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A hybrid processing method for high performance  
hydrogen-selective silica membranes.

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## Abstract

Development of high performance hydrogen-selective inorganic membrane has become an important requisite for the production of hydrogen, an energy carrier that could cater the ongoing energy revolution. This paper describes a novel, hybrid method to process high performance hydrogen perm-selective membranes by the rapid CVD modification of a sol-gel silica layer. The initial N<sub>2</sub> permeance values through a membrane were brought down by 4 orders of magnitude to  $2.74 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  within 5 minutes of CVD, while maintaining the H<sub>2</sub> permeance values as high as  $6.43 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  (H<sub>2</sub>/N<sub>2</sub> = 2300). It is likely that the reduction in the CVD zone thickness achieved by the presence of pre-existing sol-gel silica layer is the reason for the rapid modification of the pore structure to high performance membranes.

Key words: Hydrogen separation, CVD, Sol-gel, membrane reactor, silica membranes.

## Introduction

Hydrogen perm-selective membranes have attracted much interest in membrane separation applications, particularly for applications in fuel cells and membrane reactors, because of the importance of hydrogen as an energy carrier for the future [1-2]. Membrane reactors for the production of hydrogen require thermally and mechanically stable membranes with excellent hydrogen permeability and perm-selectivity. Metal composite membranes, especially thin palladium-based films/membranes on porous supports, show excellent hydrogen permeance and separation. But cost concerns and durability problems associated with their reaction with sulphur, carbon monoxide and catalyst materials limit their applications [3]. Membranes made from porous ceramics, such as microporous silica membranes, offer alternatives to palladium membranes. These membranes have long been considered as replacements to the conventional polymeric membranes for their physical, thermal and chemical stability while offering high permeability and selectivity for hydrogen [4].

Several techniques have been reported to process silica membranes, among which sol-gel synthesis [5-10] and chemical vapor deposition (CVD) [11-19] attract most attention. Sol-gel method could precisely control the pore size and pore-structure; though the retention of unreacted or partially reacted materials in the sol-gel matrix have shown to considerably affect the stability of the membranes prepared by this method. CVD methods derive chemically homogenous deposits, especially inside the mesopores of the supports. The main problem associated with CVD processing of membranes is that it only allowed deposition of a single tube

at one step and the deposition durations were normally long. Moreover, the gas permeance values were generally lower than the sol-gel counter parts, even though the stability and durability of the films were considerably better. Here we describe, a novel hybrid coating method that could drastically reduce the membrane processing effort, at the same time end-up with superior performance than the membranes made with the base technologies' when used alone. These new membranes have shown high gas permeance and selectivity.

A good membrane is determined by (a) precise control of the pore size in the molecular size region and hence having the ability to selectively filter gas and vapor molecules, (b) few pinholes and cracks and thereby avoiding nonselective molecular diffusion and (c) minimum membrane thickness to maximize the flux of permeating molecules. Attaining all these properties together in a membrane is mostly a difficult task.

Generally, sol-gel silica membranes are prepared by dip-coating a mesoporous substrate (usually  $\gamma$ -alumina) with a silica sol made using alkoxide precursor, followed by controlled drying and firing at high temperatures between 673-1073 K. In most cases, the process has to be repeated several times to ensure a defect-free membrane surface. Here, the membrane quality is greatly dependant on the sol-chemistry [15, 20-21]. CVD membranes are prepared by the reaction of gas phase precursors inside or around the mesoporous substrate pores. Especially when the reaction took place inside the substrate pores, the selectivity values reported were much higher than sol-gel membranes, though gas permeance values were lower. Here also, a strong dependency with the preparation conditions (deposition gas composition, temperature, pressure, etc.) determines

membrane quality and long CVD times were generally necessary to process high quality membranes. Earlier reports suggest a dense membrane structure for these membranes compared to sol-gel membranes as envisaged from the high activation energy measured for the permeance of small gas molecules [22-23]. As mentioned, even though the H<sub>2</sub> selectivity measured with these membrane were quite high, the H<sub>2</sub> permeance were lower ( $\sim 10^{-8}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) when compared to sol-gel membranes. Fig. 1 displays the relation of H<sub>2</sub> permeability with that of selectivity for various silica membranes at high temperatures as reported in the literature. In order to simultaneously improve the membrane gas permeance and separation performance, we have devised a new hybrid processing method involving both sol-gel and CVD procedures. This method should also assist the large scale processing of membranes and membrane bundles, by drastically reducing the CVD time and hence the total time required for fabricating high performance silica membranes, where mostly CVD time is the slowest processing step involved.

