

# Synthesis of a Multilayer Ceramic Membrane Used for Hydrogen Separation at High Temperature

M. Amanipour<sup>1</sup>, E. Ganji Babakhani<sup>2\*</sup>, A. Zamanian<sup>2</sup> and M. Heidari<sup>1</sup>

1- Chemical Engineering Department, Sharif university of Technology, Tehran, Iran

2- Gas Department, Research Institute of petroleum Industry, Tehran, Iran

Ganji@ripi.ir

## Abstract

A multilayer composite ceramic membrane was prepared by depositing a nano-scale layer of SiO<sub>2</sub> on top of a modified porous alumina support by chemical vapor deposition (CVD) method. The modification of the support was carried out by adding a graded layer of Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -alumina phase), using sol-gel method. An optimized temperature of 700 K for intermediate layer calcination was gained by XRD analysis. Cross-sectional images obtained from SEM showed that the intermediate  $\gamma$ -alumina layer had a thickness of about 2  $\mu$ m and the top selective silica layer was quite dense and uniform with a thickness of about 90-100 nm. Permeation tests showed a very good flux of 10<sup>-6</sup>-10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-2</sup> Pa<sup>-1</sup> for H<sub>2</sub> with selectivities over CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> up to 500. By performing different tests with various deposition times, it was concluded that by changing CVD time from 3 h to 6 h H<sub>2</sub>/CO<sub>2</sub> selectivity increased from 32 to 573, although H<sub>2</sub> permeation flux reduced about 50 percent.

**Key words:** Hydrogen Permeation, Ceramic Membrane, CVD, Selectivity.

## Introduction

Ceramic membranes with porous structure are known for their high performance in separation of small gas molecules from gas mixtures with selectivities and permeation fluxes greater than polymeric membranes. Therefore, they have attracted a great deal of attention in the membrane gas separation field, especially hydrogen purification [1-3]. The production of hydrogen from membrane base reformers is one of the most important applications of these kinds of membranes [4]. In order to achieve high efficiency in reformers, the membrane must be capable of separating the produced H<sub>2</sub> under harsh operating conditions and silica membranes are considered as good candidates for this purpose because of their hydrogen separation ability and large hydrogen permeability [5-6].

Silica membranes synthesized by sol-gel or chemical vapour deposition methods have been shown to be very effective for H<sub>2</sub> selective separation [7-10]. Okubo *et al.* [11] deposited silica into the pores of a porous glass with 4 nm mean pore diameter by tetraethylorthosilicate (TEOS) hydrolysis. Oyama *et al.* carried out CVD of TEOS on  $\gamma$ -alumina supports [12] and obtained thin

silica layers with very high selectivities for hydrogen (>500).

The initial membranes used macroporous supports for silica deposition and had low selectivities for gas permeation. Hwang *et al.* [13] used CVD method to deposit TEOS on a porous ceramic tube with mean pore size of about 100 nm and obtained a H<sub>2</sub>/N<sub>2</sub> selectivity of only 5.2 after 32 h of deposition. This low selectivity indicated the presence of large pore defects. A solution to this problem is adding an intermediate layer before deposition of top selective layer [14-15]. Morooka *et al.* [15] covered macroporous  $\alpha$ -alumina tubes with 110-180 nm pore size by a  $\gamma$ -alumina layer with pore size of 6-9 nm to obtain a composite support. Addition of a selective silica layer by CVD method to this modified support resulted in preparation of a membrane with H<sub>2</sub> selectivity over N<sub>2</sub> in the range of 100-1000, but low permeation fluxes of about 10<sup>-8</sup> mol m<sup>-2</sup> s<sup>-1</sup> pa<sup>-1</sup>.

In this work, we prepared a composite ceramic membrane by depositing a very thin selective silica layer on a modified porous support. The tubular  $\alpha$ -alumina support was covered with five layers of  $\gamma$ -alumina by dip-coating with different bohemite solutions using sol-

gel method and top selective silica layer was prepared by co-current CVD of TEOS at atmospheric pressure and high temperature of 873 K. Morphology of different layers of membrane was studied by SEM and the amount of permeation flux and  $H_2$  selectivities over  $CO_2$ ,  $N_2$  and  $CH_4$  at different deposition times were investigated.

