H$_2$ Permeation Properties of a Catalytic Membrane Reactor in Methane Steam Reforming Reaction

M. Amanipour, J. Towfighi, E. Ganji Babakhani, M. Heidari

Abstract—Cylindrical alumina microfiltration membrane (GMITM Corporation, inside diameter=9 mm, outside diameter=13 mm, length= 50 mm) with an average pore size of 0.5 micrometer and porosity of about 0.35 was used as the support for membrane reactor. This support was soaked in boehmite sols, and the mean particle size was adjusted in the range of 50 to 500 nm by carefully controlling hydrolysis time, and calcined at 650 °C for two hours. This process was repeated with different boehmite solutions in order to achieve an intermediate layer with an average pore size of about 50 nm. The resulting substrate was then coated with a thin and dense layer of silica by counter current chemical vapour deposition (CVD) method. A boehmite sol with 10 wt.% of nickel which was prepared by a standard procedure was used to make the catalytic layer. BET, SEM, and XRD analysis were used to characterize this layer. The catalytic membrane reactor was placed in an experimental setup to evaluate the permeation and hydrogen separation performance for a steam reforming reaction. The setup consisted of a tubular module in which the membrane was fixed, and the reforming reaction occurred at the inner side of the membrane. Methane stream, diluted with nitrogen, and deionized water with a steam to carbon (S/C) ratio of 3.0 entered the reactor after the reactor was heated up to 500 °C with a specified rate of 2 °C/ min and the catalytic layer was reduced at presence of hydrogen for 2.5 hours. Nitrogen flow was used as sweep gas through the outer side of the reactor. Any liquid produced was trapped and separated at reactor exit by a cold trap, and the produced gases were analyzed by an on-line gas chromatograph (Agilent 7890A) to measure total CH$_4$ conversion and H$_2$ permeation. BET analysis indicated uniform size distribution for catalyst with average pore size of 280 nm and average surface area of 275 m^2.g^{-1}. Single-component permeation tests were carried out for hydrogen, methane, and carbon dioxide at temperature range of 500-800 °C, and the results showed almost the same permeance and hydrogen selectivity values for hydrogen as the composite membrane without catalytic layer. Performance of the catalytic membrane was evaluated by applying membranes as a membrane reactor for methane steam reforming reaction at gas hourly space velocity (GHSV) of 10,000 h^{-1} and 2 bar. CH$_4$ conversion increased from 50% to 85% with increasing reaction temperature from 600 °C to 750 °C, which is sufficiently above equilibrium curve at reaction conditions, but slightly lower than membrane reactor with packed nickel catalytic bed because of its higher surface area compared to the catalytic layer.

Keywords—Catalytic membrane, hydrogen, methane steam reforming, permeance.

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I. INTRODUCTION

IN recent years, extensive effort is done to convert natural gas, especially methane, into products with the added values like hydrogen by direct or indirect conversion methods [1]-[5]. Hydrogen has been introduced as a clean energy carrier and attracted great attention in recent decade [1], [2]. Although direct routes are more cost effective, the approach is difficult because the activity of products is higher than methane, and the result is decrease in conversion rates. Additionally, direct partial oxidation of methane needs pure oxygen instead of using air as potential source which requires downstream cryogenic separation process to eliminate nitrogen [6].

Steam reforming is currently the most common industrial route to turn methane into hydrogen. The process is endothermic, and methane conversion is partial due to thermodynamic equilibrium conditions of reforming reactions [7]. The reactions are to be carried out at high temperatures of more than 800 ºC and pressure of about 20 bar to increase methane conversion which leads to high capital investment of reactor construction material and total energy consumption [8].

The outlet of a steam reforming reactor consists of not only hydrogen, but also methane, vapor, unreacted carbon as coke, carbon dioxide, carbon monoxide, and some other components. A separation unit should be used in order to achieve highly purified hydrogen. Pressure swing adsorption (PSA) and cryogenic distillation are common methods at industrial facilities to purify hydrogen. However, due to some restrictions regarding high energy consumption or low purity of product, new approaches are recently being utilized [2]. Membrane separation is a newly developed technique for gas purification and has a number of advantages over the conventional technologies such as lower initial and operational costs, higher operation flexibility, and low energy consumption [9], [10].

