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Characterization of a highly selective hydrogen permeable silica membrane

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The permeability properties of a new type of silica membrane for the small gas molecules CO_2, CO, Ne, CH_4, He, and H_2 are presented. The new membrane, denoted as Nanosil, has unusually high permeance for H_2, but also allows passage of He and to a smaller extent Ne, while excluding all other molecules. The membrane is formed by the decomposition of a silica precursor (tetraethyl orthosilicate) onto a Vycor glass substrate. Nitrogen physisorption isotherms of the Vycor glass substrate indicate that it is a microporous solid with slit-like pores of 3.6 nm diameter, that remains unchanged after the silica deposition. Atomic force microscopy (AFM) shows that the Vycor substrate is made up of rectangular plate-like elements of size 90 nm $\times$ 30 nm. Between the plates are found rectangular features of 4 nm breadth which are likely to be the pore mouths. The deposited silica forms a thin layer on top of these plates so as to erase fine structures and increase the average feature size to 110 nm $\times$ 50 nm.

1. Introduction

There has been considerable work reported on Vycor glass membranes [1, 2] as well as microporous silica membranes formed on inert inorganic supports such as alumina [3, 4], silica, zeolites [5], and glass [6, 7]. A recent report describes the preparation of a silica membrane deposited on Vycor glass and it's application in a membrane reactor for the conversion of methane and carbon dioxide [8]. This membrane, referred to as Nanosil, has high selectivity to hydrogen while maintaining the permeability of the original Vycor material. In this work we compare the permeability properties of the Nanosil and Vycor glass membranes, and report atomic force microscopy (AFM) images of both membrane surfaces at nanometer resolution. These images are the first application of AFM to this system, and allow visualization of the plate-like structure of the surface.

Membranes formed by the deposition of silica on Vycor glass have been reported in a number of studies. The Nanosil membrane described here differs from those of previous work in the method of preparation. For example, in one early study the silica was formed by the oxidation of SiH_4 with molecular oxygen [7]. This resulted in only moderate hydrogen selectivities and poor stabilities. In the work that was the immediate predecessor of the present study, the precursor was tetraethyl orthosilicate (TEOS) and it was decomposed at low temperature in the presence of water vapor [9] and oxygen [10]. This resulted in good selectivities to hydrogen, but permeabilities lower by tenfold over the original glass substrate. In this study we also employ TEOS as a precursor, but decompose it at an elevated temperature in an inert atmosphere. This results in a membrane with excellent permeability, high selectivity to hydrogen, and high stability.

2. Experimental

The Vycor glass membrane was purchased commercially (Corning 7930) and had a nominal pore size of 4 nm. It had a tubular geometry with an OD of 10 mm and a thickness of 1 mm. The Nanosil membrane was prepared by a chemical vapor deposition (CVD) modification of the Vycor membrane which resulted in the formation of a thin layer of silica on the surface of the Vycor glass. Briefly, the CVD procedure was carried out in a concentric tubular apparatus with the outer tube consisting of solid quartz and the inner tube holding the Vycor glass. The Vycor glass itself was a 4 cm long central section glassblown to two pieces of quartz tubing. Flows of argon were established on the outer shell side (20 μmol/s) and inner tube side (8 μmol/s) and the temperature was raised to 873 K. (Flow rates in μmol/s can be converted to cm^3 (NTP)/min by multiplication by 1.5). A flow of tetraethyl orthosilicate (TEOS,

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Aldrich, 98%) introduced through a bubbler (at 298 K) using Ar (3 μmol/s) as the carrier gas, was added to the tube side Ar flow and passed over the Vycor membrane for 12 h. More details on the preparation and stability properties of the membrane are provided elsewhere [11].

Individual gas permeabilities were determined by flowing 20 μmol s^{-1} of the pure gas at 123 kPa in the shell side and measuring the tube side (at atmospheric pressure) flow rate using a sensitive bubble flow meter. The permeance (P_i) (mol m^{-2} s^{-1} Pa) of the individual gases were obtained from the expression $P_i = Q_i/A\Delta P$, where Q_i is the flow rate on the tube side (mol s^{-1}), A is the cross sectional area (m^2) of the membrane available for diffusion, and ΔP is the pressure difference (Pa) between the shell and tube side. Characterization of the membranes by N_2 physisorption was carried out in a volumetric unit (Micromeritics ASAP 2000). Pore size distributions were obtained by applying the Barrett, Joyner and Halenda (BJH) method to the nitrogen desorption isotherm.

