

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Capture and Separation of Carbon Dioxide
from Combustion Sources**

Edited by

David C. Thomas

Senior Technical Advisor

Advanced Resources International, Inc.

4603 Clearwater Lane

Naperville, IL, USA

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Chapter 20

GRACE: DEVELOPMENT OF SILICA MEMBRANES FOR GAS SEPARATION AT HIGHER TEMPERATURES

Henk Kruidhof¹, Mieke W.J. Luiten¹, Nieck E. Benes² and Henny J.M. Bouwmeester¹

¹University of Twente, Enschede, The Netherlands

²University of Eindhoven, Eindhoven, The Netherlands

ABSTRACT

Using a polymeric gel solution route, tubular micro-porous silica membranes showing high hydrogen permeance and high gas selectivities have been prepared. Silica membranes have been coated on top of steam-stable γ -Al₂O₃ intermediate membranes inside a high-quality tubular support. Tube ends were coated with glass giving a gastight changeover between support and membranes. Single dead-end gas permeance measurements performed at temperatures > 300 °C and 4 bar pressure difference showed hydrogen fluxes > 1.10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ while H₂/CO₂ permselectivity under these conditions was found to be 80–100. H₂/CO₂ selectivity increases up to 200 with decreasing pressure down to 1 bar. Membranes were shown to be thermally stable for at least 2000 h at temperatures between 200 and 400 °C. Preliminary water-gas-shift experiments were performed at temperatures above 250 °C and showed higher than equilibrium CO conversion.

INTRODUCTION

With the development of new, highly selective inorganic membranes the possibility of using them for high-temperature gas separation and reaction became feasible. Hence, a large amount of research is currently being done on such membrane reactors on a worldwide scale. Membrane reactors can be used for selective removal of hydrogen in many equilibrium-restricted processes leading to a significant increase in conversion and yield, provided membrane permeance and selectivity are high. Moreover, by selectively removing hydrogen, strongly endothermic equilibrium-limited processes can be operated at temperatures that are significantly lower than those in conventional reactors without loss in conversion. Several types of membrane reactors are currently under investigation [1–3]. In the production of H₂ and CO₂-capture H₂/CO₂-selective gas-separating membranes can play an important role. For example, hydrogen can be removed selectively during steam reforming of various hydrocarbons, especially methane reforming, which is the major source of hydrogen in the world. In addition, selective removal of hydrogen during the water-gas-shift reaction will be an important application of an H₂/CO₂-selective membrane. Industrial separation processes based on traditional reactors are very energy intensive. The use of membrane reactors may save a lot of operating costs and may be less harmful to the environment. Because of the operating conditions in membrane reactors, as mentioned above, only inorganic membranes can be used. Besides micro-porous silica membranes, palladium membranes and zeolite membranes are also hydrogen selective. In this study, the preparation and qualities of tubular micro-porous silica membranes for use in WGS and removal of CO₂ are studied. Unfortunately, the project time was too short to investigate WGS performance in detail. Up to now only a few limited WGS experiments have been done. Investigations on properties as well as improvement of stability are still going on.

Abbreviations: WGS, water-gas-shift; Si₍₆₀₀₎, silica membranes fired at 600 °C during preparation; MAP, mono-aluminum-phosphate; MAP χ -tubes, tubular supports as treated with solutions containing $\chi\%$ of MAP; BC-solution, La-containing boehmite coating solution; SASRA, ambient steam reforming atmosphere; BET, Brunauer–Emmet–Teller.

The gas separation properties of micro-porous silica membranes are mainly based on molecular sieving. To apply H₂/CO₂-selective membranes in hydrogen-producing reactors, the membrane has to meet several demands such as high-hydrogen permeance in combination with high permselectivities for gasses like, for example, CO₂, CH₄ and CO as compared with H₂. When not considering H₂, CO₂ has the smallest kinetic diameter (0.33 nm).

Our flat state-of-the-art micro-porous silica membranes as developed a number of years ago [4,5] have a diameter of 39 mm and consist of three layers (see Figure 1): a support of α -Al₂O₃ giving the membrane its mechanical strength, a meso-porous intermediate γ -Al₂O₃ layer on top of which is an active micro-porous silica layer with a thickness of about 50 nm. The selectivity of such a flat, state-of-the-art, silica membrane meets the demands for industrial operations on condition the silica membrane has been sintered at 600 °C (Si₆₀₀). For industrial use, hydrogen permeance has to increase 1.5–2 times.