Silica membranes with molecular sieving structure are microporous ceramic membranes which separate gas species based on their adsorption behavior and kinetic diameters [11]. The performance of these membranes usually depends on the synthesis conditions and final membrane morphology. Amorphous silica membranes are commonly synthesized by using sol-gel or CVD method [12], [13]. Sol-gel is the most investigated method as it is an easy way to produce high quality membranes with high permeation flux. However, comparatively low selectivity of final membranes on one hand, and lack of reproducibility of the membranes on the other hand led researchers towards CVD route [14]. Silica membranes for gas separation are mostly manufactured in

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composite, asymmetric structure with reducing pore size from macropores (>50 nm) in substrate to micropores (<2 nm) in top layer. In this construction, the substrate acts as a mechanical support, while the top layer is the selective barrier. To generate a thin and defect-free membrane, it is essential to use an intermediate layer which provides appropriate adhesion between layers and facilitates transition from the large pores to selective layer.

Steam reforming of methane in membrane reactors with the aim of producing highly purified hydrogen is mostly performed in tubular palladium-based membrane modules packed with proper catalysts. However, some major problems like high cost of the membrane module at industrial scale, poisoning of palladium, and extremely high rates of coking on membrane surface at harsh operating condition of MSR reaction lead researchers to investigate on substitute solutions.

In this work, composite ceramic membranes with tubular structure have been used for simultaneous H_2 production and purification in steam reforming reaction. The membranes consist of a modified alumina support which is covered with an ultra-thin layer of silica layer by CVD method. This membrane is applied in methane steam reforming reaction and its performance is evaluated at different operating conditions.

II. EXPERIMENTAL

Nanocomposite ceramic membranes with graded structure were synthesized by coating a thin layer of SiO_2 on top of alumina supports. A cylindrical α-alumina microfiltration membrane (GMITM Corporation, inside diameter=9 mm, outside diameter=13 mm, length= 100 mm) with a median pore size of 0.5 micrometer and porosity of 0.35 was used as the support. Boehmite (AlOOH) sols with mean particle size of 50 to 500 nm were prepared by carefully controlling peptizing agent (nitric acid) and hydrolysis and reflux time. Briefly, 0.4 mole of aluminum tri-sec butoxide (ATSB, Merck 98%)) as precursor was added to 600 ml of distilled water and was heated up to 80 °C within half an hour. The resulting solution was kept at this temperature for a specific range of time 3 to 20h which resulted in hydrolysis of the alkoxide and formation of boehmite precipitation. A specified quantity of nitric acid with H^+/alkoxide molar ratio of 0.08–0.2 was added to the solution and refluxed. Table I demonstrates the synthesis conditions for different sols. Dynamic light scattering (DLS) analysis was used to calculate the mean particle size of each sol. The support was soaked successively in these sols and calcined at 650 °C for two hours. This process was repeated twice for each solution in order to achieve a graded substrate with an average pore size of about 50 nm. Finally, a counter current CVD method was used to form an ultra-thin, dense layer of SiO_2 on top of the substrate. The process was carried out inside a quartz module at 600 °C with Tetra Ethyl Ortho Silicate (TEOS, Merck 99.5%) as precursor. SEM (Philips-XL30) analysis was carried out to evaluate membrane structure.

Catalytic sol was prepared by solving 10 wt.% of nickel in a boehmite sol using a standard procedure. The procedure is fully expressed in literature [8]. A catalytic membrane was

achieved by covering graded membrane with this solution by sol-gel method for 15 s. BET, SEM, and XRD analysis were used to characterize this catalytic layer. The catalytic membrane reactor was placed in an experimental set-up to evaluate the permeation and hydrogen separation performance for methane steam reforming reaction (Fig. 1). The setup consisted of a tubular module where the membrane was fixed and the reforming reaction performed at the inner side of the membrane. The reactor was heated up to 600 °C and the catalytic layer was reduced at presence of hydrogen for 2 hours. Methane stream was diluted with nitrogen and added to deionized water with a steam to carbon (S/C) ratio of 3.0 and entered the reactor. A counter-flow of nitrogen was used as sweep gas through the outer side of the reactor. The produced gases were analyzed by an on-line gas chromatograph (GC) (Agilent 7890A) to measure total methane conversion and hydrogen permeation.

