Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

Edited by

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Chapter 17

SILICA MEMBRANES FOR HYDROGEN FUEL PRODUCTION BY MEMBRANE WATER GAS SHIFT REACTION AND DEVELOPMENT OF A MATHEMATICAL MODEL FOR A MEMBRANE SHIFT REACTOR

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ABSTRACT

One of the technologies for pre-combustion decarbonisation is the production of hydrogen rich fuel gas from fossil fuel feed stock by means of a water gas shift membrane reactor system. A study to develop and test hydrogen selective membranes for use in a water gas shift membrane reactor operating with sour synthesis gas has been sponsored by the CO_2 Capture Project. The aim of the project was to demonstrate a proof of concept water gas shift membrane reactor for this purpose.

As one of the potential membrane options in such a membrane reactor tubular microporous silica membranes have been made for testing with a simulated water gas shift mixture. With standard silica membranes the flux criteria can be met when no water is present in the feed. However, with water in the feed the flux drops to a value, which is a factor 3 below the target. At the start of the project it was clear that the permselectivity criterion of 100 was too high for microporous membranes, because a maximum H_2/CO_2 permselectivity of 39 was thus far measured for standard silica membranes. Selectivity improvement was focused on higher sintering temperatures, but increase of the H_2/CO_2 selectivity has not been experimentally proven. It was shown that H_2S has no detrimental effect on a standard silica membrane and the H_2/H_2S selectivity is very high. Under the process conditions, so including a relative high water concentration, the stability of the silica membrane is limited to days as expected. The hydrothermal stability has been improved by incorporating alkyl-groups in the silica structure (ECN patent pending). The modified silica membrane is stable for more than 1000 h under simulated steam atmosphere testing.

A software model of the water gas shift membrane reactor has been developed. The model simulates a counter current water gas shift membrane reactor with microporous membranes (silica and zeolite) and dense (palladium and proton conducting) membranes and copes with the isothermal and non-isothermal operation of the membrane reactor. The model is implemented as an Aspen Plus User Model (Aspen Plus, version 11.1) and is written in FORTRAN.

INTRODUCTION

The CO_2 Capture Project (CCP) is an initiative of eight major energy and oil companies to develop cost effective technologies for the capture and geologic storage of carbon dioxide.

CCP has sponsored a study on the development of technology to produce hydrogen rich fuel gas from fossil fuel feedstock by means of a water gas shift (WGS) membrane reactor system. The hydrogen rich fuel can be used as a carbon-free fuel in refinery heaters, gas turbines and for power generation. The envisioned application of a WGS membrane reactor is to convert the CO in the syngas from a gasifier to produce

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Abbreviations: WGS, water gas shift; ECN, Energy Research Centre of the Netherlands; CCP, CO_2 Capture Project; PIC, pressure indicator and controller; MFC, mass flow controller.

a hydrogen rich fuel gas stream and a CO_2 rich stream, which can be compressed for geological sequestration with minimum further treatment.

The aim of the project is to develop the WGS membrane reactor technology to proof of concept. The system is to be designed for operation with sour synthesis gas. The study was divided into two phases. Phase 1 (12 month activity) involved membrane development and testing on four different membrane materials. Preliminary process calculations have set membrane targets on a hydrogen selectivity >100 and a hydrogen permeance >0.1 mol/m^{2}s bar. The results from this work will be used to estimate membrane and reactor performances, and to determine which of the four membrane types will be selected for further development and application in a laboratory reactor system during phase 2.

The development and testing of tubular microporous silica membranes for use in the reactor, and the development of a computer simulation model of the membrane reactor are described in this chapter.

EXPERIMENTAL

Silica Membrane Preparation

To get an overview of the performance and the stability of the membrane under WGS conditions several batches of tubular silica membranes have been made according to current standard recipes [1]. The silica membranes are made in a batch process, with a maximum of 10 tubes each time. Alumina substrate tubes with a maximum length of 1 m were coated on the outside with porous intermediate layers in order to overcome the surface roughness. A so-called polymeric silica sol was made and coated on top of the intermediate layer [2]. After calcining the membranes are ready for use. The pore size of the membranes is about 5 Å and can be optimised for certain applications by, e.g. modifying the silica sol or the calcining procedure. The separation layer of these membranes consists of a very thin (<200 nm) hydrophilic amorphous silica film on the outside of a multi-layer alumina support tube (see Figure 1).

