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Steam reforming of methane in a bench-scale membrane reactor at realistic working conditions

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ABSTRACT

In this study, a bench-scale Pd membrane reactor was used to carry out the methane steam reforming reaction under realistic operating conditions: 580 °C, 28 bar(a) and GHSV values up to 950 h^{-1}. The continuous withdrawal of the H_2 product resulted in a maximum CH_4 conversion of 98% and a H_2 production rate of 0.13 $N m^3 h^{-1}$. A continuous methane conversion of 86% and a hydrogen flux of 0.1 $mol m^{-2} s^{-1}$ were achieved in the membrane reactor under these challenging conditions for almost 1100 h, demonstrating the great potential of membrane reformers for H_2 production.

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1. Introduction

Hydrogen, one of the possible energy carriers of the future, is commonly produced through steam reforming of methane (SMR):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (I)$$

And water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (II)$$

Steam reformers are fed with a mixture of natural gas and steam at high temperature. Steam reforming is an endothermic thermodynamic equilibrium reaction, requiring high temperatures to reach high conversions. An 80% conversion of methane at a temperature of 850 °C and a pressure of 35 bar is commonly reached with steam to carbon (S/C) ratios in the range of 3–4 [1]. In principle, the selective removal of hydrogen from the reaction zone enables a higher methane conversion even at lower temperatures. This principle has been experimentally confirmed in the case of palladium-based membranes [2–12].

The overall performance of a packed-bed membrane reactor is not dependent on the H_2 permeation rate of the membrane used; the basic requirement for a major increase in the reaction rate is that the H_2 production rate is in the same order of magnitude as the H_2 permeation rate of the membrane. In other words, the rate of hydrogen production generated in a given volume of the packed-bed must balance the permeation rate through the membrane area in the same volume. In addition, it is of importance to perform experiments at high gas hourly space velocities (GHSV) preferably close to the ones used in industrial applications. Typical values of GHSV in industry range from 2000 to 7000 l kg^{-1} h^{-1} [1].

In most literature on the membrane-assisted steam reformers, high methane conversions have been achieved, but at a low GHSV [5,12] typically 500 l kg^{-1} h^{-1}. The importance of matching product generation and removal was noted by Tong and Matsumura [11]. Their experiments were performed with 8 and 11 μm thick membranes with a commercially available alumina-supported nickel catalyst at GHSV in the range 400–2000 l kg^{-1} h^{-1}. In the experiments with a GHSV of 1120 l kg^{-1} h^{-1}, methane conversions higher than 70% were measured. However, it was observed that under the same operating conditions the methane conversion was similar for both membranes. It was concluded that in membrane reactor used with the 8 μm thick membrane, the rate limiting step was hydrogen production within the catalyst bed. In addition, the influence of feed flow on conversion was investigated; increasing GHSV led to decreasing methane conversion. The commercially available catalyst used in that study was designed for SMR at temperatures of 850 °C. The adaptability of this catalyst for use at lower temperatures is still not clear and needs further investigation. Methane conversions higher than 89% are reported for a membrane steam reformer with GHSV of 4000 l kg^{-1} h^{-1} at 500 °C [3].

Recently, literature on Pd-membrane reactors for pure hydrogen production for fuel cell applications has been published [13,14]. The focus was at the production of a high purity, COx-free hydrogen stream. Although this work was performed at low pressures,

Abbreviations: GHSV, gas hourly space velocities; H/C, hydrogen to carbon ratio; SMR, steam-methane reforming; S/C, steam to carbon ratio.

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Nomenclature

Fi	molar flow of component i [mol s^{-1}]
GHSV	gas hour space velocity, flow of methane over the loaded catalyst weight [l h^{-1} kg_{cat}^{-1}]

interesting hydrogen conversion rates were reported. Methane conversions of 50% were obtained with a 2 bar pressure difference over the membrane.

In this study a 3.8 μm thick Pd membrane and a Ni-based catalyst more suitable for lower operating temperatures were used. The main objective of the current work is to investigate long-term membrane reactor performance with an in-house produced hydrogen-selective Pd membrane under relevant industrial conditions, i.e. at moderate temperature, high pressure and high gas hour space velocity.