## Experimental

### Synthesis of intermediate layer

Bohemite ( $AlOOH$ ) solutions with different mean particle sizes were prepared by careful control of hydrolysis of TEOS followed by acid peptization of the bohemite precipitate obtained. The intermediate graded layer was obtained by coating with three bohemite sols with median particle sizes of 52, 94 and 592 nm. The general procedure is reported in the literature [16]. Shortly, a quantity of 0.1 mol of aluminium tri isopropilate (Merck, >98%) was added to 150 ml of distilled water and the mixture was quickly heated to 353 K in 0.5 h with high speed stirring. The solution was maintained at this temperature for 3-20 h for the hydrolysis. The resulting precipitate was then heated to 363 K and peptized with a quantity of nitric acid (Merck, 65%) with a molar ratio of  $H^+/alkoxide$  in the range of 0.1-0.25. The solution was then refluxed at this temperature for about 20 h to obtain a clear sol.

A series of thin uniform  $\gamma$ -alumina layers were coated on a macroporous  $\alpha$ -alumina support by sol-gel method. A commercial tubular membrane (GMITM Corporation, i.d=9 mm, o.d=13 mm) with a nominal pore size of 500 nm was used as support. This tube was first cut to a length of 6 cm, washed in an ultrasonic bath (BANDELIN, Sonorex digital 10P) with 10% power for 15 min and dried at room conditions for 24 h. The bohemite solutions were diluted by mixing with polyvinyl alcohol (PVA, Biochemical, M.W.=7200) as a binder in a 3 to 2 ratio. The resulting solution was then stirred at 363 K for 3 h and the support was dipped into this dipping solution and withdrawn after 10 s. The coated support was then dried in ambient air for 24 h, heated to 923 K in an electronic furnace at a rate of 1 K  $min^{-1}$  and calcined at this temperature for 2.5 h. This coating process was carried out five times by 3 different solutions in the order of decreasing sol particle size to get a graded structure intermediate layer.

### Synthesis of selective silica layer

A composite membrane was synthesised using the as-prepared multilayer support to deposit a thin silica layer by an atmospheric chemical vapour deposition (CVD) method. This results in placing  $SiO_2$  on the support by thermal decomposition of TEOS at high temperatures. The experimental setup is shown in figure 1. Shortly, the CVD process took place in a quartz tube and the silica deposited into the inner side of the support. After heating the apparatus to 873 K at a rate of 1 K  $min^{-1}$  in an inert atmosphere, an argon flow was introduced on the outer side and a dilution argon flow to the inner side of the membrane. Then a carrier gas was passed through a bub-

bler filled with TEOS at 300 K at a known flow rate using a mass flow controller, mixed with dilution flow and introduced to the inner side of the graded intermediate substrate. Table 1. shows the CVD process parameters used in one of the coatings. The concentration of species in membrane structure can be analysed by EDAX analyser. With the following flow parameters, the TEOS concentration is about 0.02 mol  $m^{-3}$ .

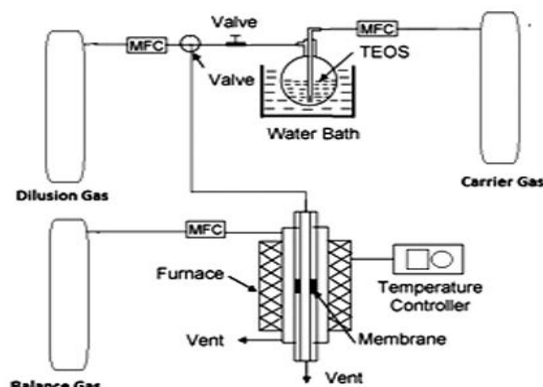


Fig. 1: Schematic of experimental CVD setup.

Table 1: CVD process parameters for silica deposition

Parameter	Amount
CVD temperature (K)	873
TEOS concentration (mol $m^{-3}$ )	0.02
Dilution gas flow ( $\mu mol s^{-1}$ )	13
Carrier gas flow ( $\mu mol s^{-1}$ )	3.5
Outer side gas flow ( $\mu mol s^{-1}$ )	17

## Results and discussion

### Calcination temperature of intermediate layer

XRD analysis was carried out to identify the alumina phase and the calcination temperature of the intermediate layer. The alumina support cannot stand temperatures higher than 1173 K. Also, if the calcination temperature is not high enough, bohemite ( $AlOOH$ ) still exists in membrane structure, which is less stable than  $\gamma$ -alumina ( $\gamma-Al_2O_3$ ). Coated supports are put in an electric furnace to be heated at a rate of 1 K  $min^{-1}$ . Fig. 2 shows two membrane samples calcined at two different temperatures. As the result of this analysis indicates, at 650 K, XRD patterns still show existence of bohemite phase in membrane. However, at 700 K, all the bohemite changes into  $\gamma$ -alumina and therefore this temperature would be suitable for calcination.

