{1.4.6}$$

The above relations are given by Langmuir (1918) and are called the Langmuir isotherm. $K = k_a / k_d$ is called *adsorption equilibrium constant*.

When the number of occupied adsorption sites, n_a , is far smaller than the adsorption capacity of the adsorbent, n_{sat} , i.e. $Kp \ll 1$, and Langmuir isotherm is reduced to the Henry type equation

$$\theta = Kp \tag{1.4.7}$$

Further, when Kp >>1, adsorption sites are saturated, and $\theta = 1$.

Langmuir adsorption isotherm and the Henry regime are showed in Fig. 1.6.



Fig. 1.6 Langmuir adsorption isotherm and Henry law

The Langmuir equation is modified when the interaction between adsorbing molecules is taken into account [33]:

$$p = \frac{1}{K} \left(\frac{\theta}{1-\theta}\right) \exp(2\mu\theta/kT) \tag{1.4.8}$$

Where 2μ represents a pair interaction energy and k is the Boltsmann constant.

1.4.4 Adsorption of water vapor on the unsupported porous silica materials

Gas sorption is largely dependent on the properties of the gas and the surface itself. H_2O molecules are polar and tend to be absorbed on the polar surfaces. The properties of silica surface depend greatly on the preparation approaches, especially on the thermal process.

1.4.4.1 Active groups on the surface of silica materials

The surface properties of silica have been widely investigated in the last decades because of the widespread use of porous silica materials as an adsorbent, catalyst support, constituent of chromatographic columns and functional membrane for separation etc.

The main active groups for H_2O adsorption are unsaturated Si atoms, hydroxyl and siloxane groups. Generally, each silicon atom on the surface of amorphous silica tends to

maintain tetrahedral coordination with oxygen atoms by being covalently bonded to an outwardly disposed hydroxyl group [34], and thus the coordination number of Si is 4. For unsaturated Si atoms, the coordination number is less than 4 because some Si-O bonds are missed or broken. Some authors [35-36] consider them as primary adsorption sites, although their concentration is apparently small, and their concentration is hard to measure. Computational modeling of water adsorption on silica and silicate glass fracture surfaces also suggests that the strongest adsorption is associated with such unsaturated Si atoms [37].

In terms of the concentration, hydroxyl and siloxane groups are dominating; their structures are shown in Fig. 1.7 [38]. Hydroxyl groups can be subdivided into free (isolated), bridged (hydrogen-bonded) and geminal OH. The type of OH groups can be distinguished by many



Fig. 1.7 Various types of hydroxyl groups on the surface of silica: (a) free (isolated) OH, (b)bridged (hydrogen-bonded) OH, (c) geminal OH and (d) siloxane group [38].

characterization techniques (e.g. FTIR, H-NMR and weight loss measurement etc), due to the difference of bond vibration frequency and the bond strength. Generally, physisorbed water can be removed at ~200°C [39]. Above this temperature, hydroxyl groups start to condense and evolve water by the interaction of adjacent pairs, and it is assumed that this reaction happens randomly. About 75% of total OH groups are removed this way [34]. Above 600°C, only free OH groups exist on the silica surface [38], and they are hard to remove due to the large distance of isolated OH, but their removal can happen by diffusion and condensation at increased temperatures. There are still a small amount of OH groups present even above 1000°C (Fig. 1.8).



Fig. 1.8 Number of the surface hydroxyl groups and the surface siloxane bridges produced by condensation of OH groups, as a function of preheating temperature [40].

Heating silica gel decreases the number of hydroxyl groups and increases the number of siloxane bridges, and therefore the concentration of siloxane groups on the surface calcined above 600°C should be the highest compared to the number of free hydroxyl groups and unsaturated Si atoms.

1.4.4.2 Water adsorption on the porous silica materials

As mentioned previously, sorption behavior depends on the nature of adsorption sites and of adsorbate, e.g. polar molecules (like H₂O) prefer hydrophilic surface. Unsaturated Si atoms and OH groups are hydrophilic, while the hydrophobicity of siloxane largely depends on the angle between Si-O bonds, where the unstrained siloxane is normally hydrophobic. In fact, many siloxane bridges are strained in porous materials, and thus siloxane groups are not

absolutely hydrophobic. The property of silica surface is changed from hydrophilic to hydrophobic as the preheating temperature is increased. In principle, dissociative adsorption of water vapor, i.e. chemisorption, occurs by breaking the siloxane bridge, called *rehydration*, yielding two adjacent OH groups.

$$\underline{=}$$
Si-O-Si $\underline{=}$ + H₂O \rightarrow 2 $\underline{=}$ Si-OH

The removal of adjacent OH groups is partly or fully reversible if calcined below 400°C [39,40], while the stability of siloxane increases with the increasing preheating temperature, with weak interaction on fully dehydrated silica above 600°C [41], even if heated up to 115°C in the saturated water vapor for 24 hours [39].

The strong adsorption of H₂O molecules on the unsaturated Si atoms is due to the strong interaction (maybe electrostatic force or weak chemical bond), and leads to a high enthalpy of interaction. Secondly, H₂O molecules are absorbed on the free OH sites via one hydrogen bond, with a 50-90 kJ/mol enthalpy. Furthermore, the adsorption of H₂O molecules on the unstrained siloxane groups (hydrophobic) and strained siloxane groups (weakly hydrophilic) is possible through the Van de Waals force, which is significant in very small pores due to the micropore confinement and the large silica surface. The enthalpy of interaction between H_2O and siloxanes is less than the latent enthalpy of liquefaction of water vapor (44 kJ/mol) due to the hydrophobicity of siloxane [41]. Since H2O molecules are highly polar, multilayer adsorption is possible [42]. Consequently, capillary condensation of water occurs in the mesopores. A. Burneau et al [39] found that the first hydration layer on the porous silica was non-uniform and involved essentially unconnected water molecules. The extent of water vapor adsorption in this layer corresponds roughly to the number of hydroxyl groups. However, H₂O molecules start clustering before their bonding to hydroxyls was complete. This is especially obvious on thermally preheated samples, due to the strong affinity of isolated hydroxyl groups & H₂O molecules and H₂O & H₂O molecules.

Water vapor sorption in the mesoporous silica materials has been studied in detail [43-47]: types IV and V isotherms with large hysteresis are typical, with an obvious increase of the amount of absorbed H_2O in the high pressure range due to the capillary condensation based on Kelvin Equation. Type IV corresponds to the hydrophilic silica surface while type V is the characteristic of hydrophobic one.