## Experimental

Pore size of the commercially available capillary substrates (NOK, Japan) was brought down to 5 nm range by applying a thin  $\gamma$ -alumina layer. A silica layer was coated over this  $\gamma$ -alumina layer using sol-gel processing. The alumina and silica sol preparation and coating conditions were based on our previous studies [9, 21, 24]. This process distributed a thin layer of silica network over the  $\gamma$ -alumina layer with some infiltration into the  $\gamma$ -alumina pores. This sol gel coated substrates were subjected to CVD using tetramethylorthosilicate (TMOS) and O<sub>2</sub> as reactants at 873 K. The CVD process parameters were selected and modified from our previous studies of counter diffusion CVD in  $\gamma$ -alumina layer [19, 25-26]. Chemical vapor deposition times of 2 hours or more were necessary in those studies to prepare a membrane giving H<sub>2</sub>/N<sub>2</sub> separation

factor of ~3000. Just as in the previous studies, TMOS was supplied through the shell side and O<sub>2</sub> was supplied through the inner side so that the reaction takes place at the point of intersection of the reactants and forms a deposit in the region. Gas permeance measurements were performed by the dead-end method and perm-selectivity values were calculated from the ratio of individual gas permeance values. XPS measurements were performed by ULVAC-PHI, Inc., Kanagawa, Japan.

## Results and discussion

The gas separation performance of a membrane prepared by 5 min of CVD is shown in Fig. 2. As shown, H<sub>2</sub> and N<sub>2</sub> gas molecules displayed activated diffusion through the membrane. The activation energy values calculated for H<sub>2</sub> and N<sub>2</sub> through the membrane were 15.56 kJ mol<sup>-1</sup> and 11.86 kJ mol<sup>-1</sup>, respectively. This data is quite different from sol-gel silica membranes as activation energy for the poorly permeating N<sub>2</sub> molecule is seldom measured or reported for sol-gel silica membranes [21]. We have previously reported that membranes prepared using the counter diffusion CVD method for 2 hours usually could show very low N<sub>2</sub> permeance through them [25-27]. Obviously, the present membrane could be presumed to have a structure formed within a very short span of CVD time, though the ideal selectivity values (H<sub>2</sub>/N<sub>2</sub> = 2300) and hydrogen permeance values achieved were in par with other reported CVD silica membranes and sol-gel silica membranes respectively. (see Figure 1).

The initial N<sub>2</sub> permeance through the silica membrane layer, before CVD reaction, was more or less similar to that through the  $\gamma$ -alumina layer without silica sol-gel coating ( $1.17 \times 10^{-6}$  mol m<sup>-2</sup>

$\text{s}^{-1} \text{Pa}^{-1}$  and  $1.99 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{Pa}^{-1}$ , respectively, at 873 K). These values also did not vary much with feed gas pressure, suggesting a defect-less substrate structure. The similarity in permeance values indicated that the sol-gel silica coating failed to completely block the  $\gamma$ -alumina pore structure or form a separation layer under the experimental conditions employed. Rather, it formed a loose network of silica particles over and into the  $\gamma$ -alumina pore structure.

The structural features of the sol-gel layer and the changes occurred in the membrane within the 5 minutes of CVD could be explained as in scheme given in Fig. 3. The silica-sol formed a thin web-like network of silica particles around the  $\gamma$ -alumina pores and pore-mouth. TMOS- $\text{O}_2$  CVD reaction deposited silica in this sol-gel silica pre-filled region, effectively concentrating the active reaction zone within this thin layer. Based on measured thickness values of similar gamma alumina membranes (2-5 $\mu\text{m}$ ) and reported values of silica membrane layer thickness (10-50nm) [9], it could be assumed that the thickness of the reaction zone could be reduced by a factor of 10-100 by this procedure. 5 minutes of reaction should obviously be sufficient for depositing enough silica to cover the already modified  $\gamma$ -alumina pore surface in this thin region.