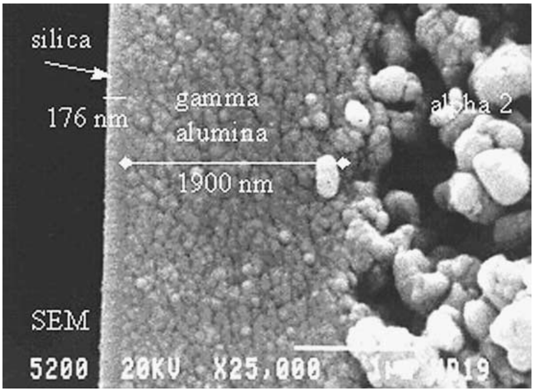

Figure 1: Scanning electron micrograph of a high-selective silica membrane.

The membrane tubes are made at a length of 1 m, an ID/OD of 8/14 mm and as a batch containing 12 tubes. Pieces of 10 cm have been cut from these tubes for use in the test programme. An overview of properties of the support and membrane layer is given in Table 1.

The silica membrane batch quality has been checked by our so-called Helium-1-point test. The Helium-1-point test gives an indication of the defect density of the membrane. By comparing the results of the He-1-point test with gas permeation tests we found that the probability for sufficient gas separation properties is high enough when the 1-point He value is below 100 mL He/min 10 cm 3 bar. Silica membrane pieces for use in the test programme have been selected based upon the He value. Gas permeation tests have been performed with silica membranes with a He value below 100 units.

TABLE 1
OVERVIEW OF PROPERTIES OF THE SUPPORT AND MEMBRANE LAYER

Layer	Coating type	Name	Compound	Thickness	Porosity	Pore *d*50/nm
1	–	Extruded tube	α-Al_2O_3	3000 μm	0.35	4000
2	Suspension	alpha 1	α-Al_2O_3	30–50 μm	0.22	180
3	Suspension	alpha 2	α-Al_2O_3	30–40 μm	0.34	170
4	Sol–gel	gamma	γ-Al_2O_3	1.5–2.0 μm	0.5	3–5
5	Sol–gel	Silica	SiO_2	50–120 nm	0.5	<1

Specifically for the separation of hydrogen from CO_2/CO/H_2O it is foreseen that further membrane development is necessary to improve the hydrothermal stability. For this stability improvement modified silica structures, which incorporates alkyl-groups (ECN patent pending) have been prepared. Small batches of tubular modified silica membranes with built in methyl groups have been made according to available recipes [3]. Addition of methyl groups in the silica structure has been done by the addition of and reaction with methyltriethoxysilane (MTES), see Figure 2. Calcination temperatures (250 or 400 °C), calcination atmosphere (air or nitrogen) and pre-treatment procedures have been varied during fabrication to determine the effect of these processing parameters on the gas separation performance. Pieces of 10 cm have been cut from these tubes for use in the test programme. The modified silica membranes have been checked for their suitability in hydrogen separation and the gas separation performance has been compared with the standard membranes.

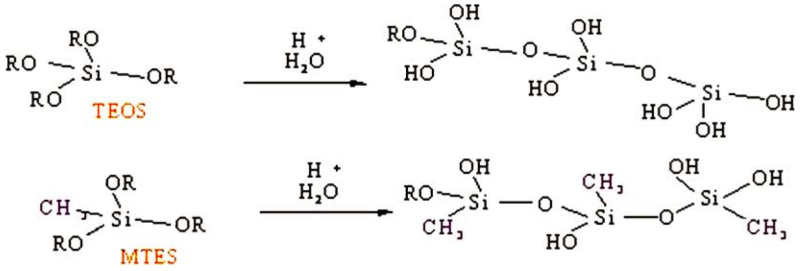

Figure 2: Simplified reaction scheme for silica and modified silica membranes.

Equipment

Low-pressure gas permeation equipment

The low-pressure (LP) gas permeation equipment, used for single gas permeation tests, is an automated set-up, which can measure gas flows through a membrane (dead-end mode) for a programmed sequence of gases, temperatures, feed pressures and average pressures. An overview of the set-up is given in Figure 3.

The flow meters and control valves of the mass flow controllers (MFC) operate independently to control the feed pressure and measure the flow. The feed pressure is measured with PIC1. The pressure difference across the membrane is measured by PIC2. The signal of this differential pressure meter controls valves K16 or K15 to keep the pressure difference at the level set. The temperature is measured and controlled by a thermocouple placed in the membrane module. The set-up is suitable for pressures up to 10 bar and temperatures up to 600 °C (restricted by the stainless steel module).

