

## ARTICLE

# Influence of Water Vapor on Silica Membrane: Adsorption Properties and Percolation Effect

Chun-lin Song<sup>a,b\*</sup>, Gang Liu<sup>a\*</sup>*a. Faculty of Materials and Energy, Southwest University, Chongqing 400715, China**b. Inorganic Membrane Group, MESA<sup>+</sup> Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands*

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The influence of water vapor on silica membrane with pore size of  $\sim 4$  Å has been investigated in terms of adsorption properties and percolation effect at 50 and 90 °C. Two methods are employed: spectroscopic ellipsometry for water vapor adsorption and gas permeation of binary mixture of helium and H<sub>2</sub>O. The adsorption behaviors on the silica membrane comply with the first-order Langmuir isotherm. The investigation demonstrates that helium flux through the silica membrane decreases dramatically in presence of H<sub>2</sub>O molecules. The transport of gas molecules through such small pores is believed not to be continuous any more, whereas it is reasonably assumed that the gas molecules hop from one occupied site to another unoccupied one under the potential gradient. When the coverage of H<sub>2</sub>O molecules on the silica surface increases, the dramatic decrease of helium flux could be related to percolation effect, where the adsorbed H<sub>2</sub>O molecules on the silica surface block the hopping of helium molecules.

**Key words:** Silica membrane, Percolation effect, Adsorption

## I. INTRODUCTION

The need for hydrogen has increased greatly in the last decades as raw material for chemical industry and clean fuel in car *etc.* Currently, hydrogen is produced mainly by two methods: reforming of fossil fuels and coal gasification. In both methods, hydrogen is mixed with a large quantity of non-desired components, such as light hydrocarbons, CO, CO<sub>2</sub>, H<sub>2</sub>O *etc.* [1, 2]. The purification or separation of hydrogen from these gases is compulsory. And this process can be done by means of membrane technology, which has a lot of advantages, such as low energy consumption and cost saving [1]. Silica-based membrane is one of the most promising candidates for hydrogen separation, and thus receives a lot of attentions [1–9].

For the transport of binary mixture through membrane with pore size less than 2 nm, Maxwell-Stefan (MS) theory is generally employed [10–14]. However, it is not suitable for the silica membrane with a pore size of  $\sim 4$  Å. In such a small pore, surface diffusion plays a very 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. In

this case, gas molecules transport along the surface concentration gradient. When energy barrier between neighboring sites is less than the heat of adsorption, gas molecules desorb from the wall surface and hop to the next unoccupied sites [15]. When binary mixture greatly defers in mobility due to adsorption, percolation effect occurs and the motion of mobile component tends to be suppressed [16]. The minimum value of coverage of the immobile or strong adsorbed component, above which the transport of the mobile molecules through the pores is blocked, is referred to as percolation threshold [17].

The transport behavior of binary mixture through zeolite membrane was investigated, where the studied gas mixture consisted of fast and weakly adsorbing hydrogen and slow and strongly adsorbing *n*-butane [15, 18, 19]. The flux of weakly adsorbing H<sub>2</sub> was reduced significantly compared to its single-component flux below 100 °C, while the flux of strong adsorbing *n*-butane was hardly changed in the presence of weakly adsorbing component. Benes *et al.* studied multi-component lattice gas diffusion, and predicted the percolation effect [17]. In principle, MS theory only predicts a linear relationship on the coverage of the immobile component and the diffusivity of the mobile component, and thus MS theory does not incorporate percolation effect. Thus, the standard mass transport descriptions used in the field of membrane separation (*e.g.* MS theory) should be used with caution.

Adsorption of water vapor in the different porous

\*Authors to whom correspondence should be addressed. E-mail: chunlinsong@swu.edu.cn, liugang13@swu.edu.cn, Tel.: +86-18883327083

materials has been successfully studied by ellipsometry [20–22]. Ellipsometry measures the optical properties of materials with high accuracy and precision, and is useful for studying water sorption on the silica surface. The adsorption isotherm of water vapor obtained by ellipsometry and the calculated pore size distribution in the mesoporous and microporous materials are consistent with traditional techniques, *e.g.* N<sub>2</sub>-sorption by powder sample and SEM by real film [21, 23]. However, the technique of N<sub>2</sub>-sorption which is used to measure the adsorption isotherms of water vapor by powder sample can not give exact information about the silica membrane on the  $\beta$ -alumina intermediate layer and  $\alpha$ -alumina support.