### Characterization of the membranes

The cross-sectional images of the modified support with  $\gamma$ -alumina layer and ultra-thin silica membrane obtained by scanning electron microscopy (SEM, Philips, XL30) are shown in fig.3 (a)-(b). Fig.3 (a) shows a graded  $\gamma$ -alumina multilayer with a porous structure coated on the support and has a thickness of about 2  $\mu m$ . As shown in figure (b), silica top layer deposited on the graded layer has a uniform, dense structure with an ultra thin thickness of about 90-100 nm. These images indicate that gas permeation through different layers of the membrane is performed by different mechanisms.

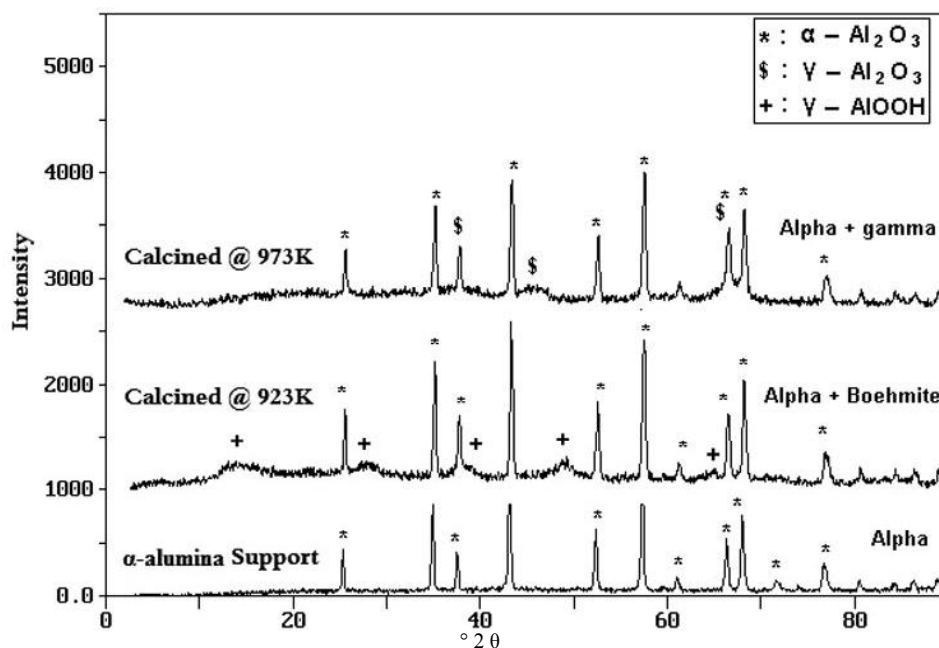


Fig. 2: XRD analysis of intermediate layer calcined at different temperatures

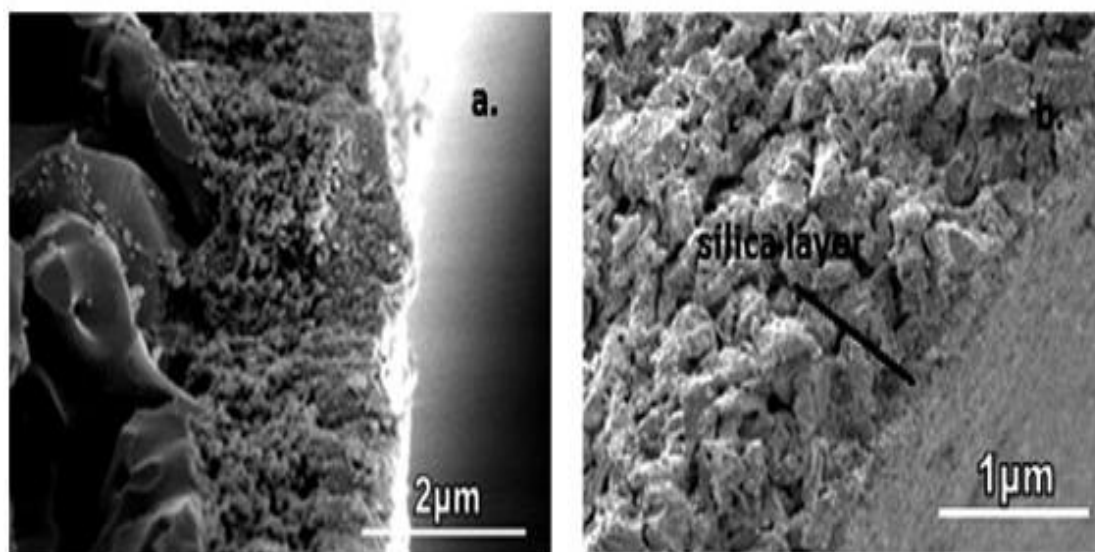


Fig. 3: SEM cross-sectional images; (a) intermediate layer; (b) silica top layer

The gas permeation tests were carried out at 973 K on  $H_2$ ,  $CH_4$ ,  $N_2$  and  $CO_2$  before and after CVD by introducing pure gases at a relative pressure of 160 kPa into the outer tube side of a quartz module. An argon flow at a known flow rate was used as the sweep gas and the composition of the permeated stream was measured by a bubble flow meter. Also a GC (Agilent, 7890A) analyser was used to determine the concentration of permeated gases. As shown in figure. 