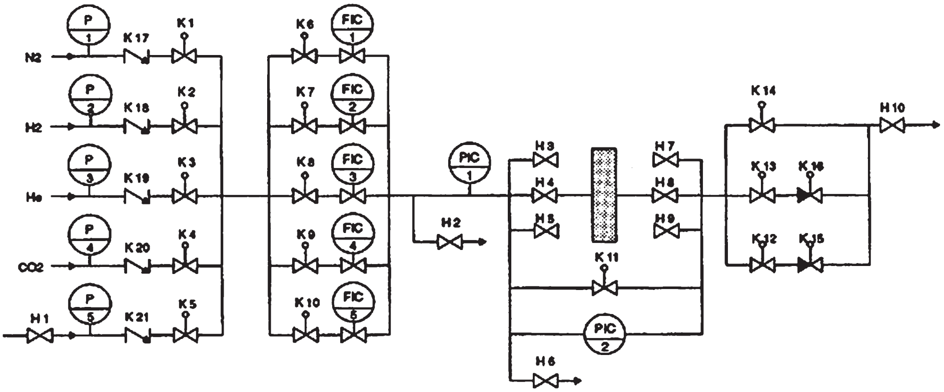

Figure 3: Low-pressure gas permeation set-up.

High-pressure gas separation equipment

A high pressure, high temperature facility for testing membranes under realistic process conditions (feed pressures up to 70 bar, temperatures up to 600 °C) has been used for separation tests. A simplified flowsheet of the installation is shown in Figure 4.

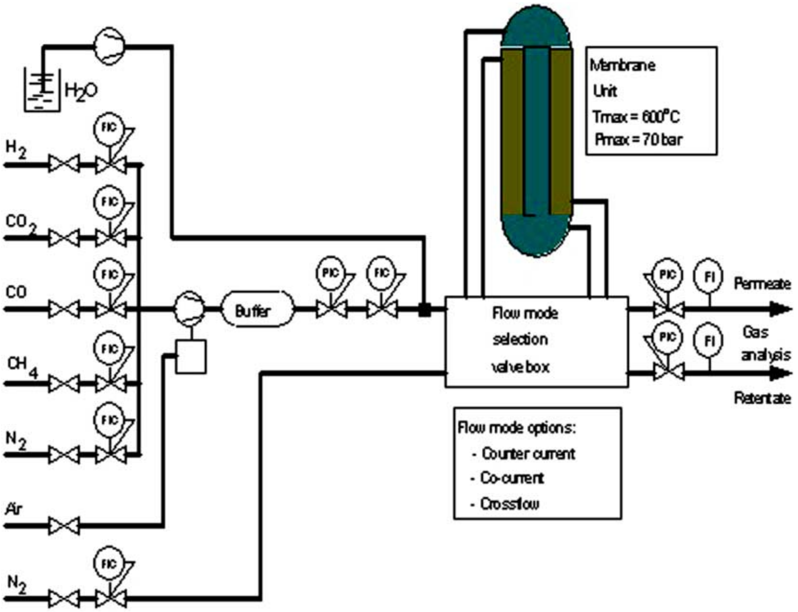

Figure 4: Simplified flowsheet of the high-pressure gas separation equipment.

The installation is laid out for use of gas mixtures without trace contaminants. Pure gases (H_2, CO_2, CO, CH_4, N_2) enter the system through MFC. Mixtures with variable compositions can be obtained by adjusting the ratio of flows through the MFC's. The gases, delivered to the installation at a pressure of approximately 5 bar, are compressed by a booster to a maximum pressure of 70 bar and are stored (temporarily) in a small storage drum (5 L.). The drum is emptied through a pressure controller, which determines the feed pressure to a MFC. This MFC determines the feed flow through the reactor/to the membrane. The feed flow through the reactor is mainly limited by the capacity of the booster. A typical value for the flow of the chosen booster at high pressure is 15 NL/min and at moderate pressures the maximum flow is 27 NL/min. After the booster, the stream is first heated to 200 °C and steam injection can take place. Feed and sweep gas are fed to the membrane module. The module is placed in an oven that can be heated to a maximum temperature of 600 °C. After the membrane the retentate and permeate pressure drops to atmospheric pressure and the flow in both streams is measured using a flow indicator. Finally the gas flows to a gas analysis device in which the composition can be determined.

Membrane steam exposition equipment

The effect of water vapour on the permeances of gases through a silica membrane is measured with set-up for steam/water vapour exposition, which is shown in Figure 5.