AFM measurements were performed with a high vacuum scanning probe microscope (JEOL JSTM 4200X). The samples were evacuated inside the microscope for two days prior to measurements to remove water layers on the surface of the samples. Without this evacuation, the water layers degraded the quality of the sample images. A cantilever with a pyramidal tip of SiN (Olympus) was used as the probe sensor. The force constant of the lever was 0.02 N m^{-1}. The surface structure of the sample was determined in the contact mode to obtain the topography. For this measurement a constant force of ~0.3 nN was set between the tip and the sample.

3. Results and discussion

The pore size distribution of the Vycor membrane determined by porosimetry was unimodal and narrow, with a mean pore size of 3.6 nm and a standard deviation of 0.5 nm (Fig. 1). There was no change in this distribution after deposition of the silica layer to form the Nanosil membrane. Evidently the pore volume contributed by the silica was negligible or inaccessible to the nitrogen adsorbent. The pore size of 3.6 nm fell in the region of Knudsen diffusion (equation 1) [12],

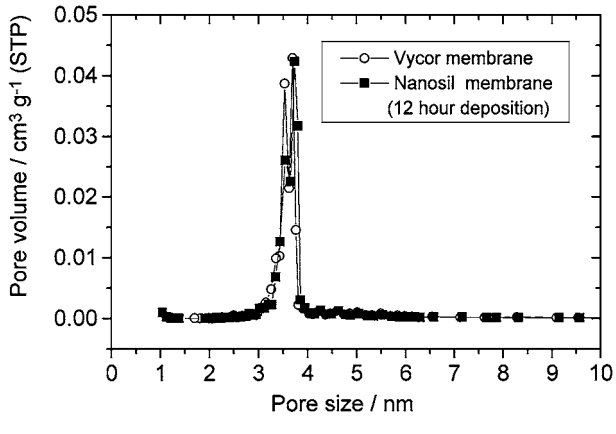

Figure 1 Pore size distributions of the Vycor and Nanosil membranes.

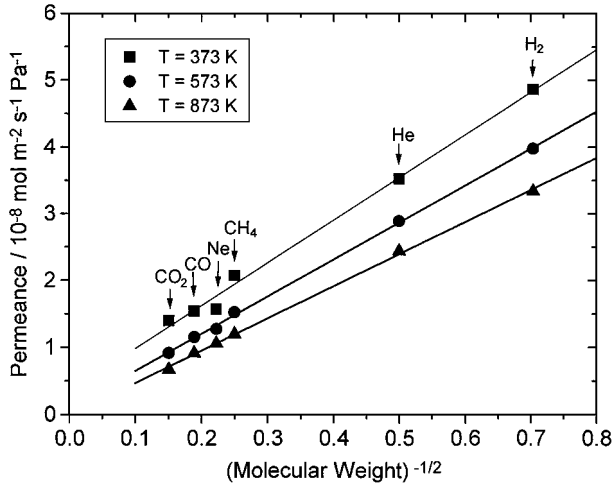

Figure 2 Permeance of light gases through the Vycor membrane.

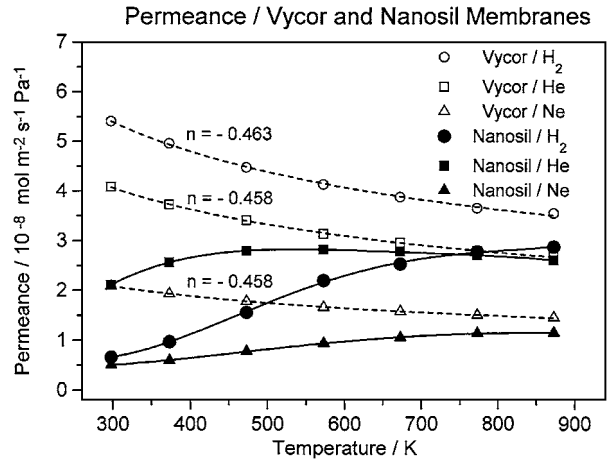

Figure 3 Temperature dependence of permeability through the Vycor and Nanosil membranes.