The CVD reaction time on this membrane was further increased up to 2 hours to evaluate the change in membrane performance. The  $\text{H}_2/\text{N}_2$  separation values almost doubled to 5000. But, even after 2 hours of CVD reaction,  $\text{N}_2$  gas maintained activated transport through this membrane; though with slightly lower activation energy of  $8.54 \text{ kJ mol}^{-1}$  compared to the initial case. The variation in membrane performance with increased CVD time is given in Table 1. Increase in the  $\text{H}_2/\text{N}_2$  selectivity values together with the  $E_{a\text{H}_2}$  values are typical of changes in



membrane structure with two types of pores, as in the case of sol-gel membranes [21], where the relative flux through the smaller pores become increasingly dominant. In the present case, the membrane structure transformed from a discontinuous network of sol-gel silica particles to a continuous and selective barrier within the first 5 minutes of CVD. With additional CVD, the membrane structure improves further with decreased non-selective diffusion, denoting a gradual transformation to a fully compact layer of silica membrane.

XPS analyses of the silica-sol-coated  $\gamma$ -alumina samples, before and after CVD reaction have shown that the modification of layer (deposition of CVD silica) occurred mostly within the existing silica infiltrated region of  $\gamma$ -alumina layer (see supplementary information attached at the end of the paper for the XPS plots). It was found that, the Si2p peak taken from the surface of sol-gel silica layer remained intact even after deposition, while the peaks collected after sputtering-out 100nm have grown significantly. Si2p collected from 200nm depth has shown marginal growth. This showed that most of the CVD reaction took place inside the  $\gamma$ -alumina layer, within the first few 100 nm's range from the surface, which was also the region where silica sol particles presumed to have infiltrated into the alumina layer. This well supported the previous discussion that the vapor phase deposition process zone area (thickness) was restricted by the silica sol-gel layer and has effectively contributed to the quick membrane formation. The high values of hydrogen permeance measured with these membranes also supported the fact that silica deposition due to CVD occurred only in a very thin layer. Thus this novel hybrid processing method could effectively be utilized for preparing membranes with much better performances than the conventional sol-gel or CVD silica membranes in a rapid manner.

Based on the XPS data and the permeance through the membrane, the structural formation process could be assumed as follows: During CVD, silica particles derived from the vapour phase will get deposited as particles/islands, whose number density will grow with deposition time, thus forming a layer of percolating silica particles along with the sol-gel deposited silica particles/islands. The presence of sol-gel layer accelerates the process of continuous layer formation by restricting the thickness of active CVD zone to the sol-gel silica modified region of  $\gamma$ -alumina membrane. The resultant membrane would be much thinner, thus reducing the membrane formation time as well as increasing gas permeance through it. Previous studies with bigger pore sized  $\gamma$ -alumina membrane also supports this theory as the gas permeance after CVD reportedly decreased with increase in the pore size of the substrate [27].

Recently, one of our groups have also scaled-up the method to make multiple membrane tube bundles in one-step and hence proved its potential as a technology ready for commercial applications.

## Conclusions

Hydrogen perm-selective membranes were prepared using a hybrid process involving the chemical vapor deposition of silica on a sol-gel silica layer coated alumina substrates. The initial  $N_2$  permeance values through the membrane were brought down by 4 orders of magnitude to  $2.74 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  within 5 minutes of CVD, while maintaining the  $H_2$  permeance values as

high as  $6.43 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  ( $\text{H}_2/\text{N}_2 = 2300$ ). The  $\text{H}_2/\text{N}_2$  separation values almost doubled to 5000, after 2 hours of CVD reaction. Permeance and separation results coupled with XPS analysis have shown that, a reduction in vapor phase deposition zone area (thickness) by the pre-existing silica sol-gel layer has effectively contributed to the quick membrane formation.