With the decrease of pore size in the microporous silica materials, the hysteresis and increase of amount adsorbed in the high-pressure range vanish [47], and the isotherm is of Type I [45,48], as shown in Fig. 1.9. There is a dramatic increase in the amount adsorbed in the low-pressure range caused by the micropore confinement and strong interaction between adsorbate and adsorbent. Generally it is assumed that the isotherm of water vapor in the micropore materials complies with Langmuir Type adsorption [49].



Fig. 1.9 Isotherms of water vapor on Zeolite 4A at four temperatures (0-101°C) [48].

1.5 Sorption measurements in the thin layer by the ellipsometry

1.5.1 The principle of ellipsometry

In this section some relevant theoretical aspects are first introduced before describing ellipsometry in more details (if not mentioned, Section 1.5.1 is based on the reference [50]).

An electromagnetic wave

Briefly, *an electromagnetic wave* is a transverse wave consisting of an electric field vector and a magnetic field vector, both of whose magnitude are a function of position and time. The electric vector and the magnetic vector are mutually perpendicular and both perpendicular to the direction of propagation. The two aspects are not independent, and the electric field vector completely determines the magnetic field vector. If only the electric field vibration is considered, the light wave can be expressed as

$$A = A_0 \sin(-\frac{2\pi}{\lambda}(x - vt) + \zeta)$$
(1.5.1)

Where A is the wave as a function of time and place, A_0 is the amplitude, λ is the wavelength, x is the distance, v is the velocity of the light, t is the time and ζ is an arbitrary phase angle.

If the time is fixed, the electromagnetic wave can be represented schematically in Fig. 1.10.



Fig. 1.10 An electromagnetic wave at a fixed time

Interaction of light with materials

To describe the interaction of light with materials, a parameter, the *complex index of* \tilde{N} , is used, which includes a real part and an imaginary part, given as

$$N = n - jk \tag{1.5.2}$$

Where n and k is called the *index of refraction* and *extinction coefficient*, respectively; j is the imaginary number (the square root of -1). For a dielectric material (e.g. glass, silica), no light is absorbed and hence k=0.

When a light beam passes from one medium into another medium, some of the light is reflected back while some of the light passes through the surface and changes the direction where the two phenomenon are called *reflection* and *refraction*, respectively (Fig. 1.11).



Fig. 1.11 The optical phenomenon of reflection and refraction

According to the law of reflection, the angle of incidence (ϕ_i) is equal to the angle of reflection (ϕ_r) , i.e.

$$\phi_{i} = \phi_{r} \tag{1.5.3}$$

The law of refraction is called "Snell's law" after its discoverer, and is given by

$$N_1 \sin \phi_1 = N_2 \sin \phi_2 \tag{1.5.4}$$

Polarized light

Most light sources emit non-polarized light that has electric field components oriented in all possible directions perpendicular to the direction of travel, while the polarized light, i.e., linearly polarized light, is referred to as the light in which all of the photons have the electric field oriented in one direction. The polarized light can be obtained by passing the light beam through an optical element or by causing the beam to make a reflection under some specific conditions. There are two cases when two linearly polarized light beams with the same frequency are combined along the same direction.

Case A: If two linearly polarized light beams whose phases are the same are combined, the obtained light beam is linearly polarized as well (Fig. 1.12).



Fig. 1.12 When two linearly polarized waves with the same frequency are combined in phase, the obtained wave is linearly polarized light as well

Case B: If two linearly polarized light beams whose phases are not the same are combined, the obtained light beam is elliptically polarized. When the difference of their phases is 90°, the obtained wave is circularly polarized light (Fig. 1.13); otherwise, it is elliptically polarized light.



Fig. 1.13 If two linearly polarized waves with the same frequency and different phases are combined, the obtained wave is elliptically polarized. In this figure, the difference of their phases is 90°, and hence it is circularly polarized.

Reflection

To describe the reflection, *the plane of incidence* is defined as the plane that includes the light beam prior to and after the reflection, and the normal to the surface is also contained in the plane of incidence as well. Furthermore, the polarized waves that are in the plane of incidence are called *p-polarized light*, and the polarized waves that are perpendicular to the plane of incidence are called *s-polarized light* (Fig. 1.14).



Fig. 1.14 Reflection of a light beam from a surface

To describe the reflection at an interface between two mediums (Fig. 1.6), *the Fresnel reflection coefficient r* is introduced, which is the ratio of the amplitude of the reflected wave to the amplitude of the incident wave for a single interface, given by

$$r_{12}^{p} = \frac{\tilde{N}_{2}\cos\phi_{1} - \tilde{N}_{1}\cos\phi_{2}}{\tilde{N}_{2}\cos\phi_{1} + \tilde{N}_{1}\cos\phi_{2}} \qquad r_{12}^{s} = \frac{\tilde{N}_{1}\cos\phi_{1} - \tilde{N}_{2}\cos\phi_{2}}{\tilde{N}_{1}\cos\phi_{1} + \tilde{N}_{2}\cos\phi_{2}} \qquad (1.5.5)$$

Where the subscript "12" denotes that this Fresnel reflection coefficient is for the interface between mediums 1 and medium 2.

The reflectance \Re is defined as the ratio of the reflected intensity to the incident intensity. The expression for a single interface is given below:

$$\Re^{\mathbf{p}} = \left| \mathbf{r}^{\mathbf{p}} \right|^2$$
 and $\Re^{\mathbf{s}} = \left| \mathbf{r}^{\mathbf{s}} \right|^2$ (1.5.6)

For multiple interfaces (Fig. 1.15), the Fresnel reflection coefficient is modified, resulting in *the total reflection coefficient R*, shown below:

$$R^{p} = \frac{r_{12}^{p} + r_{23}^{p} \exp(-j2\beta)}{1 + r_{12}^{p} r_{23}^{p} \exp(-j2\beta)} \quad \text{and} \quad R^{s} = \frac{r_{12}^{s} + r_{23}^{s} \exp(-j2\beta)}{1 + r_{12}^{s} r_{23}^{s} \exp(-j2\beta)}$$
(1.5.7)

 β is the film phase thickness and is given by

$$\beta = 2\pi \left(\frac{\mathrm{d}}{\lambda}\right) \tilde{\mathrm{N}}_2 \cos\phi_2 \tag{1.5.8}$$

Where d is the film thickness of interest.