2. Experimental

2.1. Component selection

A palladium membrane (155 cm^2, membrane length 35.1 cm and diameter 1.4 cm) was made by electroless plating [15] on commercially available alumina support having an additional intermediate layer as described in [16]. The membrane thickness was measured with Scanning Electron Microscopy (SEM) and was found to be ~3.8 μm. The membrane was mounted with low pressure compression seals [17] in the test-rig. A nickel-based pre-commercial catalyst (Sudchemie) was used for the membrane reactor experiments.

2.2. Test equipment

A simplified flow sheet of the high-pressure (up to 70 bar), high temperature (up to 600 °C) facility for testing under realistic process conditions is shown in Fig. 1. The facility contains a single-tube membrane reactor. The maximum membrane length that can be placed in the reactor is 40 cm.

The catalyst is placed in the annulus between the outside of the tubular membrane and the inside of the reactor with inner diameter of 26.2 cm. The feed is first passed over a catalyst packed-bed that serves to already convert part of the feed into syngas. The mixture then enters the annulus where the catalytic steam reforming reaction proceeds in parallel with the removal of H_2 by the membrane. The non-permeated gasses leave the reactor as the retentate. Co-current sweep is introduced inside the membrane through a central tube.

The reactor is placed in an electrically heated oven. Feed and sweep gasses are supplied through mass flow controllers and are preheated before entering the reactor. Retentate and permeate compositions are analysed with a micro-gas chromatograph (Varian 3600 GC).

Table 1
Membrane reactor tests conditions.

Test goal	Gas mixture $N_2/H_2O/CH_4$ [mol%]	Exp. conditions
Screening experiments	Mixture 1: 43/43/14	Feed flow dry [N l/min]: 1 and 3
	Mixture 2: 56/40/4	GHSV [l h^{-1} kg_{cat}^{-1}] = 760,950 N_2 sweep flow [N l/min]: 0.05 p_{feed} [bar] = 25–38 p_{sweep} [bar] = 1 T [°C] = 550–600
Long duration tests	Mixture 1	Feed flow dry [N l/min]: 3 GHSV [kg h^{-1} l^{-1}] = 950 N_2 sweep flow [N l/min]: 0.05 p_{feed} [bar] = 26 p_{sweep} [bar] = 1 T [°C] = 550
Optimization at highest GHSV	Mixture 1	Feed flow dry [N l/min]: 3 GHSV [l h^{-1} kg_{cat}^{-1}] = 950 p_{sweep} [bar] = 1 T [°C] = 550 N_2 sweep flow [N l/min]: 0.05, 0.1 p_{feed} [bar] = 5–26

2.3. Description of the experiments

In order to prevent the influence of catalyst deactivation on the methane conversion, the methane reforming experiments were performed with an excess of catalyst. The amount of catalyst used in experiments was 195.5 g (160 ml), while calculations reveal that the activity only becomes limiting below 3 g. These calculations were performed using the model presented in [18] and for the experimental conditions given in Table 1.

In screening experiments, the effect of the feed flow and composition, the feed pressure and operating temperature on CH_4 conversion was determined. The membrane selectivity performance was monitored through single gas permeation measurements with pure H_2 and N_2 between membrane reactor experiments. Subsequently, the duration tests were performed with a fixed feed composition and fixed flow for almost 1100 h. The reactor performance was determined at regular intervals.

Finally, the conversion was optimized at the highest GHSV with respect to the two membrane operating variables: feed pressure and sweep flow rate.

Between the long duration experiments and optimization experiments the membrane reformer was kept for four days in a nitrogen atmosphere. The conditions of experiments are given in Table 1.

The membrane selectivity was calculated by comparing the measured fluxes from the single gas permeation measurements. These measurements were performed for hydrogen and nitrogen at the same feed and permeate pressure.

The hydrogen recovery was calculated with following equation:

$$X_{H_2\ \mathrm{rec.}} = \frac{F_{H_2,\ \mathrm{permeate}}}{4 \cdot (F_{CH_4,\ \mathrm{feed}} - F_{CH_4,\ \mathrm{retenate}})} \cdot 100 \quad (1)$$

The CH_4 conversion was calculated in the case of membrane reforming with:

$$X_{CH_4} = \left(\frac{F_{CO_2,\ \mathrm{retentate}} + F_{CO,\ \mathrm{retentate}} + F_{CO_2,\ \mathrm{permeate}} + F_{CO,\ \mathrm{permeate}}}{F_{CH_4,\ \mathrm{feed}}} \right) \cdot 100 \quad (2)$$