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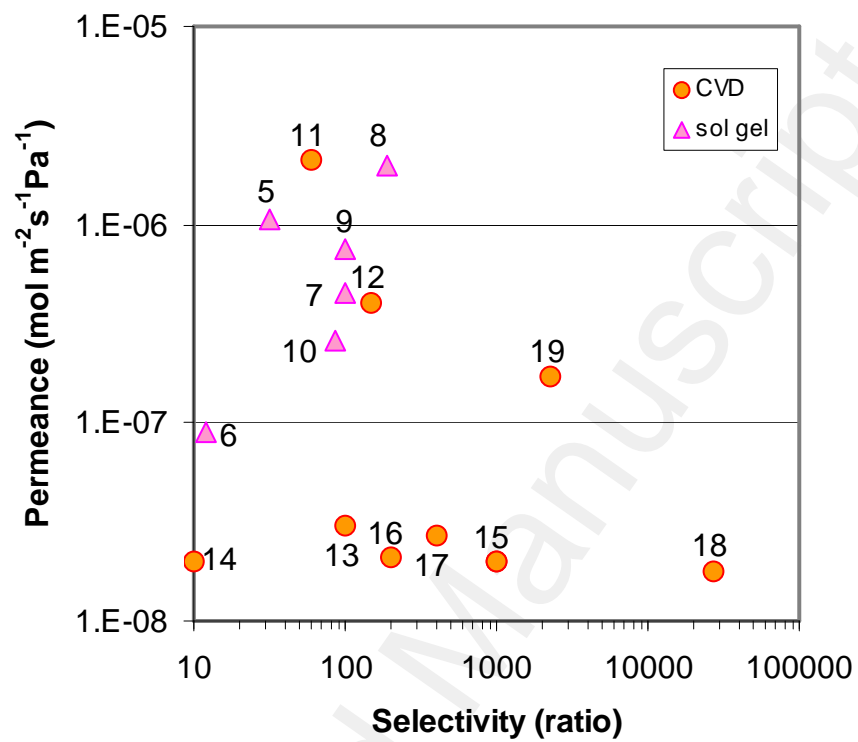


Figure 1. H<sub>2</sub> permeance and ideal selectivity values of H<sub>2</sub> with other gases reported for silica membranes at high temperatures (>673 K). Numbers represents corresponding references.

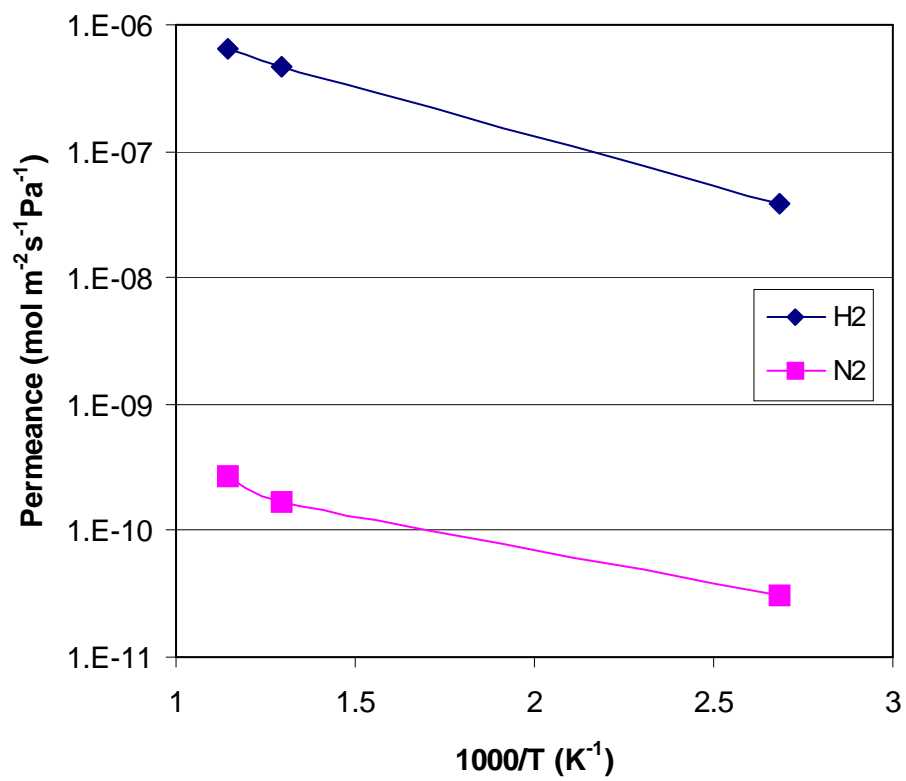


Figure 2. Membrane performance after chemical vapor depositing silica for 5 minutes at 873 K.