Table 1 gives the values for a standard Si₆₀₀ membrane as measured at 300 °C and the values required for economical industrial use, based on figures as provided by industry.

TABLE 1
PERFORMANCE OF FLAT PLATE MEMBRANES AND DEMANDS FOR COMMERCIAL
TUBULAR ONES

	BET specific surface area (m ² g ⁻¹)	
	Before SASRA treatment	After SASRA treatment
SiO ₂	0.2	<0.2
SiO ₂ /10% Ti	0.3	<0.2
SiO ₂ /10% Zr	0.5	<0.3

Since for practical applications, the flat plate geometry is considered unsuitable, the intermediate and silica layers should be placed on the inside of high-quality commercially available tubular supports. Furthermore, although the thermal and mechanical properties of micro-porous silica membranes are superior compared to those of their organic counterparts, use for H₂ separation at high temperatures and under harsh conditions requires improvement of their hydrothermal stability.

Coating a high-quality micro-porous silica layer of about 50 nm on top of a meso-porous γ -Al₂O₃ layer requires that the γ -Al₂O₃ layer is also of high quality. Such a layer usually has a thickness of about 1.5 μ m and high quality can only be obtained if coated on (tubular) supports with very smooth and defect-free surfaces. In the case of the flat micro-porous silica membranes, membrane layers are deposited on a perfect “purpose made” α -Al₂O₃ support with a perfectly smooth and polished surface [5]. High-quality tubular supports, as demanded for micro-porous membrane preparation, are not commercially available. In close cooperation with our research group, aaflo systems GmbH, Germany, developed a multi layered tubular α -Al₂O₃ support as a special product for micro-porous membrane coating. This tubular support was improved continuously and near the end of the project, this tube was of much higher quality compared with standard support tubes.

Hydrogen permselective silica top layers, stable under practical conditions, are only obtainable if the whole support including the meso-porous intermediate layer is fully stable under practical conditions. To obtain such a hydrothermally stable support, the stability of the meso-porous intermediate γ -Al₂O₃ has to be realized. It is also impossible to determine the real performance of the micro-porous silica membrane if such a membrane is applied on top of an intermediate γ -Al₂O₃ layer that does not have good stability. Non-hydrothermal stability of γ -Al₂O₃ has been reported in literature. Instabilities of γ -Al₂O₃ membranes varying from large changes in pore sizes [6,7] to large defects [8] are reported when these membranes are exposed to steam. Even complete delamination of these membranes from the α -Al₂O₃ support in hot steam

is known [5,9]. So it is clear that hydrothermal stability of the intermediate γ -Al₂O₃ layer had to be realized. Nijmeijer et al. [9] have published a method describing the preparation of hydrothermally stable γ -Al₂O₃ membranes on flat plate supports. Starting from this method La-doping of γ -Al₂O₃ has been used to increase pore stability and impede phase transition of γ -Al₂O₃ to other transition Al₂O₃-forms as described by Wefers and Misra [10]. Mono aluminum phosphate (MAP) coating of tubular supports, preliminary to boehmite coating (to obtain γ -Al₂O₃ layer) have been used to anchor the γ -Al₂O₃ intermediate membrane to the tubular α -Al₂O₃ support.

If high conversions are feasible in a membrane-WGS reactor, the water vapor pressure can be relatively low. The membrane has to be stable under practical conditions. Consequently, testing of the silica membrane has to be performed under real WGS conditions. Dependent on the results, hydrothermal stabilization of the silica top layer may be essential (doping the silica or preparing a hydrophobic membrane system). Due to lack of time for the project, no stabilization experiments could be performed on supported SiO₂-membranes. Only unsupported doped and undoped SiO₂ have been exposed to steam. Due to their relatively large pore sizes as compared with silica membranes [11,12] using zirconia/titania-based membranes for gas separation is not an option today.

For testing hydrogen permeance, permselectivity and WGS performance of tubular membrane systems, the membranes have to be fixed into a reactor. The latter means that at the end of the tubes a gastight seal has to be achieved in order to separate gas inlets and outlets. Also the changeovers from sealed support ends to membranes have to be absolutely gastight.

A seal meeting the demands for membrane fixing into the reactor as well as gas tightness of the changeovers between sealed tube-ends and membranes had to be developed.