TABLE I
SYNTHESIS CONDITION OF BOEHMITE SOLUTIONS PREPARED FOR SOL-GEL COATING

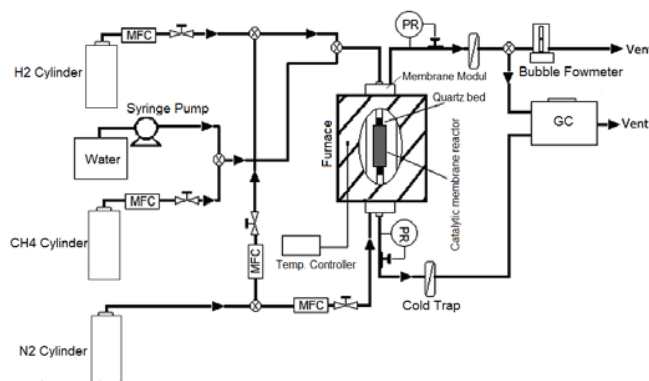| Sol Label	H^+/alkoxide molar ratio	Hydrolysis/ Reflux Time (h)[a]
S01	3	0.2 / 12
S02	15	0.2 / 6
S03	20	0.08 / 6

Fig. 1 Experimental set-up for methane steam reforming in membrane reactor adopted from [8]

III. RESULTS AND DISCUSSION

A. Membrane Characterization

Boehmite sols were characterized with DLS analysis using 1.3 as refractive index. The results showed mean particle size of 53.13, 104.3, and 451.1 nm for S01, S02, and S03, respectively. As the results indicate, higher H^+/alkoxide molar ratio causes smaller particle size in sols. This is because acid acts as a catalyst in solution and breaks the bond between the boehmite agglomerates. Moreover, lower hydrolysis time is favorable for smaller particle size, while more colloidal flocculation would be formed by polymerization reactions as the hydrolysis time proceeds.

SEM analysis was used to evaluate surface structure before and after coating, and also to estimate silica thickness of silica selective layer. As shown in Fig. 2, the α-alumina support has a completely porous structure with some pores in range of 300

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to 400 nm. After coating intermediate layers of γ-alumina with sol-gel, pore size reduces effectively and the substrate structure enters into meso-porous criteria. However, pore size distribution and even some large pores on the surface restrict its application for gas separation. The images show that after coating of SiO_2 by CVD, membrane top layer has a dense structure, and there are no specific pores left. Cross section of the final membrane confirms graded structure of the membrane and 90 to 100 nm thickness of the silica membrane after 3 h of CVD.
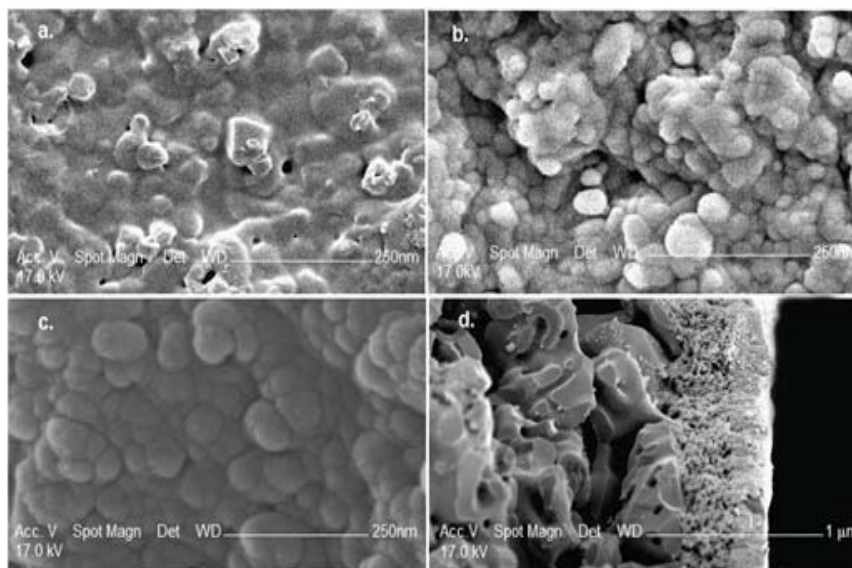
Fig. 2 SEM images from different layers of composite membrane: (a) Surface of α-alumina support; (b) Surface of graded substrate after sol-gel coating; (c) Surface of final composite membrane; (d) Cross-section of final composite membrane
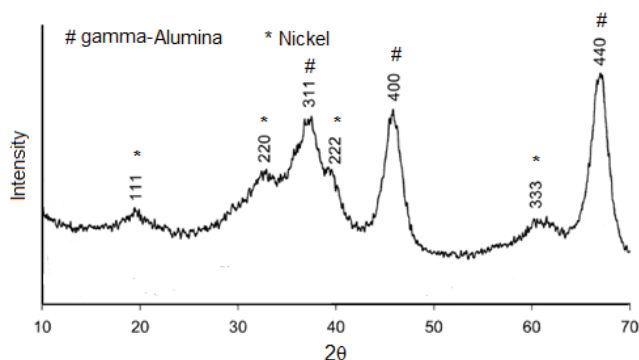