The hydrogen purity is calculated using this equation:

$$H_2\ \mathrm{purity} = \left(\frac{F_{H_2,\ \mathrm{permeate}}}{F_{H_2,\ \mathrm{permeate}} + F_{CH_4,\ \mathrm{permeate}} + F_{CO_2,\ \mathrm{permeate}} + F_{CO,\ \mathrm{permeate}} + F_{N_2,\ \mathrm{permeate}} - F_{N_2,\ \mathrm{sweep}}} \right) \cdot 100 \quad (3)$$

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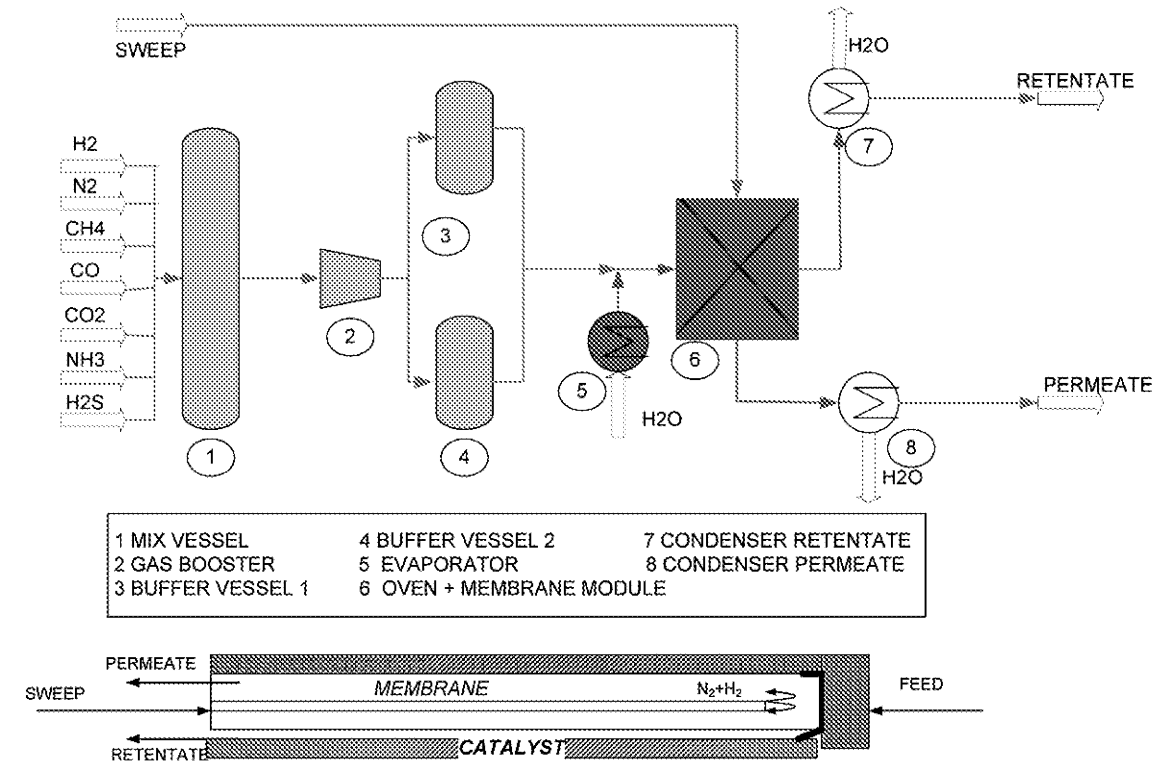

Fig. 1. Simplified flowsheet of the membrane reactor test-unit (above), and membrane module (below).

The thermodynamic equilibrium conversion was calculated using the Gibbs reactor model from the Aspen Plus simulation program.

3. Results and discussion

3.1. Membrane performance

The initial membrane and seal qualities were checked with single gas hydrogen and nitrogen permeance tests after mounting the membrane into the module. The resulting N_2 permeance was too low to be accurately determined and the membrane H_2/N_2 selectivity was estimated to be over 1800 at 6 bar feed pressure. From this it can be concluded that membrane was leak tight. The measured hydrogen flux was 1.7 mol m^{-2} s^{-1} at 525 °C and a pressure difference of 4.8 bar. Fig. 2 shows that the hydrogen permeance value obtained in this work is high in comparison with literature values determined under comparable conditions [3,19].