Fig. 1.15 Reflection of a light beam from multiple interfaces

Theoretical basis of ellipsometry

Referring to Fig. 1.14, the parameter Δ (delta) is defined as the difference of the *phase* difference δ_1 between the p-wave and s-wave of incidence and the phase difference δ_2 between the p-wave and s-wave of reflection.

$$\Delta = \delta_1 - \delta_2 \tag{1.5.9}$$

Without regard to phase, the amplitude of both p-wave and s-wave may change due to reflection. $|\mathbf{R}^{p}|$ and $|\mathbf{R}^{s}|$ are defined as the ratio of the amplitude of the corresponding reflected wave to that of incident wave.

Another parameter for ellipsometry, *the quantity* ψ , is defined as the angle whose tangent is the ratio of the magnitude of the total reflection coefficients.

$$\tan \psi = \frac{\left|\mathbf{R}^{\,\mathrm{p}}\right|}{\left|\mathbf{R}^{\,\mathrm{s}}\right|} \tag{1.5.10}$$

The last parameter for ellipsometry, the complex quantity ρ is defined to be the complex ratio of the total reflection coefficients.

$$\rho = \frac{R^{p}}{R^{s}} \tag{1.5.11}$$

Finally, the fundamental equation of ellipsometry is obtained

$$\rho = \tan \psi e^{j\Delta} = \frac{R^{p}}{R^{s}}$$
(1.5.12)

The quantities ψ and Δ are precisely measured by ellipsometry, the information about the sample is contained in the total reflection coefficients, and hence in ρ .

For dielectric materials (e.g. alumina and silica), Δ (in Eq. 1.5.12) remains close to 180° or 0°, depending on the angle of incidence.

1.5.2 Sorption of water vapor on silica layers by ellipsometry

Generally, the traditional techniques for sorption (e.g. gravimetric and volumetric methods) are convenient for powder samples, but they are not suitable to analyze the actual porous films, especially since the properties of powder and supported film are generally not identical. Ellipsometry is a non-destructive optical technique and thus suitable for the characterization of porous thin films. Recently, ellipsometry is applied to the characterization of inorganic porous films with low k materials in terms of porosity [51-56], pore size distribution [51,54,55,57] and sorption [51-55,57-59].

It is known that the optical properties of porous films are changed if the pores absorb gas molecules or are filled with liquid. The amount of the adsorbate can be calculated if the optical properties of the materials, which form the porous films, and the adsorbate are known. There are several methods for performing these calculations based on e.g. Lorentz-Lorentz equation [52,60]. N. E. Benes *et al* [52] investigated CO₂ adsorption on the porous silica film by assuming the linear relationship between the number of gas molecules absorbed in the silica film and the change in the effective dielectric function $\langle \varepsilon_e \rangle$ of the film, the later corresponding to the change of tan ψ measured by ellipsometer. The maximum adsorption of CO₂ (2.8-3.0 mmol/g) was found, which was in fair agreement with the value of ~2.7 mmol/g by gravimetric high-pressure sorption setup.

Adsorption of water vapor in the different porous films has been studied by ellipsometry [58,61-63]. Ellipsometer measures the optical properties of materials with high accuracy and precision, making this technique useful for studying water sorption on the silica film. The water vapor isotherms obtained by ellipsometry and consequent calculated pore size distributions in the mesoporous and microporous films are consistent with traditional techniques (e.g. N₂-sorption by powder samples and SEM by the real film) [62,63]. Since silica is transparent, i.e. k=0, $\cos \Delta$ can be ± 1 if a proper incidence angle is used. As a result, only tan ψ is changed by water vapor sorption. It has also been deduced theoretically that tan ψ is proportional to the amount of adsorbed H₂O molecules by A. A. Herrero (Fig. 1.16) [62], and this basic relation makes possible to relate optical parameter tan ψ to the coverage θ .



Fig. 1.16 Calculated dependence of tan ψ and water volume fraction, assuming that SiO₂ volume fraction is 0.7, pore volume is 0.3. Incident angle is 70.11° and the wavelength is 800 nm [62]

This above relationship was used to develop the adsorption isotherm of water vapor in the actual silica membrane supported by γ -Al₂O₃ by S. Kuipers [64]. The studied amorphous silica membrane has smaller pores (~ 4 Å) than that studied by other authors (larger than 1 nm). Adsorption of water vapor at two temperatures of 31°C and 55°C is well fitted with the first order Langmuir isotherm, complying with Type I isotherm.

It can be concluded that ellipsometry is a very versatile technique for investigating surfaces and thin films since it is precise, non-destructive and can provide the thickness and optical properties of the thin films, including the in situ monitoring of those properties due to an induced change.

Chapter 2

Sample preparation and experiments

2.1 Samples

The sol-gel method and procedure for the sample preparation have been described previously [4,7]. The membranes used in the gas permeation experiments are composed of two γ -Al₂O₃ layers and two silica layers to achieve high selectivity for small gas molecules, like H₂ and He. The first γ -Al₂O₃ layer reduces the roughness of α -Al₂O₃ support, providing a smooth surface to coat the second γ -Al₂O₃ layer. The samples for the ellipsometry experiments contain single γ -Al₂O₃ and silica layers, since the additional refraction and reflection at the interface of two γ -Al₂O₃ or silica layers make the analysis of optical data more complex. In this report, we assume the same material properties of once and twice coated γ -Al₂O₃ and silica layers, although the pore structure of the top layer may be affected by the roughness of the underlying layer. Each sample is employed one time in either gas permeation or ellipsometry experiment, to assure the consistent sample conditions prior to the water vapor exposure.

2.2 Experimental methods and setups

In this assignment, ellipsometry and gas permeation are the two main characterization techniques used to analyze the specific sorption of water vapor and percolation in the case of He transport through the silica membranes. H₂O and He are used for the gas permeation experiment, since they have similar kinetic diameter (2.60 and 2.65 Å for He and H₂O molecule, respectively), and both of them can enter the narrow pores in the silica layer without size exclusion, with the probability of entering the pores being related to the component concentration The variation in He permeance in presence of water vapor is measured directly as the water vapor pressure is increased, while ellipsometry is used to study the adsorption of water vapor.

2.2.1 Water vapor generator

If the desired concentration of water vapor in the gas mixture is not very high, an easy way to supply a gaseous mixture with the water vapor is by letting a gas flow through the water at a constant temperature (Fig. 2.1). There is some water vapor in the gas above the water surface, and the water vapor is carried by the He flow to the sample cell. Water vapor generator is used in the experiment of both gas permeation and ellipsometry.



