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Microporous Silica Membrane prepared using TMOS/O_3 CVD in Opposing Reactants Geometry

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Hydrogen–perm-selective silica membranes were prepared using counter-diffusion chemical vapor deposition (CVD) from tetramethylorthosilicate and ozone precursors. Thin α-alumina tubular substrate (400 ì m thickness) was used as the support on which γ-alumina coating was made to bring down the surface pore size to 5 nm. The reactants were supplied across this γ-alumina layer to form a deposit inside the pores that could effectively reduce the pore size and thus form a microporous membrane. High temperature and lower flow rates were required to form a deposit inside the γ-alumina pores. He molecules permeated fastest with activation energy of 6.4 kJ mol^{-1} while H_2 permeated with 9.7 kJ mol^{-1} and N_2 with 18.5 kJ mol^{-1}. A He/N_2 selectivity of 3200 was achieved at 300°C while the H_2/N_2 selectivity was 1190. This membrane was also found to be stable for various, heating and cooling cycles.

Key words: Silica membranes, Hydrogen separation, Chemical vapor deposition, Opposing reactants geometry, Tetramethylorthosilicate.

1. INTRODUCTION

Hydrogen is considered to be a clean, renewable and flexible carrier of energy. Most of the chemical processes that produce hydrogen are complex processes conducted at drastic conditions and the use of inorganic membranes should help to make the process simple and at less severe conditions. Last decade, much research was directed to the development of hydrogen selective inorganic membranes with considerable attention focused towards silica membranes. Silica membranes are usually in the form of silica layers placed atop rigid and porous ceramic supports such as Vycor glass, alumina, etc., using sol-gel techniques and chemical vapor deposition (CVD). The hydrogen permeance values of these membranes were reported over a wide range (10^{-7} to 10^{-9} mol m^{-2} s^{-1} Pa^{-1}) and the selectivity for nitrogen ranging up to 3000 were also found in the literature.

Silica (SiO_2) films are widely used as passivation layers in the semiconductor industry, deposited using various CVD processes. In the CVD process, a porous ceramic substrate is fixed inside a high temperature reactor and suitable vapor precursors are introduced which react to form a solid deposit over the membrane resulting in complete or partial plugging of the membrane pores. When the membrane pores are completely plugged using a suitable solid that is highly perm-selective to a certain gas (i.e., Y_2O_3 stabilized ZrO_2 for O_2, SiO_2/Pd for H_2), it may result in the formation of a composite dense membrane. This type of membrane thus delivers single component gases in the permeate side and hence could be used when high purity gases are required.

In the case of partial pore plugging membranes, perm-selectivity is decided by the pore size of the top membrane layer before CVD and it is always desirable to have very narrow pore size range. For making these types of membranes, two types of CVD configurations are possible. One is the one-sided geometry in which the reactants are made to react in the feed gas phase or on the surface of the substrate, producing a deposit on the surface of the porous substrate. Several researchers have already reported silica membranes produced by this method. The second type is the opposing reactant geometry or counter diffusion CVD in which the reactants are fed through opposite sides of a porous substrate and the reactants come into contact inside the pores of the substrate and forms a deposit inside the pores. The pore size will become narrower with the increase in the deposition layer inside the pores and finally the reaction stops automatically when the reactants could no longer pass through the narrow pores. Thus a homogeneous micropore-sized distribution could be achieved using this method.

Gavalas et al.[1] first reported a membrane made using counter diffusion CVD using SiH_4 and O_2 as reactants and could achieve a H_2 permeance of 1.3×10^{-8} mol m^{-2} s^{-1} Pa^{-1}. Tsapatsis and Gavalas[2] prepared another membrane using $SiCl_4$ and H_2O at 600-800°C and reported a H_2 permeance of 7.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a H_2/N_2 selectivity of 500. They found that a dense layer of approximately 0.5 μm thickness posed as the barrier for gases other than H_2. Megris and Glezer[3] tired to overcome the densification phenomena by using an alkylsilane $(C_3H_7)_3SiH$ in an opposing reactants geometry. This membrane was thermally stable unless exposed to oxygen environment at high temperatures but their selectivity was lower (200) when compared to the earlier membranes. Ha et al.[4] tried to make silica membrane using counter diffusion method at 700°C by sending tetraethylorthosilicate (TEOS) through the inside and O_2 through the outside of the glass support tubes but could not achieve a significant H_2/N_2 selectivity because of the high concentration of TEOS used in pyrolysis. They found that the oxygen concentration at the deposition region was very low and the initial deposition reduced the pore size to 10 Å, which is comparable to the size of the TEOS molecule. Thus the deposition got shifted towards the TEOS side and the resultant film showed the properties of silica deposited in the absence of O_2. Our group[5] has also attempted to make silica membrane using counter diffusion CVD technique using TEOS and O_2 as precursors and could achieve a He/N_2 selectivity of 950 at 40°C.