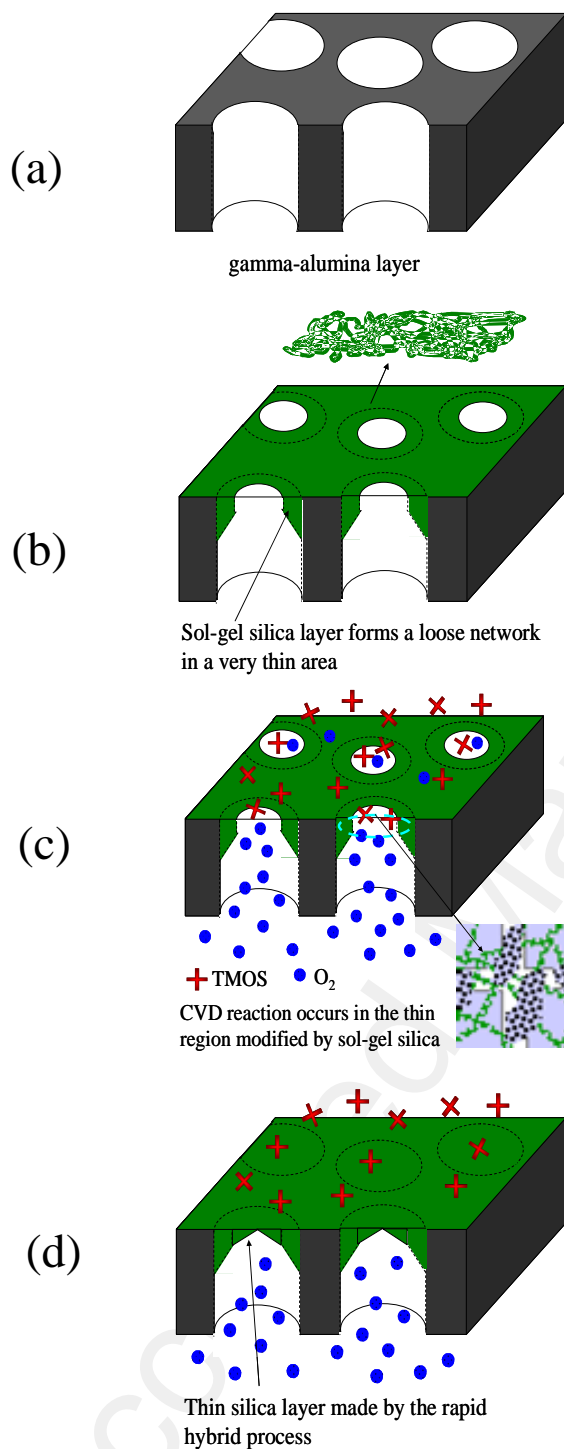


Figure 3. Membrane formation: (a)  $\gamma$ -alumina layer (b) silica sol forms a network over and into the  $\gamma$ -alumina layer (c) TMOS and oxygen are supplied through either sides of the  $\gamma$ -alumina layer where they react at the intersection region or sol-gel silica pre-filled region (silica coating effectively reduces the thickness of the zone of CVD reaction) (d) continuing deposition completes the membrane architecture.

Table 1. Single gas permeance values of H<sub>2</sub> and N<sub>2</sub> through the silica membrane at 600°C. Activation energy values were calculated for the temperature range 100-600°C. Ideal selectivity values were calculated from the single gas permeance data.

CVD reaction time	H <sub>2</sub> ( $\times 10^{-7}$ mol/m <sup>2</sup> s Pa)	N <sub>2</sub> ( $\times 10^{-11}$ mol/m <sup>2</sup> s Pa)	H <sub>2</sub> /N <sub>2</sub> (ratio)	$E_{aH_2}$ (kJ/mol)	$E_{aN_2}$ (kJ/mol)
120 min	3.27	6.51	5027	19.40	8.54
30 min	3.02	7.62	3970	18.45	12.31
5 min	6.43	27.4	2343	15.36	11.88