After the duration experiments single gas hydrogen and nitrogen permeance tests were performed and the measured H_2/N_2 selectivity was 97 at 5.2 bar feed pressure, 4.18 bar pressure difference and temperature of 600 °C. Thus, the selectivity of the membrane decreased at least 18 times after testing for 1100 h.

3.1.1. Screening experiments

Steam reforming is an endothermic reaction in the gas phase in which the number of moles increases with reaction. This means that this reaction will be favoured at high temperatures and at lower feed pressures.

To increase the hydrogen recovery in the membrane reactor a high hydrogen flux over the membrane is required, so operation at a high feed temperature and pressure is favourable. The operation at the high pressure is contrary to the reaction demand. Moreover, at high pressure the hydrogen purity will decrease because the flux of other components that are permeating over membrane by Knudsen or viscous flow will also increase.

There are also two counteracting effects that need to be balanced in selecting the operating temperature of the membrane reactor:

- Component permeation is favoured at higher temperature because of the Arrhenius temperature dependency
- Membrane life time decreases with higher temperature due to higher possibility for occurring of the leak flow over the sealing.

Table 2 shows that the maximum obtained methane conversion was 98% at p_{feed} = 28 bar, T = 580 °C and a GHSV equal to 760 l h^{-1} kg_{cat}^{-1}. The hydrogen recovery and purity at these

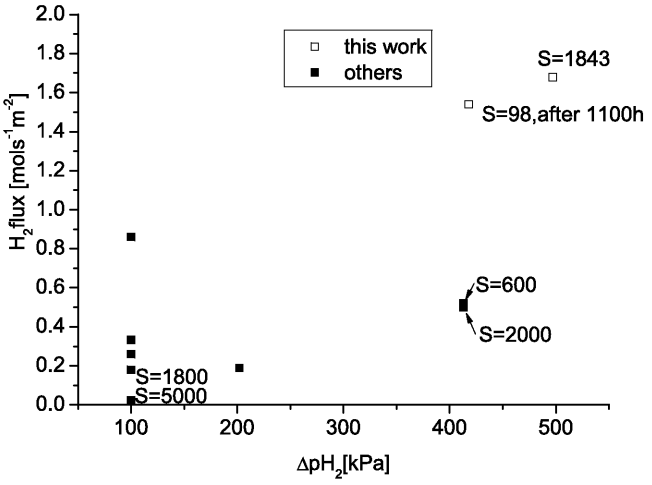

Fig. 2. Measured hydrogen flux in various literature and in this work vs. the pressure difference at S = selectivity, if not mentioned in figure selectivity was high [3,19]. Temperature was in range T = 525 ± 25 °C.

Table 2
Preliminary experimental results, $T = 560 \pm 20\,^{\circ}C$.

Time [h]	GHSV [$l\,h^{-1}\,kg_{cat}^{-1}$]	p_{feed} [bar]	X_{CH_4}	$X_{H_2\ rec}$	H_2 purity
118.8	950	35	75.3	64.5	82.6
145.2	760	28	98.5	66.2	91.1
147.12	760	42	96.1	87.8	86.5
236.64	950	24	89.8	69.4	90.5
242.64	950	25	91	71.4	90.7
261.12	950	24	90.0	71.6	90.3
284.16	950	25	89.3	67.9	89.8

conditions were respectively 66 and 92% (with 8.70% CO_2, 0.03 mol% CO and 0.18 mol% CH_4 on the dry basis). As expected a lower feed pressure leads to a lower hydrogen recovery with a higher purity. For example, in experiments with the GHSV of 760 $l\,h^{-1}\,kg_{cat}^{-1}$ the hydrogen recovery increases from 66 to 88%, while purity decreased from 92 to 86% when the feed pressure is increased from 28 to 42 bar. Since the methane conversion also depends on the feed pressure, a balance between methane conversion, hydrogen recovery and purity has to be found.

For the long duration test the optimum conditions to balance those factors were selected.

A GHSV of 950 $l\,h^{-1}\,kg_{cat}^{-1}$ was selected [1]. A feed pressure of 26 bar was selected to favour the methane conversion and intermediate temperature of 550 °C was chosen as a compromise between hydrogen permeation and membrane life time expectations.

3.1.2. Long duration tests

Fig. 3 shows that the membrane reactor had a stable performance in the long duration tests with an average methane conversion of ~86%. The obtained hydrogen recovery in these experiments was ~70% and hydrogen purity was higher than 80%. The hydrogen purity decreases with time.