Interestingly, most of the membranes prepared using counter diffusion CVD method uses TEOS as the silica source, maybe because of the fine particles generated in the process. Here we report a silica membrane made using tetramethylorthosilicate (TMOS) and O_3 as the reactants in a counter diffusion CVD method. In an earlier work, the membrane formation using TEOS and TMOS as the precursors were compared and found that TMOS yielded better perm-selective membranes than TEOS[6]. Hence a membrane was prepared using TMOS as the silica precursor.

2. EXPERIMENTAL

α-alumina capillary tubes having an average pore size of 100 nm (35 cm long; 2.7 mm diameter) supplied by NOK Co. Ltd. was used as support. Both ends of the substrate was glass-coated and only 5 cm in the middle portion was used to deposit silica. A thin layer of γ-alumina (3 ì m thick) was coated on this exposed region using the sol-gel dip-coating technique to bring down the surface pore size to 5 nm. The detail of the sol-gel technique was described elsewhere[7].

The reaction module was kept at a constant temperature between 230-300°C. TMOS (Wako, Japan) was carried by N_2 gas from a bubbler kept at constant temperature and fed to the outside of the substrate. O_3 generated in an ozonizer was introduced to the inside of the tube. The reactants diffused through the pores of the substrate, reacted and deposited inside the pores of the support. The reaction took place at atmospheric pressure. CVD conditions were optimized to the reaction procedure. The concentration of TMOS in the feed stream was maintained between 0.25-2.0 mol m^{-3} by varying the bubbler temperature (20-70°C) and N_2 flow-rate (200-500 ml min^{-1}).

Single gas permeance measurements were made simultaneously using the same setup. Thickness and surface morphology of the γ-alumina layer was observed using FE-SEM while the EDAX attachment gave the SiO_2 distribution.

3. RESULTS AND DISCUSSIONS

In order to prepare a hydrogen perm-selective membrane module with large area/volume ratio capillary tubes should be desirable. CVD conditions are highly dependant on the substrate characteristics and hence all basic CVD conditions had to be optimized to obtain a highly perm-selective membranes from such thin capillary substrates. Oxygen flow-rate as well as the voltage applied to the ozonizer determines the rate of O_3 production. Higher voltage and faster flow-rates resulted in higher concentration of O_3 in the stream. Such higher O_3 concentration yielded faster reaction and a white powdery silica deposit was observed atop the γ-alumina layer after the reaction. This could be due to the lower diffusion time of O_3 through the γ-alumina layer and the reaction took place outside the membrane region. Finally, the ozone generating voltage of 40V was used and N_2 flow rate was adjusted to obtain a TMOS concentration of 0.29 mol m^{-3} in the feed stream. The reaction was performed at atmospheric pressure conditions.

Table I. Effect of carrier-gas flow-rates on membrane permeance after 8 h of CVD. Measurements were made at 230°C at 300 torr.

No	O_2 flow rate (ml min^{-1})	N_2 flow rate (ml min^{-1})	N_2 permeance ($\times10^{-8}$ mol m^{-2} s^{-1} Pa^{-1})
1	1000	200	13.2
2	400	200	5.47
3	500	400	4.03
4	600	500	2.62
5	500	500	1.45
6	200	200	0.0043

Table I describe the relationship between the O_2 and N_2 flow-rates and its effect on membrane formation as observed through N_2 permeance values. As discussed before, higher O_2 flow rate resulted in an increased O_3 concentration in the system and produced a deposit outside the γ-alumina layer resulting in poor membrane performance. The performance increased with decreasing carrier gas ratio. Use of an O_2/N_2 ratio of 1 could lower the N_2 permeation to 1.45×10^{-8} mol m^2 s^{-1} Pa^{-1} but still the membrane perm-selectivity was in the Knudsen range. It has to be assumed here that the $O_3(O_2)$ flow-rate was still higher and the 400nm thick substrate could not induce sufficient resistance to contain the reaction inside the γ-alumina pores. Finally, when the $O_3(O_2)$ flow rate was lowered to 200 ml min^{-1} (maintaining 1:1 ratio with TMOS/N_2), a drastic improvement in the membrane

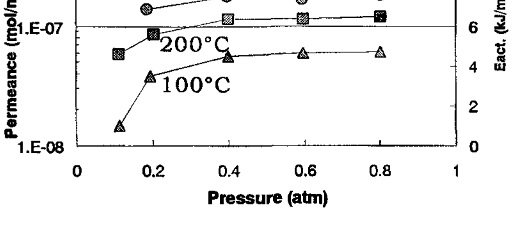

Fig. 1 Variation of H_2 permeance with pressure through a TMOS/O_3 membrane (300°C, 480 min) at different temperatures. Permeation was measured using bubble-flow method. Dotted line indicates activation energy.

performance could be achieved. Fig. 1 gives the variation of H_2 permeance through a TMOS/O_3 CVD membrane prepared at 300°C with pressure. H_2 permeation remained somewhat steady with pressure for the temperature range studied. Activation energy also showed a similar trend with pressure, maintaining a uniform value around 10 kJ mol^{-1}, indicating good membrane properties.