Ellipsometry is the most versatile tool to investigate adsorption isotherms of water vapor on the silica membrane. The principle is described as: first, silica is transparent, then  $k=0$ ; secondly,  $\cos\Delta$  can be  $\pm 1$  when a proper incidence angle is used [20–22]. As a result, only  $\tan\psi$  is changed by adsorption of water vapor on the silica membrane. It has also been deduced theoretically that  $\tan\psi$  is the value at a certain water vapor pressure, which is proportional to the amount of adsorbed H<sub>2</sub>O molecules by Herrero *et al.* [21]. Thus, it makes possible to relate optical parameter  $\tan\psi$  to coverage  $\theta$  by following equation,

$$\theta_\psi = \frac{|\tan\psi_0 - \tan\psi|}{|\tan\psi_0 - \tan\psi_{\text{sat}}|} \quad (1)$$

where  $\theta_\psi$  is the coverage calculated from ellipsometry experiments,  $\tan\psi_0$  is the value of  $\tan\psi$  without water vapor,  $\tan\psi_{\text{sat}}$  is obtained by extrapolating  $\tan\psi$  value with the first-order Langmuir isotherm, and is the theoretical maximum value.

In this study, the adsorption of water vapor in the silica membrane was measured by ellipsometry. The percolation phenomenon was investigated in the case of binary mixture containing He and H<sub>2</sub>O at low temperatures, where H<sub>2</sub>O molecules tend to be absorbed on the silica surface, rather than reacting with silica. The low mobility of H<sub>2</sub>O molecules, compared to that of He, may induce the percolation effect.

## II. EXPERIMENTS

### A. Sample preparation

The sol-gel method and procedure for sample preparation had been described previously [24]. The membrane was composed of two  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers and two silica layers to achieve high selectivity for small gas molecules, like H<sub>2</sub> and He. The first  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer reduces the roughness of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support, providing a smooth surface to coat the second  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. The silica layer was sintered at 600 °C for 3 h. Each sample was employed one time in either gas permeation or el-

lipsometry experiment, to assure the consistent sample conditions prior to water vapor exposure.

### B. Experimental methods

Ellipsometry and gas permeation are used to analyze the adsorption of water vapor and percolation in the case of He transport through the silica membranes. H<sub>2</sub>O and He were used for the gas permeation experiment, since they have similar kinetic diameter (2.60 and 2.65 Å for He and H<sub>2</sub>O, respectively), and both of them can enter the narrow pores in the silica layer without size exclusion, with the probability of entering the pores related to the component concentration. The variation of He permeance in the presence of water vapor was measured directly as water vapor pressure was increased. Ellipsometry was used to study the adsorption of water vapor.

#### 1. Water vapor generator

An easy way to supply a gaseous mixture with the water vapor is letting a gas flow enter water. The carrier gas, He in this study, was saturated with the water vapor at a constant temperature. Various water vapor pressures were obtained by adjusting the temperature of water. The wet gases were heated by a heating rope around the gas tubes to avoid the condensation of water vapor before the gases reached the membrane during all experiments. In order to achieve very low water vapor pressures, additional He was mixed with the wet gas flow to dilute the concentration of water vapor.

#### 2. Gas permeation

The studied membrane was placed in a steel cell and sealed with rubber rings, and He permeance at dry or wet atmospheres was measured. The flux of permeating gas was measured by a soap flowmeter after the gas was dried by silica gel in a long U-shape tube.

Prior to the measurements, it is essential to remove the physisorbed water molecules from the silica layer by a process called outgassing that took place at 200 °C for about 24 h under a dry He flow, until He flux was stable. To ensure that the membranes were crack-free, only the samples with high permselectivity ( $\alpha(\text{He}/\text{CH}_4) > 100$  at 200 °C) were adopted. According to the kinetic diameter of CH<sub>4</sub>, the pore size of silica membrane was  $\sim 4$  Å in this study.

He permeance ( $F_{\text{He}}$ ) was obtained by normalizing the flux of He at the permeate side with membrane area ( $S$ ) and pressure difference ( $\Delta p$ ) between the feed and permeate side.  $\Delta p$  was kept at 3.0 bar. When  $F_{\text{He}}$  was stable at certain water vapor pressure, the flux of water vapor at permeate side was calculated by the weight increase of silica gel over a long time (at least 12 h).

The silica gel was held in a long U-shape glass tube to ensure that all the water vapor was absorbed from the wet gas mixture at the permeate side. However, the measurement of water vapor flux was not accurate, since the concentration of water vapor was very low at the permeate side and the weight increase of silica gel was very small. Nevertheless, it provided a rough estimate of water vapor flux, in order to compare with He flux.  $F_{\text{He}}$  through the silica membrane was measured 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 experimental temperatures also ensure a sufficient variation of H<sub>2</sub>O mobility.