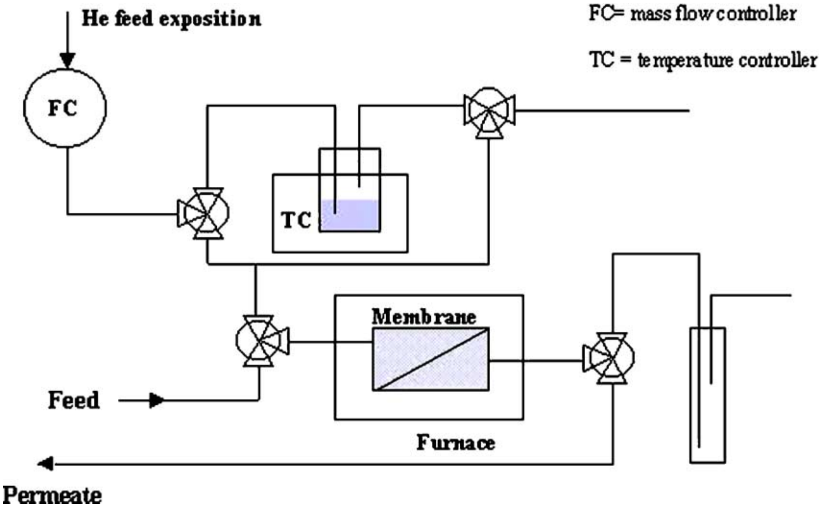

Figure 5: Set-up for steam/water vapour exposition experiments.

A helium stream controlled by a mass flow controller (0–200 mL/min) is sent to a water bubbler, set at a temperature between ~20 and 95 °C. The wetted gas stream is fed to the membrane module placed in a furnace that is set at the desired temperature, usually in the range 100–350 °C. After a certain exposure time the valves are switched to the dry gas permeance mode and the membrane is dried at the desired temperature. Then the permeances of desired gases, usually helium, can be measured. In this way a plot of the "dry" permeance as function of the exposition time can be made and the quality of the membrane can be monitored in-situ. In some cases the wet helium flux directly after exposition is measured by measuring with a separate flux tester in order to follow the relaxation of the permeance during drying of the membrane.

Water Gas Shift Membrane Reactor Simulation Model

A computer model of the WGS membrane reactor was developed to evaluate the performance of different membrane types under development in the CCP project. The WGS membrane reactor model simulates a counter-current water gas-shift membrane reactor and describes the non-isothermal and isothermal operation of the membrane reactor. The membrane reactor model is implemented as an Aspen Plus User Model (Aspen Plus, version 11.1).

In the membrane reactor hydrogen and carbon dioxide is produced in the reaction of carbon monoxide and steam; the WGS reaction. The reaction is a gas phase equilibrium reaction according to reaction scheme:

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

The reaction is moderately exothermic ($\Delta H = -41.1\,\mathrm{kJ/mol}$). The equilibrium constant K_p is defined by:

$$K_p = \frac{c_{H_2}c_{CO_2}}{c_{CO}c_{H_2O}} \qquad (-)$$

with c_i the concentration of component i (mol/m^3). K_p decreases with increasing temperature, which means that less product will be formed as the temperature rises. A simple expression for the equilibrium constant is [4]:

$$K_p = \exp\left(\frac{4577.8}{T} - 4.33\right) \qquad (-)$$

A FeCr catalyst is chosen as a starting point for the kinetic expression in this model [5,6]. The catalyst is active in the temperature range of interest (300–450 °C). Furthermore, it can tolerate small amounts of sulphuric components. The reaction rate is described by [7] using a power law expression:

$$R_{CO} = -k_1 c_{CO}^{0.73} c_{H_2O}^{0.55}(1-\beta) \qquad (\mathrm{mol/m^3}s)$$

with β, the reversibility factor:

$$\beta = \frac{c_{CO_2}c_{H_2}}{K_p c_{CO}c_{H_2O}} \qquad (-)$$

The hydrogen transport through the membrane is described by:

$$J_{H_2} = Q^0_{H_2}\mathrm{e}^{-E_a/RT}(P^n_{f,H_2} - P^n_{p,H_2})$$

where J_{H_2} is the hydrogen flux through the membrane (mol/m^{2}s); Q_{H_2}(T) the temperature dependent hydrogen permeance (mol/m^{2}sPa^n); P_{H_2} the partial hydrogen pressure on feed (f) and permeate (p) side [Pa]; n the exponent on partial pressure (–); $Q^0_{H_2}$ the temperature independent constant (mol/m^{2}sPa); E_a the activation energy for transport (J/mol); T the absolute temperature (K); R is the gas constant (J/molK)

The active temperature range of the WGS catalyst makes this equation suitable for both porous and dense membrane under investigation in the overall project. The Pd–alloy membrane and the ceramic–metal composite membrane typically work with $n = 0.5 - 1$ and for the silica and the zeolite membrane, $n = 1$. Similar equations were developed for other components than hydrogen. The membrane reactor model was used to calculate a CO_2 capture model plant as described in Ref. [8] and works well.