$$F_K = \frac{\varepsilon d_P}{\tau L}\left(\frac{8}{9\pi MRT}\right)^{1/2} = A\left(\frac{1}{T}\right)^{1/2} \quad (1)$$

$$A = \frac{\varepsilon d_P}{\tau L}\left(\frac{8}{9\pi MR}\right)^{1/2} \quad (2)$$

In these equations F_k is the permeance (mol m^{-2} $s^{-1}Pa^{-1}$), ε is the porosity, d_P is the pore diameter (m), τ is the tortuosity, L is the membrane thickness (m), R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is the temperature (K), and M is the molecular weight (kg mol^{-1}).

For the Vycor membrane it was found that the permeability of the series of gases comprising CO_2, CO, Ne, CH_4, He, and H_2 followed roughly the Knudsen equation. The effect of mass showed the expected inverse square root of molecular mass ($M^{-1/2}$) dependence (Fig. 2). The effect of temperature was close to that expected from the Knudsen equation which predicts an exponent of −0.50. The individual gases (Fig. 3, open points) gave fits with exponents of −0.458 for He, −0.463 for H_2, and −0.458 for Ne. These slight deviations from the expected value of −0.50 indicated that the transport process involved some interactions of the gases with the pore walls. The curves connecting the open points (Fig. 3) are the actual theoretical curves.

TABLE I Parameters in the Knudsen equation

Gas	n	A (exptl) mol $K^{1/2}$/ m^{-2}s Pa	A (calc) mol $K^{1/2}$/ m^{-2}s Pa	χ^2
He	−0.458	5.353×10^{-7}	4.529×10^{-7}	2.556×10^{-19}
H_2	−0.463	7.554×10^{-7}	6.392×10^{-7}	4.820×10^{-19}
Ne	−0.458	2.384×10^{-7}	2.018×10^{-7}	2.971×10^{-19}

The parameters are given in Table I, including the χ^2 values, which confirm the excellence of fit.

Values of the group $A = \frac{\varepsilon d_p}{\tau L}(\frac{8}{9\pi MR})^{1/2}$ (equation 2) were calculated using as parameters, $\varepsilon = 0.28$ [13, 14], $d_p = 3.6 \times 10^{-9}$ m, $\tau = 5.9$[15, 16], $L = 1.1 \times 10^{-3}$ m. All of these are experimental quantities and the excellent agreement between calculated and measured A values without adjustable parameters indicate that the Knudsen model is a reasonable description of the permeance of the gases through the Vycor membrane.

The permeance behavior of the Nanosil membrane displayed a completely different mass and temperature dependence from that of the Vycor membrane. Regarding mass, there was no inverse square root dependence. In fact, no other molecules aside from He, H_2 and Ne were observed to pass across the Nanosil membrane. The behavior of these small species was reminiscent of their conduct in fused silica, where they show good permeance at high temperatures [17, 18, 19]. This occurs through a solid state diffusion mechanism in which transport occurs by passage through narrow rings formed by Si-O linkages. The structure of fused silica has been described as a disordered form of β-cristobalite [20], in which solubility sites are approximately 0.30 nm in diameter [21]. The passageways consist of 5, 6, and 7 membered rings [20] which are forced to expand upon entrance of even small atoms like helium or neon. In agreement with this, the permeability also depends on the size of the diffusing species. Specifically, in solid glass permeability decreases in the order He > H_2 > Ne, which is roughly in the order of increasing kinetic diameter, but not mass. These kinetic diameters are 0.26 nm for He, 0.275 for Ne, and 0.289 nm for H_2 [22]. The enhanced permeability of H_2 in the Nanosil membrane could be due to the formation of atomic hydrogen on defects [11], but this needs to be confirmed.