### 3. Ellipsometry

The ellipsometry experiments were carried out in the Solid State Physics Group at the University of Twente, by a homemade ellipsometer, described in the literature [25]. The light beam came from the source of Xe lamp, and then passed through a filter and a rotating polarizer. Consequently, polarized light was reflected by the sample, and then analyzed. Two parameters ( $\tan\psi$  and  $\Delta$ ) were measured. The studied membrane was placed in a special cell. The cell contained double glass walls, heated up by an external oil bath to maintain the temperature. Quartz windows were placed vertically at the end of the tubes to accommodate the passing light beam. The angle relative to the normal of the sample surface was  $\sim 64.5^\circ$  to keep  $\cos\Delta$  close to  $\pm 1$ . Furthermore, the cell contained a lamp and a thermocouple behind the sample, the former being an accessory heater to obtain the temperatures. The gas delivery system was similar to that used in gas permeation experiments with the same total He flow ( $\sim 60$  mL/min).

After placing the membrane into the cell, ellipsometer was aligned and calibrated to obtain a good signal. Prior to the measurements, outgassing was carried out for about 24 h at 185 °C. The outgassing temperature was slightly lower than that in gas permeation experiment (200 °C) due to the limitation from the heater. Based on the result of gas permeation experiments, 24 h-outgassing was considered to be sufficient.

Time scan mode was utilized to measure the process of adsorption. With time scan mode, a plateau region was obtained from these scans, indicating the equilibrium at a certain  $p_{\text{H}_2\text{O}}$  during adsorption. The same temperatures (*i.e.* 50 or 90 °C) and conditions (*e.g.* gas flow) as those in gas permeation experiments were applied during the ellipsometry measurements.

## III. RESULTS

### A. Gas permeation of He in the presence of water vapor

When water vapor was applied to the silica membrane,  $F_{\text{He}}$  decreases dramatically at both 50 and 90 °C,

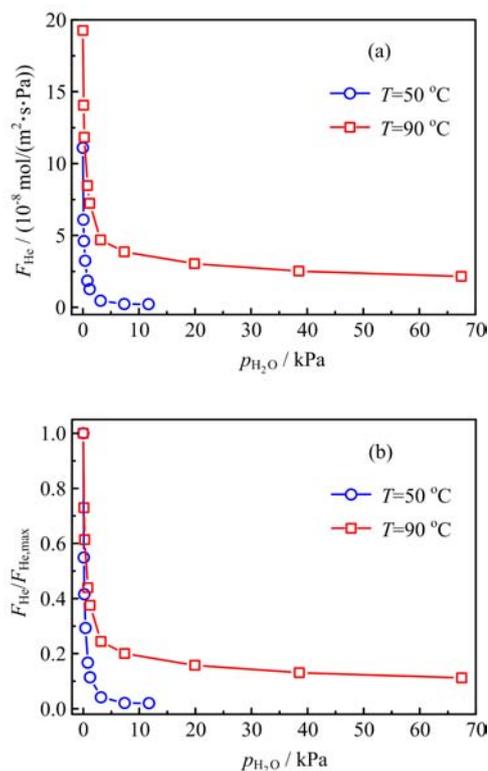


FIG. 1 He permeance ( $F_{\text{He}}$ ) (a) and relative He permeance ( $F_{\text{He}}/F_{\text{He,max}}$ ) (b) as a function of  $p_{\text{H}_2\text{O}}$  at 50 and 90 °C, taking  $F_{\text{He}}$  at  $p_{\text{H}_2\text{O}}=0$  as  $F_{\text{He,max}}$ .

TABLE I Comparison of He and water vapor flux through the silica membrane at 90 °C.

$p_{\text{H}_2\text{O}}/\text{kPa}$	H <sub>2</sub> O flux/( $\mu\text{L}/\text{min}$ )	He flux/( $\text{mL}/\text{min}$ )
1.23	29.3	5.43
3.17	45.5	4.44
7.38	83.4	4.19
19.92	40.9	3.89
38.54	47.2	3.81
67.47	41.2	3.58

shown in Fig.1(a). The performance of He permeation indicates that the effect of water vapor on the gas permeation is significant. In the low  $p_{\text{H}_2\text{O}}$  range,  $F_{\text{He}}$  decreases quickly, and it progresses slowly in the high  $p_{\text{H}_2\text{O}}$  range. Taking the data of  $F_{\text{He}}$  at  $p_{\text{H}_2\text{O}}=0$  as  $F_{\text{He,max}}$ , the relative change of  $F_{\text{He}}$  was obtained, shown in Fig.1(b). The lowest  $F_{\text{He}}$  are  $\sim 2\%$  and  $\sim 11\%$  of  $F_{\text{He,max}}$  for 50 and 90 °C, respectively.