EXPERIMENTAL

All experiments were performed on multi layered α -Al₂O₃ tubular supports prepared as a special high-quality product (aaflo systems, GmbH, Germany). Improving the inner surface roughness of these tubes and preventing defects was a continuous process during the term of the project. The coarse pore-sized (several microns) extruded tubes are coated with a number of α -alumina layers, resulting in a systematic decrease in pore size through the coated layers. The inner-most support layer has a pore size of \sim 100 nm.

For convenience and clarity, we will only deal with tubes as prepared just at the beginning of the project (first generation), tubes as prepared halfway the project (second generation) and tubes as prepared 6 months before the end of the project (third generation). Preparation and characterization of membranes were repeated every time, improved tubular multi layered supports were available. For all experiments, tubes with a length of 10 cm were used.

Tube End Sealing

For all preliminary experiments, foregoing high-temperature characterization measurements, synthetic resins and glues for tube end sealing were used. Tube end sealing based on glass as developed during the term of the project, was applied later on. These glass seals having gastight changeovers between support and membranes are applicable up to 500 °C. Synthetic seals were applied, after preparation of the whole supported membrane, while glass sealing was already applied to the tubular supports before any other treatment.

Preparation and Characterization of Tubular Steam Stable γ -Al₂O₃ Membranes

To anchor intermediate γ -Al₂O₃ layers to the tubular supports, a MAP layer was coated on the supports [9] according to the following procedure. A commercial 50 wt% MAP solution (alfa, Johnson, Matthey GmbH, Karlsruhe, Germany) was used to prepare diluted aqueous solutions, resulting in MAP concentrations varying between 0 and 5 wt%. The insides of tubular supports were brought in contact with the solutions for 10 s, after which they were dried and fired. These tubes will further be referred to as MAP_x-tubes, x being the MAP concentration of the solutions the tubes are treated with. All MAP-treated tubes were coated under class-100 clean room conditions with a 0.5 M boehmite sol, containing 6 mol % La in relation to the Al content.

La-doped boehmite sol was prepared the following way. First, 0.5 mol of aluminium-tri-sec-butoxide (ATSB 97% purity, E. Merck, Darmstadt, Germany) was allowed to react with ~ 70 mol of double-95 °C distilled water [13]. The ASTB was added drop wise to the water under a nitrogen gas flow to avoid premature hydrolysis. The temperature of the reaction mixture was >90 °C to avoid the formation of bayerite [14]. After the ASB was added, the mixture was kept at 95 °C for at least 1 h to evaporate the butanol formed. The mixture was subsequently cooled to ~ 60 °C, water added to ~ 1 L (to fill up evaporated water) and peptized with 1 M HNO₃ (E. Merck, Darmstadt, Germany) at a pH of ~ 2.8 . During the whole synthesis, the sol was stirred vigorously. The peptized mixture was refluxed for 20 h at 90 °C, resulting in a very stable 0.5 M boehmite sol with a clear white/blue appearance. Thorough mixing with the appropriate amount of a 0.3 M La-nitrate solution performed doping of this sol. The mixing was done just before preparing the coating solution to avoid possible aging effects as reported in the literature [15].

An La-containing boehmite coating solution (referred to as BC-solution) for inner tubular membrane coating was prepared by diluting 30 mL of doped boehmite sol with 20 mL of a solution containing 30 g of polyvinyl alcohol in 1 L of 0.05 M HNO₃. All MAP_x tubes were brought in contact with the BC-solution for 3 min using a rate- and time-adjustable communicating vessel system. Filling and emptying rates were 1.7 cm s^{-1} . Coating procedures were carried out under class-100 clean room conditions. After coating, the membranes were dried and fired in air at a temperature of 650 °C for 3 h using heating and cooling rates of 1 °C min^{-1} . The coating and firing procedure was repeated once and resulted finally in layers with a total thickness of 3 μm (as investigated beforehand). These La-doped and support-anchored γ -Al₂O₃ membranes were subjected to simulated ambient steam reforming atmosphere (SASRA) for 100 h at 600 °C using H₂O/CH₄ = 3/1 (by volume) at 25 bar total pressure. The experiments were performed at Sintef, Materials Technology, Norway.