Fig. 2.1 Water vapor generator

1 liquid bath; 2 water bottle; 3 heating or cooling rods

4 porous sieve; 5 temperature controller; 6 valve; 7 temperature indicator The thick and thin dashed lines denote the liquid in the bath and water in the bottle, respectively

However, there is an obvious shortcoming, since the real p_{H2O} near the membranes cannot be measured directly. To obtain the water vapor partial pressure (p_{H2O}) in the mixture of He and H₂O, p_{H2O} is estimated according to the following assumptions:

- 1. The flow is steady.
- 2. Ideal gases are used.
- 3. The water vapor pressure above the water is the equilibrium vapor pressure at the current pressure and temperature.

Hence, the carrier gas, He in this report, is saturated with the water vapor at a constant temperature. The porous sieve is used to maximize the contact interface of water and gas bubbles. As a result, various p_{H2O} are obtained by adjusting the temperature of the liquid bath. The saturated p_{H2O} at the constant temperature is independent on the total pressure above water in the low-pressure range (e.g. lower than 5 bar), and therefore, the saturated p_{H2O} can be obtained from the Handbook of Physical Chemistry at 1 atmosphere of total pressure [65].

The wet gases from the water bottle are heated by a heating rope around the gas tubes to avoid the condensation of water vapor before the gases reach the membrane during all experiments.

When the liquid used in the bath (Julabo F25, Germany) is water, the lowest bath temperature is 4°C. However, in order to achieve very low p_{H2O} near the silica membrane, additional He is mixed with the wet He flow by a modified wet gas delivery system to dilute

the concentration of water vapor (Fig. 2.2). The flow of gas is controlled by the calibrated Mass Flow Controllers (MFC).



Fig. 2.2 Normal (A) and modified (B) wet gas delivery systems

2.2.2 Gas permeation

Setup

The setup for gas permeation is showed schematically in Fig 2.3. The studied membrane is placed in a steel cell and sealed with rubber rings, and the He permeance at dry and water vapor atmospheres is measured by regulating the adjustable valve to be shut down completely or properly opened, respectively. The valve is operated in such way to keep a certain pressure difference between the feed gas and permeate side. The flow of permeate gas is measured by a soap flowmeter after the gas is dried by silica gel with moisture indicator in a long U-shape tube.



Fig. 2.3 Homemade gas permeation setup MFC: mass flow controller; PC: pressure controller; PM: pressure meter

Permeation measurement

Prior to the measurements, it is essential to remove the physisorbed water molecules from the silica layer by a process called *outgassing* that takes place at 200°C [34,38] for about 24 hours under a He flow and a high pressure difference (~3 bars), until the He flux is stable. The samples with high permselectivity (α (He/CH₄)>100 at 200°C) are adopted, i.e. the membranes are considered to be crack-free.

The He flux (F_{He}) is obtained by normalizing the flow (N) of dry He at the permeate side with the membrane area (S) and pressure difference (ΔP) between the feed and permeate side. ΔP is measured by PM in Fig 2.3, assuming no pressure loss from PM to the membrane. ΔP is kept at about 3.0 bar, rendering p_{H2O} negligible compared to ΔP .

When F_{He} is stable at certain water vapor pressure, the flow of water vapor at permeate side is calculated by the weight increase of silica gel over a long time (e.g 12 hours). The silica gel is held in a long U-shape glass tube to make sure that all the water vapor is absorbed from the wet gas mixture at the permeate side. However, this method is not accurate, since the concentration of water vapor is very low at the permeate side and the increase of weight is very small. But it can provide a rough estimate of water vapor flow, in order to compare it with He flow.

He flux through the silica membrane is measured at different temperatures of water $(T(H_2O))$ while the temperature of membrane (T(mem)) is kept at 50 or 90°C. Since the studied silica membrane is considered to be stable in the presence of water vapor below 100°C, the selected T(mem) ensure a sufficient variation in H₂O mobility, compared to the much higher mobility of inert He gas. T(H₂O) is increased gradually, with the highest T(H₂O) being slightly lower than T(mem), and thus avoiding the condensation of water vapor in the membrane.

2.2.3 Ellipsometry

Ellipsometer

The ellipsometry experiments are carried out in the Solid State Physics Group at the University of Twente, by a homemade ellipsometer (Fig 2.4). The light beam comes from the source of Xe lamp, and then passes through a filter and a rotating polarizer. Consequently, the polarized light is reflected by a sample, and then analyzed. Two parameters ($\tan \psi$ and Δ), related to the optical properties of the sample, are measured. The studied membrane is placed in a special cell [64] (Fig 2.5). The cell contains double glass walls, heated up by an external oil bath, maintaining the temperature. Quartz windows are placed vertically at the end of the tubes to accommodate the passing light beam. The angle relative to the normal of the sample





Fig. 2.4 Scheme of a homemade ellipsometer

Fig. 2.5 The cell for ellipsometry experiment [64]

surface is ~64.5° to keep $\cos\Delta$ close to ± 1 [50]. Furthermore, the cell contains a lamp and a thermocouple behind the sample, the former being an accessory heater to obtain the temperatures higher than the maximum oil bath temperature (110°C). The gas delivery system is similar to that used in gas permeation experiments with the same total He flow (~60 ml/min).

Measurement

After placing the membrane into the cell, ellipsometer is aligned and calibrated to obtain a good signal. Prior to the measurements, the outgassing is carried out for about 24 hours at 185°C. The outgassing temperature is slightly lower than that in gas permeation experiment (200°C) due to the heater limitation. The brightness of the lamp within the cell disturbs the signal and causes that the process of outgassing cannot be recorded *in situ* (Replacing the lamp with an electric heater was an option to solve this problem). A one-day outgassing is considered to be sufficient based on the result of gas permeation experiments.

Two scanning modes are applied to characterize the sorption of water vapor in the silica layer: *energy scan* and *time scan*. When the sorption reaches its equilibrium at each water vapor pressure, the *energy scan* is performed over the range of energy values from 1.5 to 3 eV, to obtain optical properties of silica layer and determine a suitable energy value for the *time scan* series. For the investigated sorption process, the higher the optical sensitivity at certain E values, the better the data to calculate the coverage of water vapor on the silica surface. For example, the energy value, 2.2 eV, where all *energy scans* overlap, is not suitable for the *time scans*, whereas E=2.35 eV is more appropriate (Fig. 2.6).