RESULTS AND DISCUSSION

Single Gas Permeance

Standard and modified silica membranes have been tested in single gas (H_2, CO_2, N_2, CH_4) permeation tests at 350 °C and a maximum feed pressure of 10 bar. The performance at 350 °C, 10 bar feed pressure and a pressure difference of 1 bar for the silica membranes is given in the Table 2. Silica membranes with a lower selectivity have a high H_2 flux.

Maximum selectivity and selectivity improvement

Standard silica membranes all made according to the same recipe show a variation in hydrogen permeance and H_2/CO_2 permselectivity. In order to know the range of variation an inventory has been made of the 22 membranes made and tested in a period of 2 years. Only two of these membranes had a H_2/CO_2 selectivity between 30 and 40 (Figure 6) showing that it is extremely difficult for these membranes to reach a

TABLE 2
PERFORMANCE OF STANDARD AND MODIFIED SILICA MEMBRANES

Temperature	**350 °C**		**450 °C**	
Membrane type	**H_2 flux (mol/m^{2}s bar)**	**H_2/CO_2 permsel**	**H_2 flux (mol/m^{2}s bar)**	**H_2/CO_2 permsel**
Modified silica (N_2 calcined)	0.2	7	0.3	9
Modified silica (Air calcined)	0.2–0.8	4–8	0.1–0.9	5
Standard silica	0.1–0.3	5–15	–	–

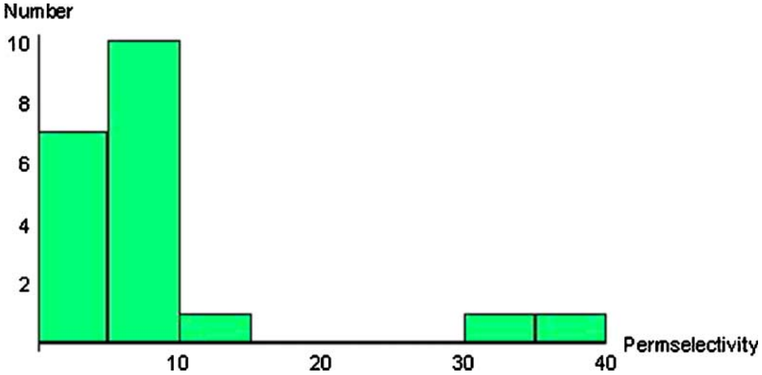

Figure 6: Number histogram of H_2/CO_2 permselectivities at 350 °C and $P_{av} = 9.5$ bar.

reproducible performance well above these values. One should also consider that the membrane test samples are taken from membrane tubes made at an industrial scale of 1 m length.

The average H_2/CO_2 permselectivity was between 5 and 15. The membrane used in the hydrothermal test had an H_2/CO_2 permselectivity higher than average (=29.7). An overview of the performance of three standard silica membranes with increased selectivity is given in Table 3. When the membranes have an H_2/CO_2 permselectivity which is a factor 3–4 higher than standard they have a hydrogen flux that is a factor 5–10 lower. From this data it is expected that the hydrogen permeance of a silica membrane with a H_2/CO_2 selectivity of 50 would be in the range of 0.01–0.005 mol/m^{2}sbar, which is well below the target permeance

TABLE 3
OVERVIEW PERFORMANCE STANDARD SILICA MEMBRANES

Temperature	**350 °C**	
Membrane type	**H_2 flux (mol/m^{2}s bar)**	**H_2/CO_2 permsel**
Average	0.1–0.3	5–15
X2M62Si07	0.041	39
X65Si02	0.016	33
XT51Si53	0.037	29.7

of 0.1 mol/m^{2}sbar for this application. Increasing the selectivity will cause definitely a decrease of the flux through the membrane, which is without doubt detrimental to the economic feasibility.

A possibility for increasing the selectivity of the silica membranes would be calcination at 600 °C. In the PhD work of R. De Vos [9] it was reported that the H_2/CO_2 selectivity increases with at least a factor of 10 when the sintering temperature is increased from 400 to 600 °C. The hydrogen permeance measured at higher temperature (300 in stead of 200 °C) decreased with at least a factor of 3 (Table 4).

TABLE 4
HYDROGEN PERMEANCE AND H_2/CO_2 SELECTIVITY OF SILICA MEMBRANES

Membrane	**Avg H_2 permeance (mol/m^2 s Pa)**	**H_2/CO_2 selectivity**
Si400 (200 °C) R. de Vos	1.64×10^{-6}	7.5
Si600 (300 °C) R. De Vos	6×10^{-7}	70–139
Si400 (200 °C) ECN	5.4×10^{-7}	9–13.6
Si600 (200 °C) ECN	5.1×10^{-7}	7.7
Modified Si250 (350 °C) ECN	$7.6–3.1 \times 10^{-6}$	4.1–4.5
Modified Si450 (350 °C) ECN	$3.9–9.3 \times 10^{-6}$	4.2–5

Temperatures at which the hydrogen permeance was measured are given in parenthesis.