More data on catalyst post-analysis performed after these experiments can be found in recent literature [18]. Pieterse et al. [18] reported that the significant amount of carbon deposition was found after these membrane reactor tests. However, it is suspected that in the time-span of the experiments the effect of C-deposition on the catalyst activity can be masked by the over dimensioned catalyst amount. Thus, the decrease of the hydrogen purity in the experiments is probably not caused by catalyst deactivation.

Possible reason for hydrogen purity decrease is an increase of the leak flow. This was confirmed with single gas measurements

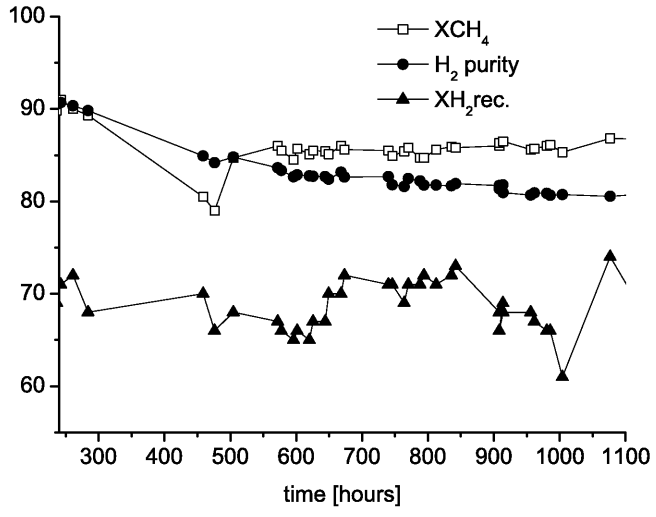

Fig. 3. Measured methane conversion, hydrogen purity and hydrogen recovery in the long duration membrane reformer experiments for conditions in Table 1.

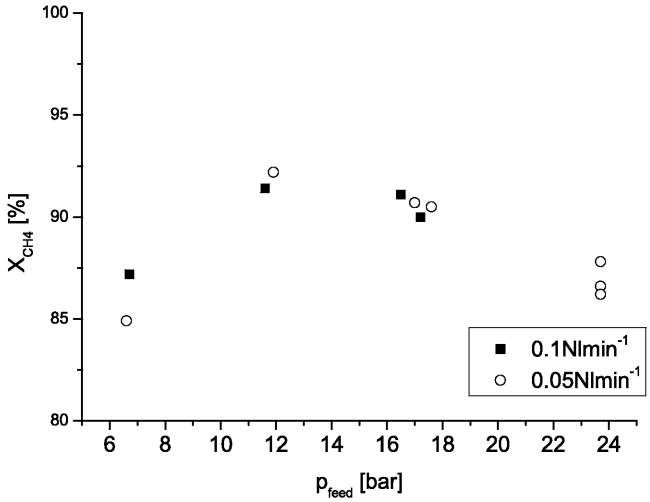

Fig. 4. Conversion vs. feed pressure for different sweep flows at $550 \pm 20\,^{\circ}C$ and GHSV = 950 $l\,h^{-1}\,kg_{cat}^{-1}$.

performed after the long duration tests in which it was found that the membrane selectivity decreased 18 times. More detailed analysis of the permeate composition showing decrease in hydrogen purity and fluxes of permeating compounds during these tests are given in Figs. 6 and 7. Fig. 7 shows that the hydrogen and methane fluxes were constant in the long duration experiments while the CO_2 and CO flux increased indicating increase in the leak flow. Since the CO_2 is also product of the reaction it is expected that because CO_2 flux increases during the long duration experiments, while the CH_4 and H_2 fluxes are constant, the methane conversion will also increase. However, Fig. 3 shows that the methane conversion in long duration experiments is not affected by the increase in the leak flow. This can be explained by the possible position of the leak. If the leak is positioned at the sealing where feed leaves the membrane, the methane conversion will not be affected by increase of the leak flow.

3.1.3. Optimization of the methane conversion

Fig. 4 shows the results of variations in feed pressure and sweep flow rate with the aim to increase the conversion above the target of 90% at the highest GHSV. A maximum conversion of 92% was found at a feed pressure of 12 bar, which was slightly higher than in the screening experiments at the same GHSV. At lower feed pressures the flux of hydrogen through the membrane was lower and thus the hydrogen removal was limiting. Increased pressure causes the equilibrium partial pressure of H_2 within the catalyst bed to decrease. No influence of the sweep flow was found, meaning that the sweep side mass transfer for hydrogen transport in the membrane reactor was not the rate limiting step.