4, before deposition of silica layer, permeation fluxes are very high and in the order of  $10^{-5}$ - $10^{-6}$   $mol\ m^{-2}\ s^{-1}\ Pa^{-1}$ . This is due to the porous structure of the substrate, which causes the permeation of gases through Knudsen diffusion mechanism. This mechanism predicts that gas permeance would have a dependency on the inverse square root of temperature. Thus, increasing the temperature lowers the permeance values in multi-layer

substrate. Using CVD deposition, there is a reduction in fluxes, but  $H_2$  selectivities increase rapidly, which is because of adding selective  $SiO_2$  dense layer on top of the  $\gamma$ -alumina multilayer.

As shown in the figure, for the first 3 hours of deposition, there is a large decrease in fluxes, which can be explained by the fundamental change in permeation mechanism. It is claimed that gas permeance through this dense silica layer is achieved by an activated diffusion transport through the membrane [17]. This theory is based on a mechanism involving jump of gas molecules between solubility sites of the dense silica layer. These sites have a very small size less than 0.3 nm. Therefore, membrane structure can exclude permeance of gases with larger kinetic diameter like  $CH_4$  (0.38 nm) or  $CO_2$  (0.33 nm).

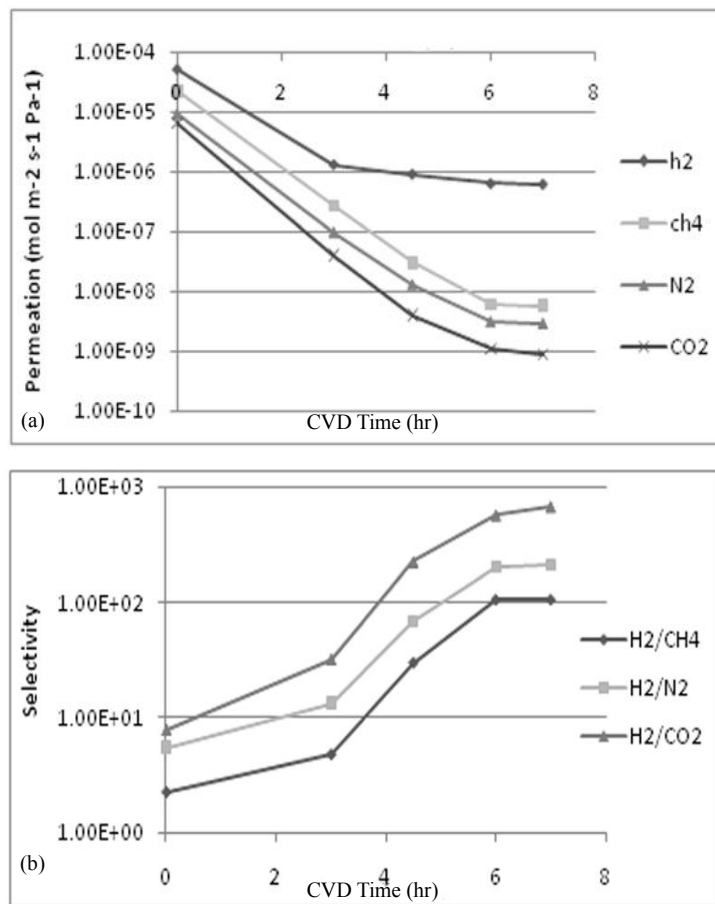


Figure 4: (a) permeation fluxes of four different gases at 973 K; (b) H<sub>2</sub> selectivity over other gases