Before and after SASRA treatment, pore sizes of the membranes were determined by means of permporometry to establish (non) pore growth and (non) ongoing sintering during hydrothermal treatment. The method and the equipment used for the measurements have been described in detail elsewhere [16]. In the meantime, though the apparatus has been modernized, the principle remains the same. The method is based on capillary condensation of cyclohexane in the meso-porous membrane until all pores are filled followed by emptying the membrane pores when the cyclohexane partial pressure above the membrane has been reduced. From oxygen permeance data as a function of the cyclohexane partial pressure, the pore size distribution can be calculated using the Kelvin equation [17].

The adherence of the γ -Al₂O₃ membranes was investigated in the following way. After SASRA, tubes were sawn through lengthwise and observed by SEM. (JEOL 5800 and/or FEG SEM). The so-called "Scotch tape test" was also done after SASRA. The test has been described elsewhere [18]. In this test, a piece of Scotch tape was applied firmly with the sticky side onto the membrane surface and torn off rapidly. If the membrane layer was torn off together with the tape, it was concluded that destruction of the membrane had occurred. For membranes that did not show any sign of destruction, as far as applicable the pore-size was measured by permporometry.

Preparation and Characterization of Tubular Micro-Porous Silica Top Layers

Polymeric silica sols [13] were prepared by acid-catalyzed hydrolysis and condensation of tetra-ethyl-ortho-silicate (TEOS, 98%, Aldrich) in ethanol. A mixture of acid and water was carefully added to a mixture of TEOS and ethanol under vigorous stirring. During the addition, the reaction mixture was cooled in an ice bath to avoid premature hydrolysis. After completion of the reaction, mixtures were heated for 3 h in a water bath under continuous stirring. The reaction mixtures had a final molar TEOS/ethanol/water/acid ratio of 1/4/6.5/0.085. The reaction mixtures were cooled to ambient and diluted 19 times with ethanol to obtain the final Si-coating solutions.

MAP_{0.5} tubes were brought in contact with the Si-coating solutions for 10 s using a rate- and time-adjustable communicating vessel system. Filling of the tubes was done fast, while after the 10 s coating, emptying rates were slow. Coating procedures were carried out under class-100 clean room conditions. After coating, the membranes were dried and fired in air at a temperature of 600 °C for 3 h using heating and cooling rates of 0.5 °C min^{-1} . The coating and firing procedure was repeated once. In Figure 1, a schematic supported silica membrane on top of a meso-porous intermediate layer is shown.

SiO₂ layer thickness was measured by means of XPS (Physical Electronics Quantera, Scanning X-ray Microscope) using etching rates of 18 nm min⁻¹. Selectivity of the membranes was measured by means of single gas permeance measurements of H₂, CH₄, N₂ and CO₂ using homemade equipment. Dead-end measurements were performed at 150–350 °C under a pressure difference of 1 and 3 bar. The principle of the measurements for flat plates is described elsewhere [8, p. 28,29]. Measurements on tubular membranes principally do not differ from flat plate membrane measurements, except from being measured in tubular modules. Sealing of the membrane in the module was done with graphite rings under pressure.

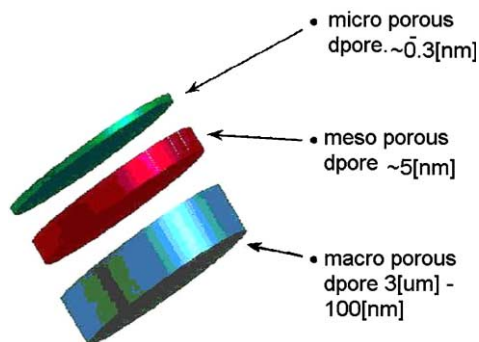


Figure 1: Schematic silica membrane with intermediate meso-porous γ -Al₂O₃ layer on multi layered support.

Silica Stability and Doping of Unsupported Silica

The thermal stability of silica membranes as prepared on steam stable intermediate meso-porous γ -Al₂O₃ layers has been measured by exposing the membrane to different (dry) gasses and temperatures for about 3 months (~2000 h). Temperatures up to 450 °C were applied. During 3 months, the membrane was exposed to several temperatures and gasses, heating and cooling conditions. As a reference, hydrogen permeance at 250 °C and 3.8 bar pressure difference was used and measured a few times.