Time scan is utilized to measure the process of adsorption and desorption in time. With the *time scan* mode, a plateau region is obtained from these scans, indicating the equilibrium at a certain p_{H2O} during adsorption/desorption. *Time scan* is performed at a single wavelength estimated by the *energy scans*.

The same temperatures (i.e. 50 and 90°C) and conditions (e.g. gas flow) as those in gas permeation experiments are applied during the ellipsometry measurements.



Fig. 2.6 Energy scans at different temperatures of water bath $(T(H_2O))$ where the membrane temperature (T(mem)) is 90°C

Coverage vs tany

Since silica is a transparent material, $\cos\Delta$ remains constant (±1) and $\tan\psi$ suffices as the only measured parameter related to the water vapor sorption.

Tan ψ has been proved to be linearly proportional to the adsorbate coverage θ [62], making it possible to relate tan ψ and θ . Consequently, tan ψ is substituted by θ as follows:

$$\theta_{\psi} = \frac{|\tan\psi_0 - \tan\psi|}{|\tan\psi_0 - \tan\psi_{sat}|}$$
(2.1)

Where θ_{ψ} is the coverage calculated from ellipsometry experiments.

 $tan\psi_0$ is the value of $tan\psi$ without water vapor (i.e. the dry value)

tan ψ is the value at a certain p_{H2O}

 $tan\psi_{sat}$ is obtained by extrapolating $tan\psi$ value with the first-order Langmuir isotherm, and is the theoretically maximum value.

Chapter 3 Results

3.1 Gas permeation in the presence of water vapor

Prior to the gas permeation experiment, an outgassing process is carried out at 200°C with a dry He flush, He flux becomes stable after approximately 24 hours with a small fluctuation, shown in Fig. 3.1, indicating that a one-day outgassing is sufficient to remove the physisorbed H₂O molecules in the pores of silica layer.



Fig. 3.1 Time dependence of He flux at 200°C during the outgassing process



Fig. 3.2 He flux over time at different $T(H_2O)$ and T(mem)=50 and $90^{\circ}C$ Where the numbers in the bracket (1/N) denote the ratio of the wet and dry He flow

As soon as water vapor is applied to the silica membrane, F_{He} decreases dramatically at both T(mem) (i.e. 50 and 90°C) (Fig 3.2). For each T(H₂O), F_{He} becomes stable after a long time (~one day). The performance of gas permeation indicates that the effect of water vapor on the gas permeation is significant, even at low T(H₂O).

Water vapor partial pressure (p_{H2O}) around the membrane is assumed to be the saturated p_{H2O} at corresponding temperature under 1 atmosphere of total pressure. Consequently, Fig 3.3 is obtained by using the value of stable flux at each T(H₂O). In the low p_{H2O} range, F_{He} decreases quickly, and it progresses slowly in the high p_{H2O} range.



Fig. 3.3 He permeance (F_{He}) as a function of p_{H2O} at T(mem)= 50 and 90°C

Since the mobility of gas molecules increases with increasing temperature, the initial value, i.e. F_{He} values without water vapor ($F_{He}(dry)$), is dependent on T(mem). Fig 3.4 is obtained by normalizing F_{He} with $F_{He}(dry)$. The lowest F_{He} after water vapor adsorption are only ~2% and ~11% of $F_{He}(dry)$ for T(mem)= 50 and 90°C, respectively, implying that this effect play a more important role at the lower T(mem), which is in accordance with the lower mobility of the pore-blocking component (H₂O).



Fig. 3.4 The dependence of normalized F_{He} and p_{H2O} at T(mem)= 50 and 90°C

Although to a small extent, water vapor is permeating through the membrane due to the presence of the potential gradient of pressure and concentration from the feed gas side to the permeate one. The flow of water vapor is two-order of magnitude lower than that of He at the same conditions, even in the range of high occupancy (Table 3.1), and H₂O flow hardly changes largely with p_{H2O} and θ_{W} .

T(H ₂ O)	<i>р_{Н20}</i>	ΔΡ	Coverage θ_{ψ}	H ₂ O flow	He flow
(°C)	(kPa)	(kPa)		(ml/min)	(ml/min)
10.0	1.23	384	0.369	2.93E-02	5.43
25.0	3.17	385	0.588	4.55E-02	4.44
40.0	7.38	384	0.703	8.34E-02	4.19
60.0	19.92	383	0.802	4.09E-02	3.89
75.0	38.54	383	0.858	4.72E-02	3.81
89.0	67.47	383	0.930	4.12E-02	3.58

Table 3.1 Comparison of He and water vapor flows at T(mem)=90°C

Note: Coverage θ_{ψ} is calculated from Equation (2.1) with the data from ellipsometry experiments

3.2 Water vapor adsorption in the microporous silica layer

After complete *outgassing*, the sorption of water vapor is measured *in situ* by ellipsometry. The parameter $tan\psi$ obtained from the ellipsometer changes with the amount of H₂O molecules absorbed in the silica layer.

A typical series of changes in tan ψ due to the water vapor adsorption in the silica layer measured by the mode of *time scan* are shown in Fig 3.5. T(H₂O) is increased gradually by controlling the water bath temperature. For the dry sample and each T(H₂O), *energy scans* are carried out after a stable tan ψ is obtained, corresponding to the flat regions of Fig 3.5, yielding Fig 3.6 and Fig 3.7. The energies used for *time scans* are determined by the *energy scan* experiment at the dry condition (see Fig. 2.6).



Fig. 3.5 *Time scans* for H₂O adsorption in the silica layer at a constant T(mem) and different T(H₂O) conditions
Where the numbers in the bracket (1/N) denote the ratio of the wet and dry He flow



Fig. 3.6 Energy scans for the equilibrium of water vapor adsorption at T(mem)=50°C



Fig. 3.7 Energy scans for the equilibrium of water vapor adsorption at T(mem)=90°C

To calculate coverage θ from tan ψ , the tan ψ values at corresponding T(H₂O) are obtained from the flat region of the *time scan* series. As mentioned in Chapter 2, tan ψ_{sat} is derived by extrapolating tan ψ value with the first-order Langmuir isotherm [64]. The detailed values are listed in Table 3.2 & 3.3.