3.1.4. Comparison of membrane reactor with equilibrium conversion

Fig. 5 compares the equilibrium with the experimentally obtained CH_4 conversion. The equilibrium conversion decreased as expected with a pressure increase and increased with a temperature increase. In the membrane reactor the conversion can both decrease or increase with increase in the feed pressure.

From the figure it can be noticed that calculated equilibrium conversion for two experimental conditions at 150–200 h was higher than for other experimental conditions. The reason for this is that these two experiments were performed with higher N_2 dilution (Mixture 2 in Table 1). Since the N_2 dilution for Mixture 2 is 56% compared to 43% for Mixture 1, the partial pressures of steam

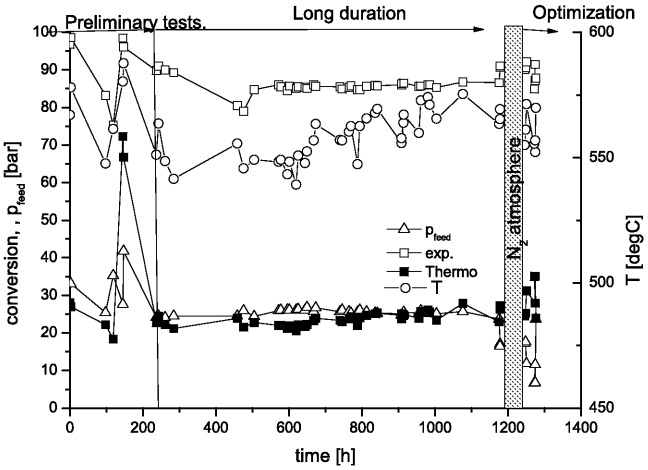

Fig. 5. Experimental (Exp.) vs. equilibrium conversion (Thermo.) at 550 ± 30 °C.

and methane were lower for Mixture 1, resulting in a higher thermodynamic methane conversion for Mixture 2.

Fig. 5 shows that in the membrane reactor a maximum methane conversion of 98% was achieved compared to the equilibrium conversion of 26%. Thus, the maximum increase of methane conversion due to performing reaction in the membrane reactor was 72%.

3.1.5. Membrane selectivity and hydrogen flux

The permeate stream composition, after substracting the nitrogen sweep, is presented in Fig. 6. The hydrogen purity in the experiments was always higher than 80%, depending on the feed pressure, with a maximum of 95%.

The measured amount of CO in the permeate was in all cases lower than ~150 ppm, while the CO_2 content in the permeate reached rather high values of ~13%. The measured amount of CH_4 in the permeate side was 2.5 mol%.

In the long duration experiments, the CO_2 content increases from 11 mol% to 15 mol%, and CO content increases from 71 to 129 ppm with time. The CH_4 content at the permeate side was rather constant, while H_2 content decreased with time.

The reason that CO_2 permeates so much while the CO content stays rather low can be explained by withdrawal of hydrogen from the thermodynamic equilibrium mixture that contains low CO amount. At the operating condition of the long duration experiments (26 bar, T = 580 °C and mixture composition given in Table 1) gas at the thermodynamic equilibrium contains 0.44% CO, 4.60% CO_2, 17.88% CH_4, 19.73% H_2 and 57.34% H_2O. The calculated fluxes for different components permeating membrane in the long duration experiments are presented in Fig. 7.

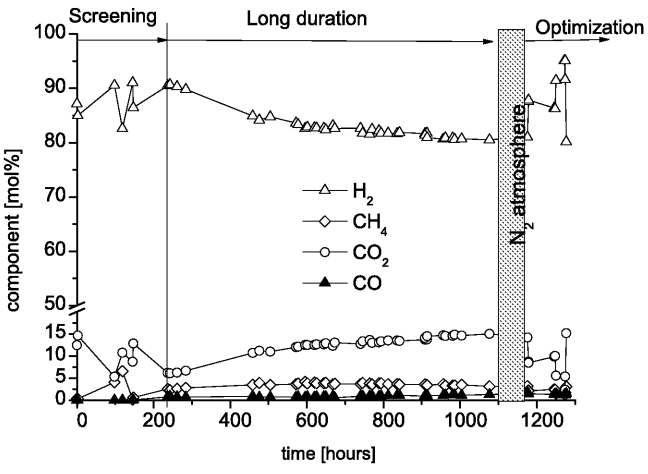

Fig. 6. Composition of the permeate stream without the nitrogen sweep with conditions given in Table 1.