Silica has been doped with zirconia and titania by adding Ti-butoxide and Zr-butoxide, respectively to silica sols. Amounts of 10 mol% with respect to silica have been added. For preparing unsupported membranes, sols were poured onto a dish, dried and fired at 600 °C in the same way as described for supported silica membrane preparation. Non-doped and doped samples were exposed to SASRA conditions (total pressure 25 bar, H₂O/CH₄ is 3/1, 600 °C, SINTEF, Norway). Before and after SASRA treatment, the BET-specific surface area was measured (Quantachrom's Monosorb BET analyser). XRD recordings were compared from samples before and after SASRA treatment. (X-ray diffractometer, Siemens D5000)

WGS performance of membranes as prepared inside second-generation supports was tested (ITM-CNR, Italy).

RESULTS AND DISCUSSION

γ -Alumina Stabilized Intermediate Layers

In the Scotch tape test as applied after SASRA treatment, most γ -Al₂O₃ layers were released from the support when the supports were not treated with MAP. Figure 2 shows a crack in the membrane–support interface as observed after SASRA treatment.

Besides the bad coherency, no further damage could be observed. γ -Al₂O₃ layers coated on MAP_x supports, with $x > 0.4\%$ did not show any release from the support after the Scotch tape test. As suggested by Nijmeijer et al. [9] this beneficial effect may be attributed to chemical bonding between the membrane layer and the support. Preliminary gas permeance measurements performed on samples treated with high MAP

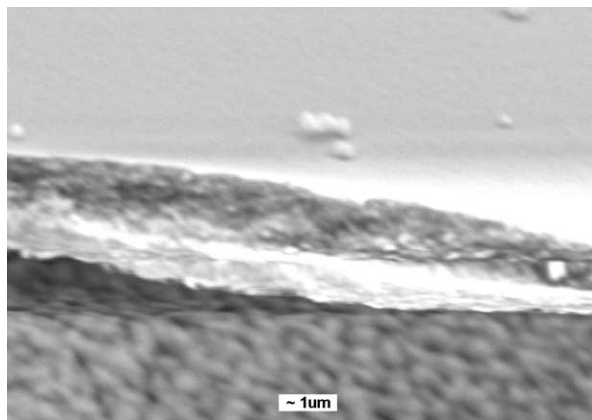


Figure 2: Detaching γ -alumina layer from the support.

concentrations ($> \sim 3\%$) showed a reduced gas flow as compared with non-treated samples. MAP penetrates the pores while using relatively high-concentrated solutions for support coating and later on this results in partial blocking of the pores.

Several repetitions of the γ - Al_2O_3 layer preparation on $\text{MAP}_{0.5}$ supports showed good anchored layers every time, again indicating 0.5% is a suitable MAP concentration for pre-treatment of the tubular supports. This concentration to pre-treat tubular supports was used for all further experiments.

Permporometry measurements performed before and after SASRA treatments did not show differences in pore size. The diameter of the pores was determined to be $5.5(\pm 1)$ nm and (6 ± 1) nm for and after SASRA treatments, respectively. Nijmeijer et al [9] report comparable steam-stable SASRA properties of γ - Al_2O_3 membranes on flat plated supports. They applied MAP on top of flat supports before boehmite coating. The latter procedure also includes doping of the boehmite sol with 6 mol% La. The amount of MAP as needed for a good coherence between support and membrane appeared to be much lower in the case a tubular support was used. As discussed by Nijmeijer et al., the interfacial stress between support and membrane may play an important role on membrane stability. They suggest that phosphate bonds are important to overcome this interfacial stress.

Because the penetration depth of the γ -layer into the support and also the shape of the support may influence the coherency and the tensile stresses as built up in the γ - $\text{Al}_2\text{O}_3/\alpha$ - Al_2O_3 interface, the amount of MAP may be different when flat supports have been used.

So it may be concluded that tubular γ - Al_2O_3 membranes have been prepared, hydrothermally stable in a steam environment at a temperature of 600 °C and a total pressure of 25 bar ($\text{CH}_4/\text{H}_2\text{O} = 1/3$), for at least 100 h.

Membrane Characterization

Figure 3 shows an XPS recording as obtained by etching of the membrane layer by layer. Etching (Ar^+) rates of 18 nm min^{-1} were used and the atomic concentrations of Si and Al (and O) were determined continuously. The figure gives the atomic concentration as a function of etching time.