Due to the presence of the potential gradient of pressure and concentration from the feed gas side to the permeate one, H<sub>2</sub>O molecules also permeate through the silica membrane. The flux of water vapor is two-order of magnitude lower than that of He at the same conditions, an example is indicated in Table I.

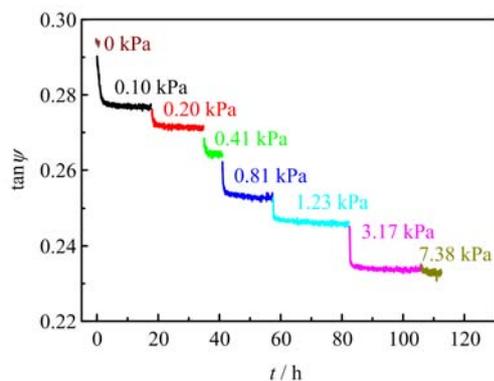


FIG. 2 Time scans at 2.60 eV for H<sub>2</sub>O adsorption at different  $p_{\text{H}_2\text{O}}$  in the silica layer.

### B. Water vapor adsorption in the microporous silica layer

After complete outgassing, adsorption of water vapor was measured *in situ* by ellipsometry. The parameter  $\tan\psi$  changes with the amount of H<sub>2</sub>O molecules adsorbed in the silica layer. A typical series of changes in  $\tan\psi$  are shown in Fig.2.

To calculate coverage  $\theta$  from  $\tan\psi$ ,  $\tan\psi$  at corresponding  $p_{\text{H}_2\text{O}}$  was obtained from the flat region of time scan series.  $\tan\psi_{\text{sat}}$  was derived by extrapolating  $\tan\psi$  value with the first-order Langmuir isotherm. Based on the above calculation, adsorption isotherms of water vapor were obtained, and shown in Fig.3. The coverage increases dramatically in the low  $p_{\text{H}_2\text{O}}$  range. In Fig.3, a larger adsorption equilibrium constant ( $K$ ) exists at the lower temperature, indicating a stronger interaction between H<sub>2</sub>O molecules and the silica surface. The isotherms comply with the first-order Langmuir isotherm.

In order to investigate the existence of multilayer adsorption, the adsorption in the high  $p_{\text{H}_2\text{O}}$  range was measured again to include more points during a consequent set of measurements at 50 °C, as shown in Fig.4. The good fitting implies no evidence of multilayer adsorption.

## IV. DISCUSSION

### A. Influence of water vapor on gas permeation

At the studied temperatures, the influence of water vapor on the gas permeation through the microporous silica membrane is significant. At high  $p_{\text{H}_2\text{O}}$  range, H<sub>2</sub>O molecules almost suppress the movement of He. Similar phenomena had been observed in the previous literature of silica membrane [26], as well as in zeolite [11, 27].

The gas transport of the 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 mo-

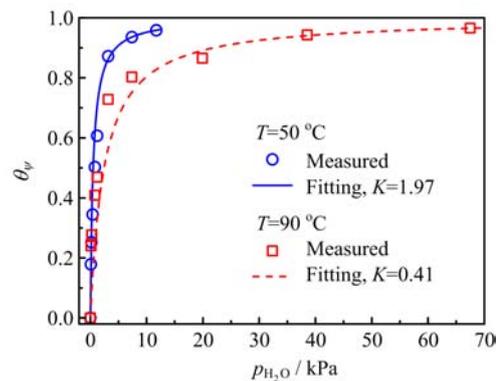


FIG. 3 Adsorption isotherms of water vapor in the silica layer at 50 and 90 °C.  $K$  is the adsorption equilibrium constant, calculated from the first-order Langmuir isotherm.

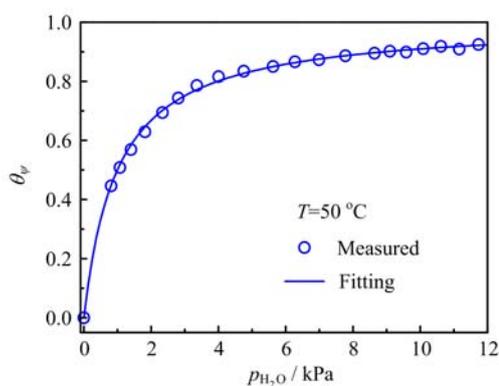


FIG. 4 Adsorption isotherm of water vapor in the silica layer at 50 °C, fitting by the Langmuir isotherm.

bile and weakly absorbing one significantly [28, 29]. Referring to Table I, polar H<sub>2</sub>O molecules are relatively immobile, because H<sub>2</sub>O molecules tend to be adsorbed on unsaturated Si atoms, hydroxyl groups and strained siloxane bridges in the silica layer. The lower the temperature, the stronger the interaction between H<sub>2</sub>O molecules and silica surface, resulting in a stronger blocking effect of H<sub>2</sub>O molecules on He permeation at lower temperature.