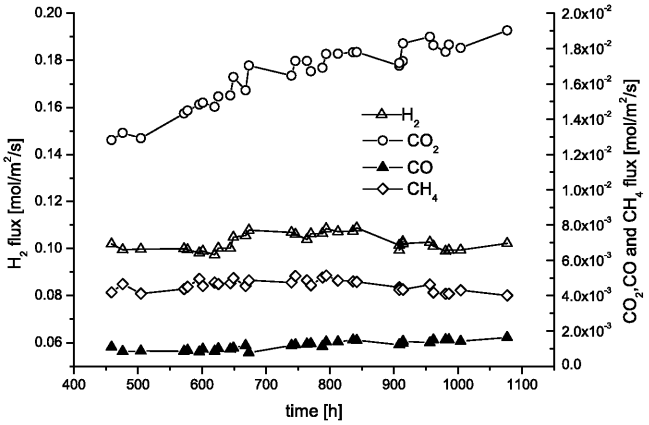

Fig. 7. The CO, CO_2, H_2 and CH_4 flux in the long duration experiments.

This figure shows that CO_2 and CO flux increased with time, confirming the increase in the leak flow. The H_2 and CH_4 flux were constant with time. As measured selectivity at the end of these experiments was 98, it is expected that hydrogen flux will remain the same in the long duration experiments because contribution of the leak to the total hydrogen flux is small. Since in the long duration experiments the measured methane conversion was the same, while the leak flow increased it is expected that also methane flux will increase in time. However, the calculated methane flux was rather constant. There is no apparent or obvious reason why the flux remained constant.

Fig. 8 shows the hydrogen flux through the membrane in the reactor as a function of the hydrogen partial pressure drop (Δp_{H_2}) over the membrane: the driving force. This value is calculated from the average of the hydrogen partial pressure differences at the membrane reactor inlet and the outlet. For the calculation of the inlet H_2 partial pressure the thermodynamic conversion of the feed was assumed. This is fairly good assumption because of the fast steam reforming kinetics and the fact that in the used configuration the feed is first let over a packed bed of catalyst without membrane (see Fig. 1).

Fig. 7 shows that the measured hydrogen flux was in range of 0.08–0.12 mol m^{-2} s^{-1}. As expected the flux decreases with a decrease in the driving force. The measured flux in pure hydrogen

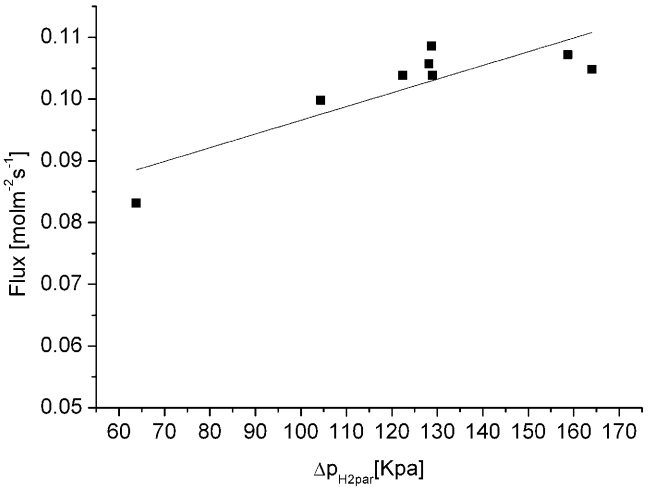

Fig. 8. Measured hydrogen flux vs. driving force T = 550 ± 20 °C, dots – experimental, line – linear fit.

measurement was 1.7 mol m^{-2} s^{-1} at 525 °C and a pressure difference of 4.8 bar.

If the flux obtained in membrane reactor experiments is linearly extrapolated to a value of the driving force for the pure hydrogen measurements, the calculated hydrogen flux is approximately 6 times lower than the measured pure hydrogen flux. For this extrapolation it was assumed that the pressure exponent for hydrogen permeation is equal to 1. This is a fairly good assumption since the membrane thickness was estimated at 3.8 μm and for such thin membranes the distance for bulk diffusion will become increasingly short. Thus, the hydrogen transport through the membrane will not be governed by Sieverts' law that gives a pressure exponent of 0.5 but by the other processes such as surface effects, gaseous flow through defects, or transport resistance through the substrate [20] that gives a pressure exponent of 1.0.