It can be observed, that after an etching time of about 1 min, the Si concentration is decreasing while the Al concentration is increasing. From the latter observations, it can be concluded that the SiO_2 -layer thickness on top comes to ~ 18 nm. After a total etching time of about 4 min the Al signal becomes constant, indicating a SiO_2/γ - Al_2O_3 intermediate layer of about 60 nm. The silica layer thickness is rather thin and increasing the thickness probably will improve reproducibility. Just at the end of the project, support tubes were of a quality high enough to perform real systematic coating experiments. For this

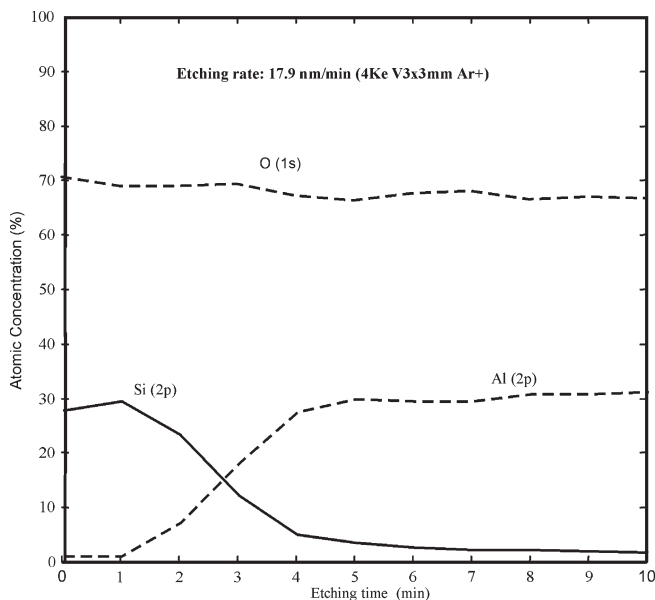


Figure 3: Silica layer thickness as measured by XPS.

reason, experiments such as layer thickness in relationship to selectivity and reproducibility are still under investigation.

Gas permeance measurements of hydrogen and methane as performed on silica membranes coated on tubular first generation supports showed very bad selectivity. When tubular supports of the second generation were used, the results were much better but selectivity was still moderate and reproducibility was bad. Membranes prepared on third generation support tubes gave high H_2 -permeance values mostly combined with high selectivities for H_2 , relative to several gasses. At the moment, reproducibility on preparation of these tubes is still under investigation.

Table 2 shows permeance values of several gasses as obtained for a membrane coated on a third generation support. The meso-porous intermediate layer has a thickness of $3 \mu\text{m}$ and glass based end sealing has been applied (silica top layer 20 nm, changeover layer Si/Al 60 nm).

An explanation of the different behavior of gasses at different temperatures and pressures is outside the scope of this chapter and has been reported in detail elsewhere [19].

Figure 4 shows H_2 permeance as a function of temperature at a pressure difference of 3.8 bar while Figure 5 gives permselectivities as compared to H_2 as a function of pressure difference at 350°C . Finally, Figure 6 gives permselectivities as a function of temperature at a pressure difference of 3.8 bar.

Experiments are still going on. Measurements at relatively high temperatures are also being carried out. The permeance values obtained at different temperatures are compared with small state-of-the-art flat plate membranes. Hydrogen permeance has been increased just as the H_2/CO_2 permselectivity. So concerning hydrogen permeance and selectivity, this tube is meeting the demands. At the moment, reproducibility has not been investigated in detail but without doubt this has to be improved. Tubular supports still need improvement and systematic experiments on tubular membrane coating are needed. However, the obtained results make it clear that high-quality tubular gas separating membranes can be produced.