Regarding temperature, the Nanosil membrane displays a completely different behavior from the Vycor substrate (Fig. 3, solid points). Instead of decreasing as temperature is increased, the permeability of the Nanosil membrane increases. This is consistent with an activated diffusion mechanism. However, the increase is not unlimited, the permeability curves of the three gases increase at first but then bend over as they near the Vycor limit. This is because the transport of species occurs in series through the Vycor and Nanosil portions, and eventually, at high temperatures the transport is limited by the Vycor. The curve for He even shows a decline, in line with the behavior for the Knudsen mechanism. The permeability of H_2 shows a dramatic increase above 400 K, eventually resulting in a greater permeability than even He. This is remarkable given that the kinetic diameter of H_2 is larger than that of He.

In order to obtain better insight into the nature of the Nanosil membrane, its structure was probed with atomic force microscopy. A direct comparison was made with the Vycor glass membrane. Since its introduction [23] AFM has been increasingly used to study inorganic materials [24] at unprecedented resolution. The technique offers considerable advantages over electron microscopy in its two common forms to study membranes. In the case of scanning electron microscopy (SEM) the resolution is not high enough, and in the case of transmission electron microscopy (TEM) sample preparation, e.g., by replica techniques, is difficult and can introduce artifacts [25]. For membranes AFM has been applied mostly for the study of polymeric membranes [26, 27, 28], although there have been reports of its use for the investigation of inorganic micro- and ultra-filtration membranes [25, 29].

Results for the Vycor and Nanosil membranes obtained in the present study are shown in Fig. 4. The top panels show images of the Vycor glass at increasing magnification. At low magnification (500×500 nm^2) the surface structure of the Vycor membrane is found to consist of rectangular, plate- or tile-like elements. These elements overlap each other like shingles on a roof, but in a random manner. At first glance most of the plates appear to be of a large size, but closer examination reveals that there are also regions between these plates containing smaller elements. Thus, the distribution of sizes appears to be bimodal. A rough count of approximately 20 plates reveal that the dimensions of the larger plates are 90 ± 15 nm $\times$ 30 ± 7 nm, while those of the smaller tiles are 30 ± 10 nm $\times$ 16 ± 4 nm. At higher magnification (100×100 nm^2) the edges between plates are visible, constituting what appear to be the pore entrances. From the highest magnification (50×50 nm^2) image the dimensions of the edge features are about 4 nm, about the order of the average pore size (3.6 nm) obtained from porosimetry. Porosimetry also indicates that the pores are slit- or rectangular-shaped supporting the view that the pores are formed by the spaces between the plates.

The bottom panels (Fig. 4) show images of the Nanosil membrane. At low magnification (500×500 nm^2) the surface structure is now seen to consist of globular, elongated particles which again overlap each other. Compared to the plate-like elements in the Vycor, these particles are more rounded and are larger, with dimensions of 110 ± 20 nm $\times$ 50 ± 13 nm. At high magnification (100×100 nm^2) it can be seen that the fine features between particles have been largely eliminated. The results are consistent with the deposition of a fine silica layer on top of the Vycor membrane. This is shown in the lower right of Fig. 4. The thickness of the layer can be approximated as 10 nm, one-half the difference between the dimensions of the Vycor plates and the Nanosil globules. This thickness is consistent with the permeability properties of the Nanosil, and is much smaller than the thickness (500 nm, 0.5 μm) achieved by conventional CVD of SiO_2 [30]. The results presented here for the