Several silica membranes have been made and were sintered at 400 and 600 °C. However, as shown in Table 4 both silica membrane types as made by ECN gave the same hydrogen permeance and H_2/CO_2 selectivity. Also increasing the sintering temperature of the modified silica membranes did not show an increase of selectivity.

H_2S permeation

A standard silica membrane has been tested with pure H_2S at different temperatures (up to 100 °C) to determine the permeance and the selectivity of the membrane in feeds containing H_2S. The H_2S permeance is very low (5–6 10^{-4} mol/m^{2}sbar at 50 °C), which gives a H_2/H_2S permselectivity of more than 400. After three days of testing with H_2S the single gas helium flux test indicates no detrimental effect on the silica when exposed to H_2S.

Gas Separation

Gas separation tests without water

Gas separation tests with a simulated WGS mixture (H_2:CO_2:CO:N_2 = 35:22:2.5:40.5) have been performed with a standard silica membrane. With pure gases this membrane had a hydrogen permeance of 0.1 mol/m^{2}sbar and a H_2/CO_2 permselectivity of 13.6 at 350 °C. First measurements are performed without water to see the effect of a gas mixture on the hydrogen permeance and the selectivity. The water is balanced in these tests with nitrogen.

In Figure 7 it can be observed that the membrane is capable of producing a hydrogen rich stream containing about 75% hydrogen from a feed stream containing only 35% hydrogen. Carbon monoxide and nitrogen permeate hardly through the membrane. From the retentate composition it can be observed that there is a significant depletion of hydrogen in the feed. Especially when the driving force is high ($dP = 14$ bar) the feed is depleted in hydrogen from 35 to 8% over a membrane of only 10 cm length. In other words: the hydrogen recovery increases with an increase of the driving force. However, one should consider that this is offset by a decrease in the hydrogen concentration in the permeate.

The membrane data (Figure 8) show that the hydrogen permeance increases slightly with temperature. Also the nitrogen and carbon monoxide permeance increase with temperature, which indicates for these molecules the main transport is through small pores and not through defects, as defect flow is governed by Knudsen diffusion and/or viscous flow and thus decreases with a temperature increase. The carbon dioxide permeance decreases with temperature probably because of the fact that this molecule strongly adsorbs on

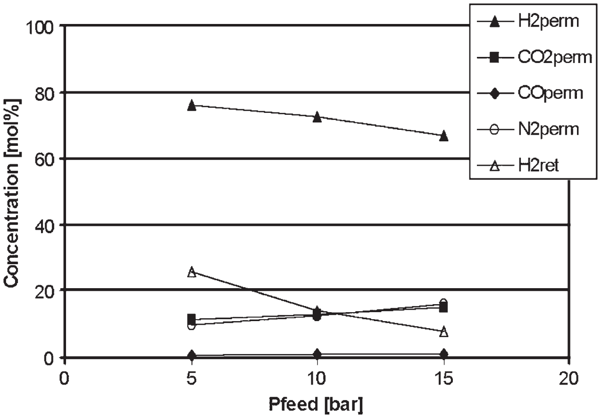

Figure: 7: Permeate and retentate concentrations as a function of feed pressure at 450 °C.

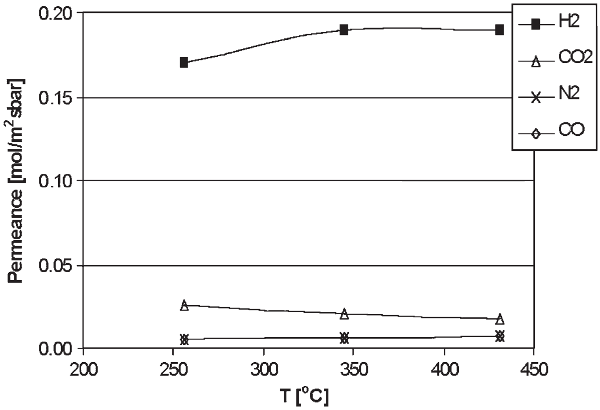

Figure 8: Permeances as a function of temperature ($P_{\text{feed}} = 5$ bar, $P_{\text{permeate}} = 1$ bar).

the surface and it is commonly known that this surface adsorption (and flow) decreases with an increase in temperature.