Fig. 3 XRD patterns for 10 wt.% Ni/ Alumina catalyst

The catalytic layer was characterized in terms of average pore diameter, surface area, and porosity by BET (Micrometrics, ASAP 2010) analysis. The results showed an average pore size of 280 nm, surface area of 280 $m^2.g^{-1}$, and porosity of 30%. These results are well in agreement with the physical properties of γ-alumina intermediate layer [15]. It means that 10 wt.% of Ni which is added to the alumina does not affect its physical properties. This is a critical issue when the membrane is used for gas separation. Therefore, this layer should cause the lowest restriction to permeation of gas molecules. X-ray diffraction (XRD) analysis was used to characterize the crystal structure of the catalyst after 3 h of calcination at 550 °C, and to ensure that no promoter is remained in the catalyst structure. As shown in Fig. 3, resulting patterns show standard peaks for nickel and γ-alumina with mesoporous structure in the catalyst with good dispersion of nickel on alumina substrate. According to the diffraction patterns, alumina has an amorphous structure, while Ni shows cubic crystal shapes.

B. Permeation Tests of Membrane Reactor

First, an equimolar ratio of H_2, CH_4, CO, CO_2 was used to evaluate the membrane properties in gas permeation. A differential pressure of 1 bar is used as the driving force for permeation. Effect of temperature was investigated for three different membranes with CVD time of 3, 4.5, and 6 hours, respectively. Separation factor was defined as permeation ratio of hydrogen to the mixture and was evaluated by analyzing an on-line gas chromatograph (GC) (Agilent 7890A) output. The results, shown in Fig. 4, indicate that gas permeation increases by increasing operating temperature. These permeation values are considerably higher than the reported permeability values through silica membranes even at lower temperatures [16]. The increasing trend of permeation is in contrast with Knudsen diffusion as the dominant permeation mechanism in γ-alumina membranes where gas permeability has reverse dependency on square root of temperature. The results confirm permeation mechanism via an activated molecular sieving in which gas molecules jump between adjacent void sites of the dense layer to pass the membrane [17]. Moreover, it is clear that although gas permeability decreases with higher CVD time, due to formation of thicker dense layers, H_2 separation factor increases because of better formation of this layer and less probable defects which may reduce membrane performance.