$T(H_2O)($ °C $)$	p_{H2O} (kPa)	tanψ (-)	Coverage θ_{ψ}
Dry	0	0.3006	0
4.0(1/8)	0.10	0.2886	0.179
4.0(1/4)	0.20	0.2836	0.252
4.0(1/2)	0.41	0.2774	0.344
4.0	0.81	0.2667	0.503
10.0	1.23	0.2596	0.607
25.0	3.17	0.2418	0.872
40.0	7.38	0.2374	0.936
49.0	11.74	_	0.959

Table 3.2 Adsorption parameters of water vapor at T(mem)=50°C, tany_{sat}=0.2331 and E=2.60 eV

T(H ₂ O)(°C)	p_{H2O} (kPa)	tanψ (-)	Coverage θ_{ψ}
Dry	0	0.3244	0
4.0(1/6)	0.14	0.3120	0.240
4.0(1/3)	0.27	0.3101	0.276
4.0	0.81	0.3033	0.409
10.0	1.23	0.3002	0.469
25.0	3.17	0.2869	0.728
40.0	7.38	0.2830	0.802
60.0	19.92	0.2798	0.865
75.0	38.54	0.2758	0.942
89.0	67.47	-	0.965

Table 3.3 Adsorption parameters of water vapor at T(mem)=90°C, tan ψ_{sat} =0.2728 and E= 2.40 eV Note: tan ψ_{sat} and the *italic* numbers are derived by the first-order Langmuir isotherm; coverage θ_{ψ} is calculated from Equation (2.1). Based on the above calculation, the isotherms of water vapor adsorption are obtained, as shown in Fig 3.8. According to the IUPAC classification, they are typical isotherms of gas adsorption in microporous materials, where the coverage increases dramatically in the low p_{H2O} range. Larger K value occurs at the lower T(mem), indicating a stronger interaction between H₂O molecules and the silica surface. The isotherms comply with the first-order Langmuir isotherm, except in the low p_{H2O} range where the real coverage is slightly higher than the fit curve.



Fig. 3.8 Isotherms of water vapor adsorption at 50 and 90°C $K = k_a / k_d$ is the adsorption equilibrium constant, calculated from the first-order Langmuir isotherm where the pressure is in [kPa]

In order to investigate the existence of multilayer adsorption, the adsorption in the high p_{H2O} range is measured again to include more points during a consequent set of measurements at T(mem)= 50°C, as shown in Fig 3.9. The results indicate that the mesopores and large defects are absent in the studied membrane.





Chapter 4 Discussion

4.1 Influence of water vapor on gas permeation

At the studied relatively low T(mem), the influence of water vapor on the gas permeation through the microporous silica membrane is obvious, even in the low p_{H2O} range. At high p_{H2O} range, water vapor almost suppresses the movement of He. Similar phenomena have neen observed in the previous research of silica membrane [7,30], as well as in the system of zeolites [49,66]. At high temperatures and in water vapor atmosphere, silica membrane could be viscously sintered or damaged [7]. Since the studied membranes are sintered at 600°C for 3 hours, viscous sintering and deterioration would not happen at low temperatures below 100°C, although some researchers claimed that these would be the case at 110°C [67]. Rehydration is also avoided at such low temperatures [39], and thus we believe that the pore size and microstructure remained unchanged during our experiments.

The gas transport in a multi-component mixture depends largely on the adsorption capacity of different gas molecules. As a result, the immobile and strongly absorbing component blocks the movement of the mobile and weakly absorbing one significantly [16-17]. At the investigated temperatures, polar H_2O molecules are relatively immobile compared to the inert He (Table 3.1), due to the presence of unsaturated Si atoms, hydroxyl groups and strained siloxane bridges in the silica layer that serve as adsorption sites for H_2O molecules. The lower the temperature, the stronger the interaction between H_2O molecules and polar silica surface, resulting in a stronger blocking effect of H_2O molecules on the inert gas permeation at lower temperature.

Although He flux decreases to a large extent in presence of water vapor, it does not vanish under the investigated conditions. The reasons may be the following: first, the adsorbed H₂O molecules diffuse along the concentration gradient through the pores, and thus He can transport along with H₂O. However, even at high p_{H2O} , He flow is still much higher than H₂O flow (Table 3.1). Second, even if all active sites are occupied by H₂O molecules, perhaps there are some big pores in the silica membrane, resulting in the suppressed He transport along the pore surface, but allowing the He transport along the center of these big pores. As a result, F_{He} at the highest p_{H2O} are ~2% and ~11% of F_{He}(dry) for T(mem)= 50 and 90°C, respectively.

4.2 Water vapor adsorption in the microporous silica layer

The obtained adsorption isotherms of water vapor in the silica layer are the characteristic in the microporous materials, according to the IUPAC classification, and they generally comply with the first-order Langmuir isotherm. The results are consistent with the literature [45, 47-49, 64, 70]. The studied silica layer has an average pore size of ~4 Å, slightly bigger than the kinetic diameter of the polar H₂O molecule (2.65 Å) which has a strong interaction with the active sites on the adsorbent (silica): unsaturated Si atoms, free hydroxyl groups and strained siloxane bridges [71]. As a result, at the low p_{H2O} range coverage θ increases dramatically, which causes a large decrease in He flux in the gas permeation experiment. The greater the K value, the stronger the interaction of the adsorbates and adsorbents, and hence, the more molecules are absorbed at lower temperature.

A small deviation of measured points from the ideal Langmuir isotherm may be due to the heterogeneous adsorption. Basically, the first-order Langmuir isotherm assumes energetically equivalent adsorption sites. However, polarized H₂O molecules can be absorbed on several types of active sites in the following order of decreasing enthalpies of interaction: unsaturated Si atoms, free hydroxyls and siloxanes. Although the amount of unsaturated Si atoms is small, their interaction with H₂O molecules is likely to be very strong, and thus these sites are first occupied [37]; free hydroxyl groups are hydrophilic, interacting with H₂O molecules *via* only one hydrogen bond and the enthalpy of interaction is below the enthalpy of liquefaction of water (44 kJ/mol) [41]. Most H₂O molecules are absorbed on these abundant hydrophilic sites at the beginning of adsorption, while the siloxane bridges are hydrophobic, except in the case of the strained ones, and they play a more important role in the smaller pores due to their large population. The enthalpy of interaction between H₂O molecules and silica decreases with increasing the coverage/pressure. Therefore, the heterogeneous adsorption can be the reason that the real adsorption isotherm deviates from the ideal first-order Langmuir isotherm, with significant deviations in the low pressure range because the stronger interaction makes the real coverage higher than the prediction from the ideal first-order Langmuir.

The absence of multilayer adsorption indicates that all the pores are in the range of micropores and that the studied membranes are crack-free.