TABLE 2
GAS PERMEANCE VALUES AND SELECTIVITY OF A SILICA MEMBRANE AS OBTAINED FOR
THIRD GENERATION TUBES

Temperature (°C)	dp (bar)	Permeance ($\text{mol m}^{-2} \text{s}^{-2} \text{Pa}^{-1}$)				Selectivity		
		H ₂	CH ₄	N ₂	CO ₂	H ₂ /CH ₄	H ₂ /N ₂	H ₂ /CO ₂
150	3.8	2.8E-07	3.8E-09	3.7E-09	1.2E-08	75	77	25
	1.0	2.9E-07	1.9E-09	3.2E-09	5.1E-09	148	87	54
200	3.8	3.9E-07	1.6E-09	2.3E-09	1.0E-08	241	166	37
	1.0	3.5E-07	6.5E-10	2.2E-09	4.1E-09	534	154	84
250	3.8	6.0E-07	1.2E-09	1.6E-09	8.4E-09	495	367	72
	1.0	5.4E-07	5.1E-10	1.5E-09	2.4E-09	1064	355	230
300	3.8	9.7E-07	1.10E-09	3.3E-09	1.2E-08	889	297	80
	1.0	9.5E-07	4.13E-10	3.3E-09	6.0E-09	2311	288	159
350	3.8	1.2E-06	1.1E-09	3.6E-09	1.24E-08	1164	344	100
	3.0	1.2E-06	9.5E-10	3.6E-09	1.17E-08	1301	348	106
	2.5	1.2E-06	8.8E-10	3.6E-09	1.11E-08	1419	348	112
	2.0	1.3E-06	7.8E-10	3.5E-09	1.02E-08	1612	356	124
	1.5	1.2E-06	6.5E-10	3.5E-09	8.72E-09	1911	349	142
	1.0	1.2E-06	4.8E-10	3.5E-09	6.20E-09	2562	353	199

During the permeance measurements, in total lasting about 2000 h, no big alteration in hydrogen permeance and selectivity could be observed. After 2000 h, it was observed that hydrogen permeance as well as methane permeance had increased $\sim 20\%$ as measured at the reference temperature of 250 °C. It can be concluded that under the experimental conditions, the membrane appeared to be thermally stable.

Long-term experiments, however, should be repeated and extended in order to establish thermal stability for long periods of use. It should be clear whether the increase in permeance can be attributed to a slow degradation of the membrane at moderate temperatures or whether possible membrane degradation is caused by higher temperature use. Unsupported standard membranes such as TiO₂ and ZrO₂ doped ones did not show any crystallization after SASRA treatment. As shown in Table 3, BET analysis, however, showed a decrease in surface area indicating that sintering is going on if silica is exposed to steam of relatively high pressures.

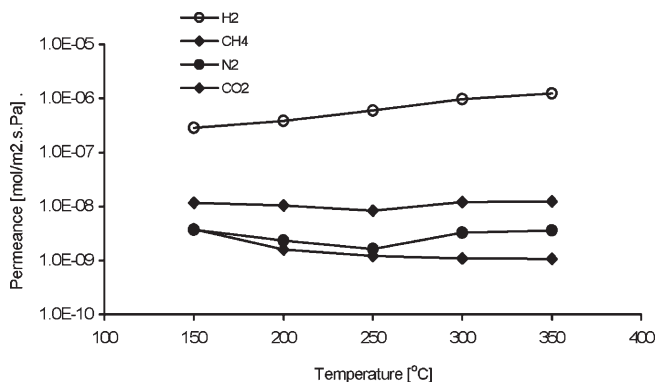


Figure 4: Hydrogen permeance as a function of temperature at a pressure difference of 3.8 bar.

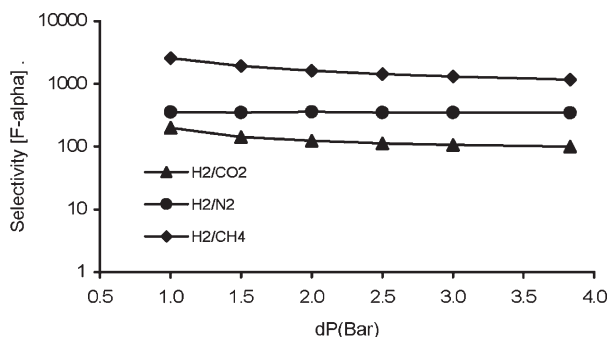


Figure 5: Permselectivities in relation to hydrogen as a function of pressure difference at 350 °C.

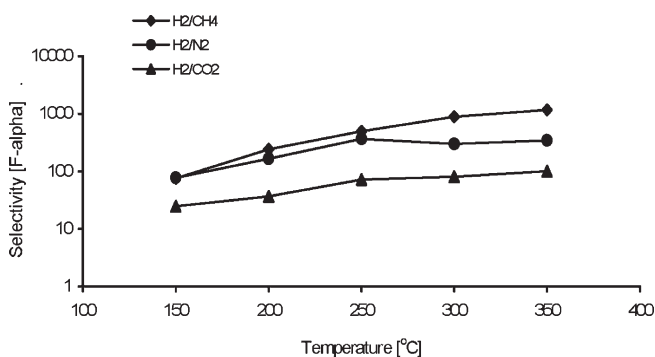


Figure 6: Permselectivities in relation to hydrogen as a function of temperature at a pressure difference of 3.8 bar.