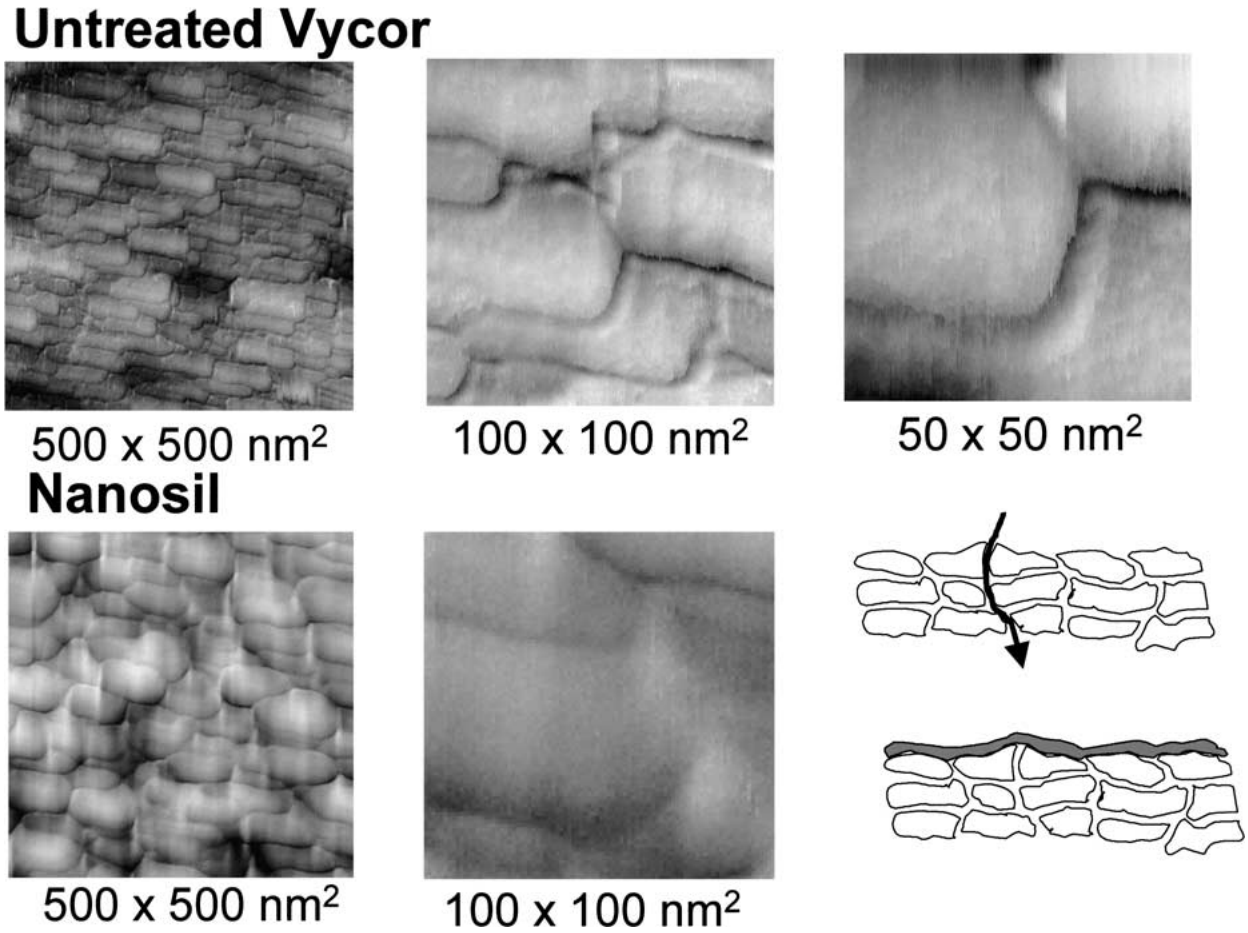

Figure 4 Atomic force micrographs of the Vycor and Nanosil membranes.

characterization of the Vycor and Nanosil membranes advance our present understanding of the materials by providing high resolution images of the surface structure not achieavable by such techniques as small angle diffraction and electron microscopy [30, 31].

4. Conclusions

A new type of composite silica membrane denoted as Nanosil was prepared by the chemical vapor deposition of a silica precursor on Vycor glass. The permeation properties of this membrane towards the small gas molecules H_2, He, Ne, CH_4, CO, and CO_2 were investigated. It was found that the permeation mechanism changed from a Knudsen type mechanism for the Vycor glass to an activated diffusion mechanism for the Nanosil membrane. Only H_2, He, and Ne permeated through the Nanosil membrane. Atomic force microscopy indicated that the Vycor consisted of plate like structures of tens of nanometers in size, and that the Nanosil membrane was formed as a thin silica layer of about 10 nm thickness on top of this structure.

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