4.3 Percolation effect

Distinct decrease of the mobile component (He) permeance with increasing coverage of the immobile component (H₂O) (Fig. 4.1) at investigated temperatures is indicative of the percolation behavior, which is more pronounced at lower temperature, where the mobility of molecules is lower.



Fig. 4.1 The dependence of He permeance on the coverage θ of water vapor at T(mem)= 50 and 90°C(a) real He flux (b) normalized He flux

The basic assumptions from Section 1.2.2.2, implying incontinuous movement of the gas molecules in the narrow pores are appropriate in case of the ideal lattice representation of the microporous material, and consequently, it is suitable only for the qualitative analysis of the transport phenomena considered in this study, since the real pore network in the silica layer is more complex. Optionally, a narrow pore can be imagined as a rolled 2-D lattice (Fig. 4.2),

where gas molecules are hopping from one to the other near unoccupied site under the gradient in chemical potential and pressure.



Fig. 4.2 The concept of an unfolded pore and gas hopping in a 2-D lattice

Filled circle represents the site with one molecule (occupied), intersection represents a vacancy (unoccupied) and arrow represents the hopping of molecules

A narrow pore can be imagined as a cylinder obtained by closing the 2-D lattice along the two blue horizontal borderlines



Fig. 4.3 Percolation in a 2-D lattice

Filled and unfilled circles denote the immobile and mobile molecules, respectively.

Arrow represents the hopping direction of molecules

(A) When a small amount of immobile molecules is present in the lattice, the mobile

molecules can transport through the network

(B) When more sites are occupied by the immobile molecules, the movement of the mobile molecules is blocked, denoted by the dashed line.

In case of a binary mixture of components greatly differing in mobility that diffuse through a porous medium, percolation can happen when a connected cluster of immobile molecules extends from one side of the lattice to the other. When the coverage of immobile molecules is beyond the percolation threshold, the mobile molecules can hardly move through the lattice, even under a large potential gradient (Fig. 4.3).

In such a lattice, the coordination number of an active site, indicating the degree of freedom (here referred to as site connectivity), may be higher than that in the 2-D lattice, since the molecules can also jump to the sites on the opposite wall of the narrow pore, rather than only be confined in the lattice plane. The high percolation threshold observed in Fig. 4.1 also implies that the investigated silica pore is more complex (irregular, heterogeneous, with the molecules hopping in the lattice at different frequencies) than the ideal 2-D lattice model. Therefore, the irregular lattice, heterogeneous sites and gas molecules hopping to the sites on the opposite wall of narrow pores may cause the percolation to happen at the high coverage of immobile H_2O .

In principle, He flux should vanish when the percolation occurs. Certain low He flux at high H_2O coverage may be caused by the presence of larger pores in which the basic assumptions (Section 1.2.2.2) are not valid, since He molecules can be transported along the pore center, rather than by hopping over the lattice sites. On the other hand, H_2O molecules may also permeate slowly through the membrane due to the chemical potential gradient and He can move along with them. But the contribution from the movement of H_2O is less than that from the big pores, since H_2O flow is much lower than He flow even at high temperature (Table 3.1).

However, regardless of the chosen lattice model for the silica material, the presence of percolation behavior should be taken into account when using standard mass transport descriptions in the field of membrane separation, e.g. Maxwell-Stefan theory, which does not incorporate the percolation phenomena, since it only predicts a linear relationship of coverage of the immobile component and diffusivity of the mobile component. The relevance of this percolation behavior for the validity of MS theory was shown by Benes et al [13] (see Fig 1.3 in this report) by Monte Carlo simulations, and is experimentally qualitatively observed in this study.

Chapter 5 Conclusions

Based on the detailed discussion, some concise conclusions are given:

- He flux through the silica membrane decreases dramatically in the presence of water vapor, even in the low p_{H2O} range due to the effect of blocking by the strongly absorbed H₂O molecules.
- Ellipsometry is a sensitive and nondestructive characterization technique and thus suitable to study the sorption phenomenon *in situ* in the actual membrane layers, where other convenient methods (e.g. gravimetric and volumetric methods) fail.
- The isotherms of water vapor adsorption in the silica layer obtained from ellipsometry are of Type I according to the IUPAC classification, complying with the typical adsorption behavior in the microporous materials. These results are in accordance with the average pore size of the studied silica membrane (~4 Å). The adsorption isotherms generally comply with the first-order Langmuir isotherm, with a slight deviation probably caused by the heterogeneous adsorption of H₂O molecules at different active sites on the silica surface.
- The transport of gas molecules through such small silica pores can be envisioned by assuming that the gas molecules are hopping from one occupied sites to the other unoccupied ones under the potential gradient.
- Because of the strong interaction with silica surface, H₂O is immobile compared to the inert He. For the increased coverage of water vapor, He permeance is affected by the percolation phenomena. The irregular lattice, heterogeneous sites and gas molecules hopping to the sites on the opposite wall of narrow pores may cause the transition in normalized He flux to happen at the high coverage of immobile H₂O. He flux does not vanish even at the highest coverage of immobile H₂O molecules likely due to the presence of big pores in the silica layer.
- The presence of percolation behavior should be taken into account when using standard mass transport descriptions in the field of membrane separation, e.g. Maxwell-Stefan theory, which does not incorporate the percolation phenomena, since it only predicts a linear relationship of coverage of the immobile component and diffusivity of the mobile component.

Suggestions

Measuring the real p_{H2O} around the membrane

Although several attempts have been carried out to obtain the really saturated water vapor atmosphere by passing the gas through the water and to avoid the condensation of water vapor along the gas tubes, an obvious shortcoming in the water vapor delivery system is that the real p_{H2O} around the membrane is not obtained directly. Gas chromatography (GC) or Mass Spectroscopy (MS) would be an option, but the gas mixture should be heated before it reaches GC/MS, resulting in a more complex setup. Perhaps, putting a pressure indicator and a small humidity sensor near the membrane is the most suitable way.