Gas separation experiments without water were repeated with a comparable silica membrane. With pure gases this membrane had a hydrogen permeance of 0.17 mol/m^{2}s bar and a H_2/CO_2 permselectivity of 7.5 at 350 °C. This membrane is also capable of producing a hydrogen rich stream containing about 85% hydrogen from a feed stream containing only 37% hydrogen (Figure 9). Carbon monoxide and nitrogen permeate hardly through the membrane. These results compare well with the previous membrane. The hydrogen concentration in the permeate is even higher now, as less depletion of hydrogen on the feed side occurs at the higher feed flow rate used now (15 NL/min in stead of 5 NL/min). From these separation measurements a maximum selectivity of 18 is obtained for H_2/CO_2. The hydrogen permeance, derived from the hydrogen partial pressure driving force is for both silica membranes well above 0.1 mol/s m^{2}bar, which is the target permeance for the application.

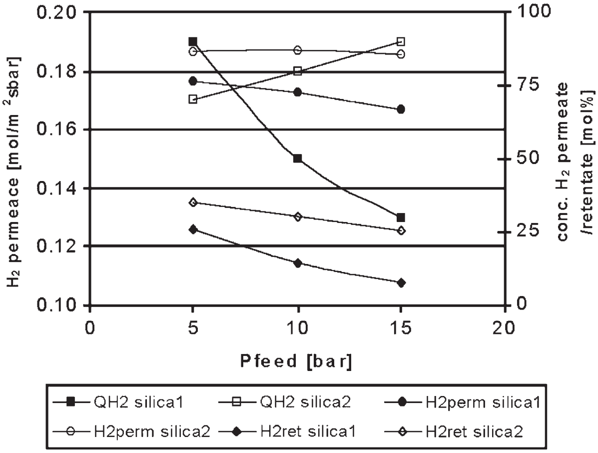

Figure 9: Hydrogen permeance, permeate and retentate concentrations for two silica membranes at 450 °C.

Gas separation tests with water

Experiments with the second membrane were continued, now with water added to the feed (H_2:CO_2:CO:H_2O = 29.3:15.2:1.8:53.7). The measurements have started at 350 °C, then 250 °C and finally 450 °C measurements have been performed.

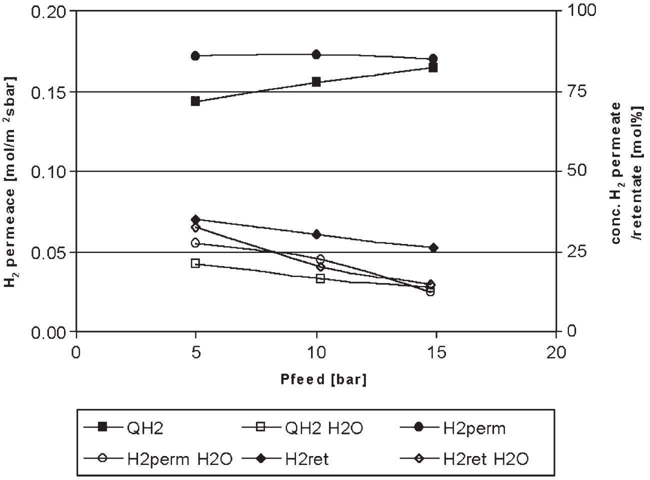

Figure 10: Hydrogen permeance, permeate and retentate concentrations with and without water in feed mixture at 350 °C.

From these measurements and checking of the membrane performance between these temperatures it is clear that the membrane quality (pure silica membrane) decreased already during the measurements at 250 °C. When comparing the measurements at 350 °C without water with the measurements with water in the feed it is clear that both the hydrogen purity in the permeate and the hydrogen permeance are decreased by the water present in the feed stream (Figure 10). The hydrogen permeance, derived from the hydrogen partial pressure driving force has a maximum value of 0.031 mol/s m^2 bar, which is below the target permeance of 0.1 mol/m^2s bar.

Hydrothermal Stability Testing

Before hydrothermal testing the prolonged exposition to elevated temperatures was investigated. Thermal cycling of a standard silica membrane from 50 to 350 °C under dry helium flow shows a slow increase in helium permeance in time. The hydrothermal stability for both silica and modified silica membranes has been tested. In these tests the membranes are exposed to a helium water vapour mixture (70 kPa water with 80 mL/min He) at 350 °C. During exposition the He and CH_4 permeability have been measured at certain time intervals to monitor the change in membrane performance.