## Conclusion

A hydrogen selective membrane composed of a nano-scale silica layer deposited on a graded alumina support by CVD method was successfully prepared to operate at high temperatures. Crystal structure of the intermediate layer was investigated and an optimum calcination temperature for  $\gamma$ -alumina layer was obtained by XRD analysis. SEM images confirmed the preparation of different layers as expected and indicated that the structures of intermediate and top layers are quite different, which resulted in a fundamental difference in permeation mechanisms through these layers. Permeation tests showed that as silica deposition proceeded, H<sub>2</sub> selectivities considerably increased, which is supposed to be related to the hopping mechanism of permeation in dense layer.

## References

- [1] R. Ramachandran, R.K. Menon, *An overview of industrial uses of hydrogen*, Int. J. Hydrogen Energy 23 (1998) 593.
- [2] R.W. Van Gemert, F. Petrus-Cuperus, *Newly developed ceramic membranes for dehydration and separation of organic mixtures by pervaporation*, J. Membr. Sci. 105 (1995) 287–291.
- [3] N. Wynn, *Dehydration with silica pervaporation membranes*, Membr. Technol. 2001 (2001) 10–11.
- [4] Yasushi Yoshino, Takehiro S., *Development of tubular substrates, silica based membranes and membrane*

*modules for hydrogen separation at high temperature*, J. Membr. Sci. 267 (2005) 8–17.

- [5] J. Lin, I. Kumakiri, B.N. Nair, H. Alsayouri, *Microporous ceramic membranes: review*, Sep. Purif. Meth. 31 (2) (2002) 229.
- [6] R.J.R. Uhlhorn, *Ceramic Membranes For Gas Separation*, PhD Thesis, University of Twente, Cap. 2, 1990, ISBN 90-9003618-0.
- [7] R.M. De Vos, H. Verweij, *High-selectivity, high-flux silica membranes for gas separation*, Science 279 (1998) 1710–1711.
- [8] L.J.P. Van Den Broeke, W.J.W. Bakker, F. Kapteijn, J.A. Moulijn, *Binary permeation through a silicalite-1 membrane*, AIChE J. 45 (1999) 976–985.
- [9] J. Sekulic, M.W.J. Luiten, J.E. Ten Elshof, N.E. Benes, K. Keizer, *Microporous silica and doped silica membrane for alcohol dehydration by pervaporation*, Desalination 148 (2002) 19–23.
- [10] M. Tsapatsis, S. Kim, S.W. Nam, G.R. Gavalas, *Synthesis of hydrogen permselective SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> membranes from the chloride precursors*, Ind. Eng. Chem. Res. 30 (1991) 2152.
- [11] T. Okubo, H. Inoue, *Introduction of specific gas selectivity to porous glass membranes by treatment with tetraethoxysilane*, J. Membr. Sci. 42 (1989) 109.
- [12] A.K. Prabhu, S.T. Oyama, *Highly hydrogen selective ceramic membranes: application to the transformation of greenhouse gases*, J. Membr. Sci. 176 (2000) 233.

- [13] G.J. Hwang, K. Onuki, S. Shimizu, H. Ohya, *Hydrogen separation in H<sub>2</sub>-H<sub>2</sub>O-HI gaseous mixture using the silica membrane prepared by chemical vapor deposition*, J. Membr. Sci. 162 (1999) 83.
- [14] Y. Yoshino, T. Suzuki, B.N. Nair, H. Taguchi, N. Itoh, *Development of tubular substrates, silica based membranes and membrane modules for hydrogen separation at high temperature*, J. Membr., Sci. 267, 2005 8.
- [15] S. Yan, H. Maeda, K. Kusakabe, S. Morooka, Y. Akiyama, *Hydrogenpermeable SiO<sub>2</sub> membrane formed in pores of alumina support tube by chemical vapor deposition with tetraethyl orthosilicate*, Ind. Eng. Chem. Res. 33 (1994) 2096.
- [16] Yunfeng Gu, S. Ted Oyama, Ultrathin, *hydrogen-selective silica membranes deposited on alumina-graded structures prepared from size-controlled boehmite sols*, J. Memb. Sci. 306 (2007) 216–227.
- [17] Yunfeng Gu, Pelin Hacıoğlu, S. Ted Oyama, *Hydrothermally stable silica–alumina composite membranes for hydrogen separation*, J. Memb. Sci. 310 (2008) 28–37.