Gas permeation

1) Based on percolation theory, one component should be absolutely immobile, implying that there is no driving force for their transport. Although the mobility of He and H₂O is greatly different, due to the presence of H₂O chemical potential gradient, water molecules can diffuse and even transport along with the He molecules, causing the He flow not to decrease to zero. The driving forces for H₂O diffusion include the chemical potential gradient and the friction between He and H₂O molecules. The friction should be negligible compared to the chemical potential gradient since the mass of H₂O molecule is much larger than that of He, and there is a strong interaction between polar H₂O molecule and silica. Therefore, H₂O molecules would not move in absence of the chemical potential gradient. Since chemical potential is related to the partial pressure in the gas atmosphere, the easy way to obtain such condition would be to keep the same partial pressure at feed and permeate side, shown schematically in Fig. A. Same partial pressure at feed and permeate sides $P_{\rm H2O}^{\rm I} = P_{\rm H2O}^{\rm 2}$ and $P_{\rm total}^{\rm I} = P_{\rm total}^{\rm 2}$. The carrier gas for water would be changed into methane (CH₄) at the permeate side, since its dynamic diameter is too large to pass through the narrow silica pores.



Fig. A The schematic way to study percolation

Although there would be no total pressure difference at both sides, for the inert gas, i.e. He, there would still be a concentration gradient present, enabling it to diffuse through the membrane. In case of the same water vapor pressure at both sides , H₂O molecules would not transport from side 1 to side 2, and thus, the real condition for percolation would be achieved. Consequently, the permeance of the inert gas at different water vapor pressures could be recorded under these conditions. To achieve this aim, two water baths and an MS or GC are necessary. The former would be used to generate water vapor and the later to analyze the concentration of different components in both sides. In the absence of pressure difference at the two sides, high temperature is necessary to keep the water vapor from condensing in the intermediate layer due to the capillary phenomenon, or only low water vapor pressure should be used.

Possibly, another problem can be the fact that the He permeating from side 1 to side 2 would dilute the concentration of water vapor, so that the adjusting of the water vapor pressure is necessary by changing the temperature of water bath at the permeate side during the experiment.

2) In this assignment, some relatively low temperatures are used to achieve a large difference of mobility between He and H_2O molecules and to avoid the rehydration of silica surface by water vapor. Further decrease in temperature may be beneficial for reducing the mobility of water molecules even more with regard to the expected shift of the percolation threshold to the lower coverage values. Since the mobility of H_2O increases more quickly than that of He with increasing temperature, the effect of percolation vanishes if their mobilities are similar. The behavior should comply with Maxwell-Stefan theory. Therefore, the equivalent He permeance in presence of H_2O at high temperature should be interesting.

3) The membranes with two γ -Al₂O₃ layers and two silica layers have been selected for the gas permeation to assure crack-free membrane and high selectivity, but it would be useful to measure the permeance of the membranes with single γ -Al₂O₃ and silica layers, which are consistent with the samples for ellipsometry experiment, although more defects are not desired for gas permeation.

Adsorption of water vapor

1) In this report, the coverage is calculated from the data of tan ψ from the *time scan* at constant energy. In the relative way, the amount of H₂O absorbed molecules can be calculated [52], but the necessary data from α -Al₂O₃ and γ -Al₂O₃ layers is just planed to be measured.

2) The presence of a shift from high to low energy in the *energy scans* recorded during the water vapor adsorption may indicate the possible water vapor adsorption in the γ -Al₂O₃ layer. Therefore, it is necessary to measure the adsorption in the γ -Al₂O₃ layer separately.

Desorption of water vapor

1) The desorption of water vapor from the silica layer is currently measured under a dry He flush, and the whole process is recorded *in situ* by the ellipsometer. The lower final tan ψ value (tan ψ_{final}) after desorption, compared to the initial value (tan ψ value at dry condition), indicates that the adsorption process is irreversible at the corresponding temperatures (Table A). For the desorption at 50°C, θ_{ψ} decreases from 98.0% to 22.7%, while it decreases much more from 93.0% to 15.9% at 90°C. The observed irreversible sorption at corresponding temperatures is consistent with the results of S. Inagaki *et al.* for the mesoporous silica powder [46-47].

Temperature of	tanybegin(-)	$tan\psi_{final}(-)$	$tan\psi_{dry}(-)$	Coverage	Coverage
desorption (°C)	_		_	$\theta_{\psi}(\text{begin})$	$\theta_{\psi}(\text{final})$
50.0	0.2031	0.2469	0.2644	0.98	0.227
90.0	0.2335	0.2593	0.2640	0.930	0.159

Table A. Desorption parameters measured by ellipsometry at 50 and 90°C

Note: $tan\psi_{begin}$ and coverage $\theta_{\psi}(begin)$ are the values at the beginning of desorption

 $tan\psi_{final}$ and coverage $\theta_{\psi}(final)$ are the values at the equilibrium of desorption $tan\psi_{drv}$ is the values at the dry condition

coverage θ_{ψ} is calculated from Equation (2.1)

2) Water vapor desorption at 50 and 90°C is shown in Fig B. Considerable number of H_2O molecules remain in the silica layer after desorption at the corresponding temperatures of adsorption, indicating a very strong interaction of water and silica. However, it is possible to remove all the physically absorbed H_2O molecules by significantly increasing temperature. The duration and shape of desorption curves at 50 and 90°C are different because of the difference in implemented temperatures and dry He flows.

Seemingly H_2O molecules desorbs from the silica layer in steps, indicated by the three steps in the desorption curve at 90°C (shown in Fig B). Steps could correspond to: a) the different sorption sites in the silica layer, or b) to the three distinguishably different pore sizes corresponding to the different layers of the membrane.

a) Different groups on the silica surface calcined at 600°C can be distinguished: siloxane groups, free hydroxyl groups and unsaturated Si atoms [38,40]. The heats of adsorption on these groups increase in the same order [37,41], corresponding with the increased difficulty of the H₂O desorption in the same order. From Fig. B, it seems that H₂O molecules desorb from all sites, in other words, the vibration of H₂O molecules at corresponding temperatures can overcome the energy of interactions between the adsorbates and adsorbents. Thus, H₂O

molecules on the different sites should desorb at the same time, but with different desorption rates. Therefore, there would not be a flat range between the two steps, which is in contradiction with the results of our experiment. The desorption from the confined narrow pores should be different from that from a flat surface, and the whole process should include desorption from the sites of weak interaction and diffusion along the pores. It is possible that the molecules desorbing from the sites of weak interaction are absorbed on the sites of strong one. Further study is necessary to relate the steps to the adsorption sites (e.g. by using IR reflectance spectroscopy that can give both information on type and relative amount of molecules or bonds).

b) Second, the steps may come from different layers with different pore sizes, which can be examined by changing the number of layers, to determine if the number of steps corresponds to the number of layers.



Fig. B Water vapor desorption at 50 and 90°C

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Appendix

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