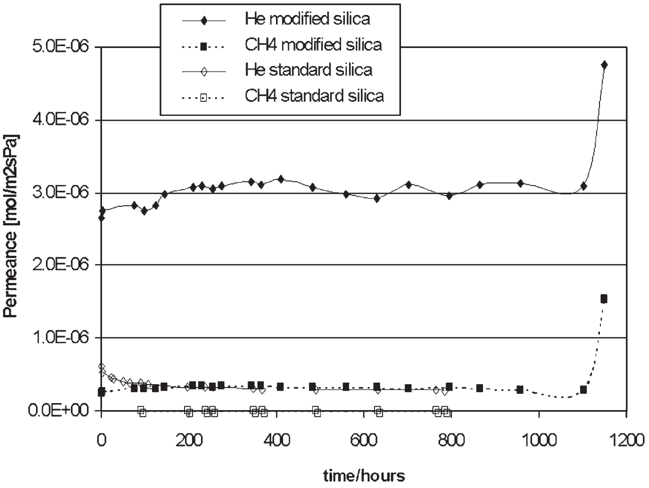

Figure 11: He and CH_4 permeance as a function of time for a standard and a modified silica membrane at 350 °C.

The results of the measurements are given in Figure 11. In the first 200 h the standard silica membrane shows a decrease in the helium and methane permeance of a factor 2. After this period the flux is more or less constant. There is hardly any change in selectivity (48 at the start and 41 after 874 h for He/CH_4) as both fluxes have decreased.

The modified silica membrane shows a slight increase in the permeance after the start of the measurement and after about 200 h this value is constant. The selectivity He/CH_4 is always 10 ± 1. After about 1150 h on stream both the helium and methane flux increased and the selectivity dropped. Post-test analysis of the sample revealed that the sudden flux increase is probably due to crack formation and not by change of the pore system.

CONCLUSIONS

The maximum H_2/CO_2 permselectivity measured at 350 °C for standard silica membranes calcined at 400 °C is 39. At a H_2/CO_2 permselectivity of 50 the hydrogen permeance is expected to be between 0.01 and 0.005 mol/m^2 s bar. Increase of the H_2/CO_2 selectivity by increasing the sintering temperature of the silica membranes could not be experimentally proven at ECN. It is hardly expected that H_2/CO_2 selectivities above 100 can be achieved reproducibly with this type of membrane, certainly if produced at large scale.

H_2/H_2S selectivity was measured to be at 400. This indicates that only undetectable trace amounts of H_2S will permeate through the membrane. Three days testing with H_2S has no detrimental effect on a standard silica membrane. Exposition of a standard silica membrane to steam at 350 °C shows as expected a decline in permeance and selectivity. In 15 days the H_2/CO_2 selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. A silica membrane modified by building in methyl groups has been on stream in wet gas stability testing for 1000 h and shows stable and reproducible performance. However, the modified silica membrane has systematically lower selectivities due to larger pores because of the modification.

Gas separation with a dry gas mixture showed that from a feed stream containing 35% hydrogen a permeate stream containing 75% hydrogen could be derived. This performance is achieved with a membrane with a H_2/CO_2 selectivity of 13.6, which is far below the target of 100. The hydrogen permeance, derived from the hydrogen partial pressure driving force during gas separation testing with a dry gas mixture is well above 0.1 mol/s m^2 bar, which is the target permeance for the application. The presence of water in the feed mixture reduces the hydrogen permeance and thus hydrogen purity in the permeate compared to the tests without water.

The final conclusion is that silica membranes can meet the flux criteria when no water is present in the feed, but the H_2/CO_2 selectivity criterion of 100 is too high for porous silica membranes. A value of 9 has been reached for the silica membrane under simulated process conditions. Under these process conditions, so including water, the stability of this silica membrane is limited to several days. Modified silica membranes have an improved hydrothermal stability, but a systematically lower selectivity. Summarising it can be concluded that porous silica membranes are not suitable for this application.

RECOMMENDATIONS

Although it seems almost utopia to reach the economic selectivity and flux targets for a WGS reactor application of sol/gel silica membranes, future research should at least concentrate on significantly increasing the H_2/CO_2 selectivity while maintaining the flux also in environments containing water. As the molecular sizing of H_2 and CO_2 are very near this will be an utmost challenge. If this challenge could be beaten then also the long-term stability in water containing environments needs to be improved significantly. Following this the final hurdle of reproducible large scale manufacturing should be taken. Based on these observations it is obvious to recommend not pursuing currently the path for silica membranes in WGS membrane reactor applications. However, in other applications where no water is present such as hydrocarbon separation this membrane can be a good candidate.

More promising candidates for this application are dense membranes like thin layer palladium alloy membranes, which can produce very high purity hydrogen at high flux. Although the hydrogen flux of these membranes has been improved in the last years, higher productivity at high permselectivities is still needed to become economically feasible for large-scale applications. Also for these membranes other important issues need to be resolved like long-term material stability and membrane performance in realistic environments, development of feasible manufacturing processes suitable for large scale production and reliable seals, fittings, module and reactor designs.

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