Although He flux decreases to a large extent in the presence of water vapor, it does not vanish under the investigated conditions. The possible explanations are: (i) the adsorbed H<sub>2</sub>O molecules diffuse along the concentration gradient through the pores, and thus He transports along with H<sub>2</sub>O; (ii) even if all active sites are occupied by H<sub>2</sub>O molecules, resulting in the suppressed He transport along the pore surface. Due to the pore distribution in the silica membrane, He could transport along the center of those big pores, even when the surface of those big pores is occupied by H<sub>2</sub>O molecules.

## B. Water vapor adsorption in the microporous silica layer

The obtained adsorption isotherms of water vapor in the silica layer are characteristic in the microporous materials, and they generally comply with the first-order Langmuir isotherm. The results are consistent with the literature [27, 30–32]. At the low  $p_{\text{H}_2\text{O}}$  range, coverage  $\theta$  increases dramatically. The greater  $K$  value implies the stronger the interaction of the adsorbates and adsorbents. The greater  $K$  value at 50 °C shows more molecules are absorbed.

## C. Percolation effect

Distinct decrease of the mobile component (He) permeance with increasing coverage of the immobile component ( $\text{H}_2\text{O}$ ) (shown in Fig.5) at investigated temperatures is indicative of percolation effect. Percolation effect is more pronounced at lower temperature, because the mobility of molecules is lower.

It is reasonably assumed that incontinuous movement of gas molecules in the narrow pores are appropriate in the case of microporous material [15]. Consequently, it is suitable for the qualitative analysis of the transport phenomena considered in this study. In the case of binary mixture of components greatly differing in mobility, percolation happens when a connected cluster of immobile molecules extends from one side to the other. When the coverage of immobile molecules is beyond the percolation threshold, the mobile molecules can hardly move through the pore, even under a large potential gradient [16].

The relative  $F_{\text{He}}$  as a function of the coverage of water vapor is shown in Fig.5. Obviously, the presence of percolation effect should be taken into account when using standard mass transport descriptions in the field of membrane separation, *e.g.* MS theory. The relevance of percolation effect for the validity of MS theory was also pointed out by Benes *et al.* [17]. It is worth noting that percolation effect was experimentally observed in this study: at 50 °C, the percolation threshold is around 0.6, and increases as the temperature increases to 90 °C. The change of percolation threshold is based on that the mobility of  $\text{H}_2\text{O}$  molecules increases with increasing temperature.

## V. CONCLUSION

Helium flux through the silica membrane decreases dramatically in the presence of  $\text{H}_2\text{O}$  molecules, due to percolation effect by the strongly absorbed  $\text{H}_2\text{O}$  molecules. The adsorption isotherms of water vapor in the silica layer comply with first-order Langmuir isotherm. Because of the strong interaction with silica surface,  $\text{H}_2\text{O}$  molecules are considered to be immobile compared to He. With increasing coverage of  $\text{H}_2\text{O}$

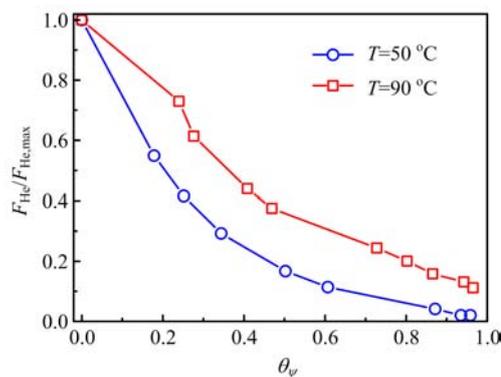


FIG. 5 The dependence of the relative He permeance ( $F_{\text{He}}/F_{\text{He,max}}$ ) on the coverage of  $\text{H}_2\text{O}$  molecules at 50 and 90 °C.

molecules on the silica surface, the decrease of He permeance can be explained by percolation effect. Thus, the presence of percolation effect should be taken into account when using standard mass transport descriptions, *e.g.* MS theory, in the field of silica membrane.

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