The lower value of hydrogen flux measured in the mixture can be attributed to:

1) Decrease of the hydrogen flux due to adsorption of the other components such CO, CO_2 and H_2O on the Pd surface
2) Concentration polarization effect [21,24,28].

A number of studies were carried out to determine the effect of the gasses such as CO, CO_2 and H_2O on the hydrogen flux [22–27]. Sakamoto et al. [22] found that the presence of CO at the temperatures lower than 500 °C can significantly decrease the hydrogen flux. At 450 °C the measured decrease in hydrogen flux was 30%. However, since the operating temperature in our experiments is 100 °C higher it is expected that the 6 times decrease in flux is not the only result of CO poisoning. There is some disagreement over the effect of CO_2 and H_2O on hydrogen flux. In some studies it is suggested that these two gases significantly reduce hydrogen flux [25], while in some opposite is claimed [23,24,27].

In the work of Gallucci et al. [28] it was theoretically shown that in the packed bed membrane reactor in the case of membranes with high hydrogen permeation rate the hydrogen transport can be highly limited by concentration polarization effect. For the membranes with high permeation rate it was calculated that hydrogen rate fraction at the membrane decreased approximately 4 times because of the mass transfer limitation of hydrogen transport from the catalyst bed to the membrane. In the work of Peters et al. [24] the extent of permeation reduction as a function of the gas composition, gas velocity, temperature, pressure was determined. It was determined that hydrogen permeance in the water gas shift mixture (60% H_2, 19.2 mol% CO_2, 15.4% H_2O, 4% CO and 1.2% CH_4) decreased ~10 times compared to pure hydrogen permeance. These experiments were performed with 2 μm thick membrane at the feed pressure of 20 bar, temperature of 400 °C, linear gas velocity of 0.22 m s^{-1}. The major contribution to the hydrogen permeation decrease was attributed to the concentration polarization and the surface effects, where the surface effects are mainly due to CO adsorption at the surface. Experiments carried out in this work were done at the same linear gas velocities as in Peters et al., feed pressures of 28 bar and temperatures of 550 °C. Since, the contribution of surface effects to the permeation reduction decreases with increase of temperature, it is expected that 6 times permeance reduction calculated in this work can be attributed to the concentration polarization effect.

4. Conclusions and recommendations

Membrane reactor experiments were performed at moderate temperature and pressure conditions and with GHSV of typically half of the industrial value. The obtained methane conversion at these conditions was higher than 90% with high hydrogen purity (80–95%) and a reasonably high recovery 60–80%. The maximum obtained methane conversion was 98% at 28 bar and a temperature of 580 °C. In addition, a stable membrane reactor performance for almost 1100 h was achieved. The average conversion during this long duration test was 86%. Further, as expected the methane conversion decreased with an increase of the GHSV. To achieve a conversion higher than 90% for the highest GHSV possible in these experiments, it was determined that the feed pressure needed to be decreased to 10–15 bar. In the membrane reactor experiments a maximum increase of 72%-points in methane conversion was achieved compared to thermodynamic conversion.

Next to the high hydrogen purity, the CO content measured in the permeate was low and in the range of 59–154 ppm. The permeate had CO_2 concentration of approximately 12%. This concentration increased in time in the long duration experiments notifying the increase of the leak flow.

In addition to this, the application of this membrane reactor for production of hydrogen rich gas for ammonia production was evaluated. There are two advantages of membrane reactors for ammonia feed production:

1) The energy efficiency of the process can be increased by operating the reactor at the lower temperature.
2) The cost of the syngas production could possibly be decreased due to a reduction in the number of process steps; removal of the hydrogen from the reaction zone in the membrane reactor allows complete methane conversion in one reaction step. The pure hydrogen stream will be withdrawn at the permeate side. In this way it is possible to skip high temperature, low temperature shift reactors and purification steps. However, it should be noted that syngas entering the ammonia synthesis loop has the carbon oxides content less than 50 ppmv [29].

From the obtained experimental results it can be concluded that the measured impurities level in the permeate are not satisfying for production of H_2 enriched gas for ammonia production and because of that purification steps such as CO_2 removal and methanation cannot be skipped. The further work focusing on the improving of the membrane selectivity and decreasing impurities level in the permeate to the acceptable values is required.

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