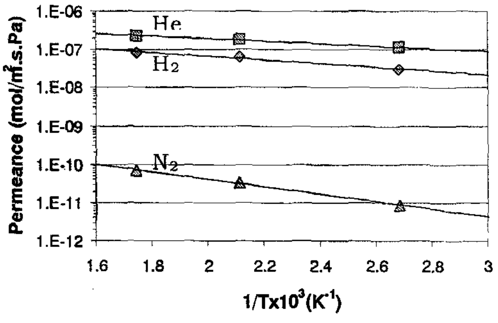

Fig.2 Arrhenius plot of TMOS/O_3 CVD membrane (300°C, 480 min).

Fig. 2 shows a more detailed Arrhenius plot for gas transport through this membrane. Among the gases studied, He permeated fastest with an activation energy of 6.4 kJ mol^{-1}. N_2 permeated the least with an activation energy value of 18.5 kJ mol^{-1}. The activation energy and permeation values of N2 indicate that the membrane has only a few defects. A He/N_2 selectivity of 3270 was achieved at 300°C (0.8 atm), which increased with decreasing temperature. H_2 permeated with activation energy of 9.7 kJ mol^{-1} and gave a H_2/N_2 selectivity of 1190 at 300°C (0.8 atm).

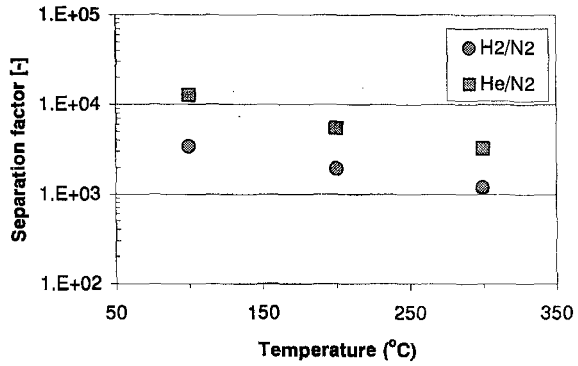

Fig.3 Variation of H_2/N_2 and He/N_2 slelectivity with measurement temperature (0.8 atm). H_2 and N_2 permeation were measured under vacuum while He was measured using bubble-flow method.

Fig.3 describes in more detail how the H_2/N_2 and He/N_2 selectivity ratio values varied with temperature. As the measurement temperature increases, the selectivity decreased. This is obvious as the activation energy value of N_2 is higher than that for He and H_2.

Table II Effect of O_2:N_2 flow rates and synthesis temperature on H_2/N_2 selectivity for a TMOS/O_3 CVD membrane.

O_2:N_2 flow rate (L min^{-1})	H_2/N_2 selectivity at	
	230°C	300°C
05 : 0.5	2.8	8.6
0.2 : 0.2	3.4	646.3

The effect of temperature and precursor flow-rate on membrane performance is given in Table II. When the precursor flow-rate was fixed at 0.5 L/min to maintain a ratio of O_2:N_2 = 1, an appreciable increase in membrane performance could not be achieved. It has to be assumed here that the precursors would not have stayed enough in the membrane pores because of their faster flow conditions and hence enough deposit might not have formed inside the pores. To confirm this point, we lowered the precursor flow-rate to 0.2 L/min while maintaining the ratio of O_2:N_2 = 1. At 230°C, the membrane formed did not have any appreciable selectivity (H_2/N_2 = 3.4). But when the temperature was raised to 300°C, a drastic improvement in the membrane performance could be achieved (H_2/N_2 = 646.3). Results indicate that lower flow rates of the reactants and higher temperature (high reactivity) helped the formation of a good deposit layer inside the gamma alumina layer.

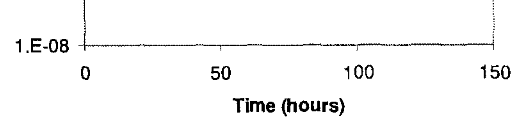

Fig. 4 Variation of H_2 permeance through the TMOS/O_3 CVD membrane after various cycles of heating and cooling.

The stability of the membrane was evaluated by monitoring the variation in H_2 permeation values through the TMOS/O_3 CVD membrane after heating and cooling cycles (Fig. 4). Each point in the Fig. 4 represent one heating cycle in which the temperature was brought from room temperature to 300°C in a very fast rate (10°C min^{-1}). Measurements were made at 300°C. Results indicated that the membrane produced could withstand various temperature cycles.

4. CONCLUSION

H_2 perm-selective silica/alumina composite membrane was successfully prepared using counter diffusion CVD method with TMOS as the silica precursor and O_3 as the reactant. Thin capillary α-alumina tubes were used as supports. γ-alumina was coated atop the α-alumina substrate. The reactants diffused through the gamma alumina layer and reacted inside the pores to form a deposit there. It was observed that slower precursor flow conditions and higher temperature conditions were prerequisites to form a deposit inside the γ-alumina pores. He permeated fastest through the membrane with activation energy of 6.4 kJ mol^{-1} while H_2 permeated with 9.7 kJ mol^{-1} and N_2 with 18.5 kJ mol^{-1}. A He/N_2 selectivity of 3273 was achieved at 300°C while the H_2/N_2 selectivity value was 1190. This membrane performance was also found to be stable for cyclic heating and cooling.

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