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Performance of the synthesized composite membrane was evaluated for methane steam reforming at a temperature range of 500-800 °C. The results are shown in Fig. 5. These results indicate that for all three membranes hydrogen removal has a positive effect on methane conversion comparing to equilibrium conditions. This is well in agreement with the Le Chatelier's principle which claims that the system adjusts itself to the new condition by shifting changes to the other side of the reaction [18]. It is shown that although membranes with longer CVD time and higher thickness have better selectivity, they have lower CH4 conversion because of lower permeance through membrane wall. This indicates that permeation flux has a dominant effect on the conversion of reactants in MSR reaction in membrane reactors.
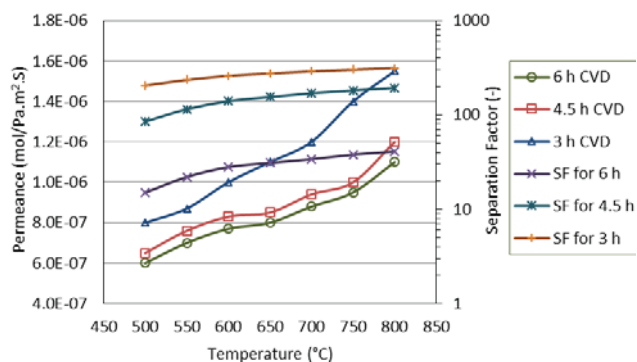

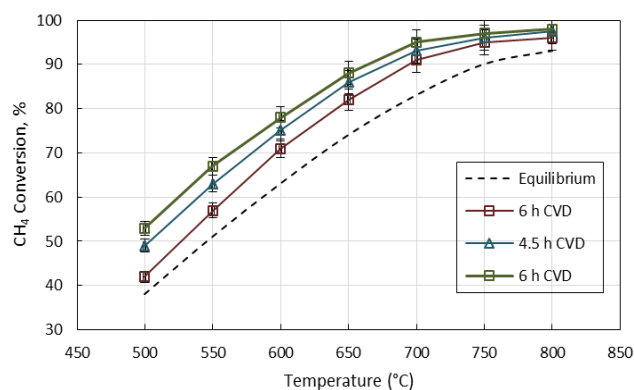Fig. 4 Permeance and separation factor of three membranes with different CVD times

Fig. 5 Methane conversion as a function of temperature for catalytic membrane reactors in MSR reaction

Effect of differential pressure on reaction and permeation side of the membrane was investigated in a range of 1 to 10 bar at 600 °C. The experimental conversions in the MR for three membranes and the equilibrium methane conversions were plotted in Fig. 6. These plots show a decreasing trend for both equilibrium and MR curves with increasing pressure because steam reforming is thermodynamically favored in lower pressures due to net increase of moles in reaction. CH4 conversion in membrane reactor is clearly increased in comparison with the equilibrium curves because of selective separation of hydrogen which in turn results in shifting the reaction to products side. These results clearly demonstrate

improvement of methane conversion in a MR with an appropriate membrane comparing to common packed bed reactors. Although the composite silica/alumina membrane which is synthesized in this research has a good permeation and separation properties, decreasing trend of conversion with increasing pressure shows that H_2 permeation is not high enough and cannot fully compete high reaction rate of reforming and overcome the effect of increase in moles in the reaction zone.
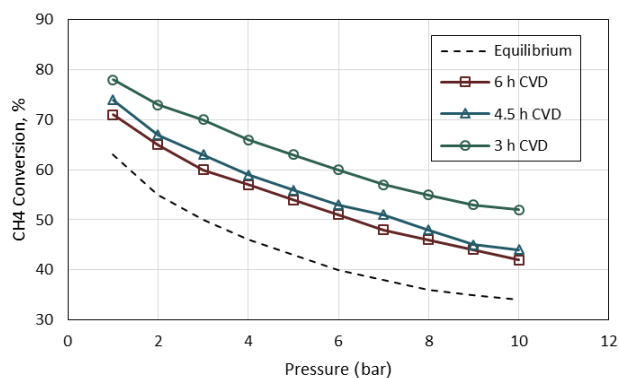

Fig. 6 Methane conversion as a function of pressure

IV. CONCLUSION

Catalytic membrane reactors were successfully prepared by coating a Ni/ Al_2O_3 on top of a nano-composite silica- alumina membrane. The final membrane showed great permeation properties and good separation factor for hydrogen at high temperatures. This membrane was used as a membrane reactor in methane steam reforming reaction, and the results confirmed CH_4 conversion higher than equilibrium even at low temperatures. These results offer ceramic membranes with appropriate structure as a good substitution of costly palladium membrane, with even higher conversions due to their high permeance.

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