TABLE 3
BET SPECIFIC SURFACE AREA BEFORE AND AFTER SASRA TREATMENTS AT 600 °C
AND A PRESSURE OF 25 BAR

Gas	State-of-the-art flat plate S ₁₆₀₀ -membrane (dp = 4 bar, 300 °C)		Commercial demands (tubular shape under practical circumstances)	
	Permeance (10 ⁻⁷ mol m ⁻² s ⁻¹ Pa ⁻¹)	Permselectivity (in proportion to H ₂)	Permeance (10 ⁻⁷ mol m ⁻² s ⁻¹ Pa ⁻¹)	Permselectivity (in proportion to H ₂)
H ₂	6.5	–	>10	–
CO ₂	0.12	54	Low as possible	>50
CH ₄	<0.01	>650	Low as possible	~500

The ongoing sintering may lead to a decrease in pore sizes of supported membranes, when such a membrane is exposed to steam. Experiments under practical conditions have to be performed to establish real performance of the membranes, because only such experiments give the real circumstances the membrane has to withstand.

First WGS experiments were achieved at ITM-CNR (Italy). Membranes as coated on second-generation tubular supports were used. Despite the relatively moderate quality as compared with third generation tubes, promising results were obtained and above 250 °C higher than equilibrium CO conversion was found. The results are reported by ITM-CNR elsewhere in this book.

Experiments on third generation tubes are still ongoing and also WGS experiments will be performed later on. Hydrothermal stabilization of the silica membrane may be needed, but the influence of the steam-stabilized γ -Al₂O₃ layer on the supported (not stabilized) silica membrane has also to be investigated. A supported silica membrane will only be hydrothermally stable on a steam-stable meso-porous intermediate layer and under relatively mild conditions hydrothermal stability may be better than expected when coated on such a layer.

CONCLUSIONS

With the preparation of steam-stable γ -Al₂O₃ membranes inside tubular supports, the first step in preparation of hydrothermally stable gas-separating membranes has been made. Besides steam stability of the support, stability of the intermediate meso-porous layer is also necessary for testing and preparing supported hydrothermally stable gas-separating membranes. The method is very similar to hydrothermal stabilization of γ -Al₂O₃ on top of small flat plate supports. As compared to flat membranes, in case of tubular supports the amount of MAP needed for good coherency is clearly less but still required. Care should be taken that MAP concentration of the solutions as used for pre-treating the supports is not too high otherwise permeance will be reduced because of pore blocking later on.

Quality of the support tubes is of enormous importance. Irregularities and defects make micro-porous membrane preparation almost impossible, even when using rather thick intermediate meso-porous layers. Especially when gas-separating properties are wanted, the support tubes have to be very smooth on the membrane coating side.

End seals of high quality and stability at relatively high temperatures are needed, because here too no leakage is allowed. Special attention has to be paid to the changeover region between sealing and membranes.

It has been proven that high hydrogen fluxes combined with high selectivities are obtainable on tubular membranes and these membranes are stable at higher temperatures for at least 2000 h when applied to dry gas separation. It may be important to extend long-term experiments.

The next step may be improvement of hydrothermal stability to make the membrane applicable for H₂/CO₂ separation and CO₂ capture under wet conditions.

The first WGS experiments showed promising results, however, no long-term experiments were performed. Short-term as well as long-term experiments should be done, using tubular third generation supports.

RECOMMENDATIONS

In cooperation with tube manufacturers, support tubes have to be improved further. Defects inside the tubes should be minimized and much smoother inner surfaces are needed. If tubes of higher quality are obtained scaling up of tubular membrane preparation to be used in several applications seems to be likely.

Membrane preparation experiments should continue on more improved supports in order to improve reproducibility and performance.

Short- and long-term WGS experiments on tubular membranes should be carried out in order to establish the performance under practical conditions.

Research on hydrothermal stability of silica membranes on steam-stable supports needs continuation just as likely research on improving the hydrothermal stability of silica membranes.

Long-term experiments on (dry) gas separation at relatively high temperatures (300–450 °C) should be extended in order to establish the durability of the thermal stability of the membranes at higher temperatures.

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