ELSEVIER

Catalysis Today 40 (1998) 191–200

CATALYSIS TODAY

Comparative study of the partial oxidation of methane to synthesis gas in fixed-bed and fluidized-bed membrane reactors. Part II – Development of membranes and catalytic measurements

T. Ostrowski[a], A. Giroir-Fendler[b], C. Mirodatos[b], L. Mleczko[a,*]

[a] *Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*
[b] *Institut de Recherches sur la Catalyse, CNRS, F-69626 Villeurbanne-Cedéx, France*

Abstract

The catalytic partial oxidation of methane (CPOM) to synthesis gas was carried out in fixed-bed and fluidized-bed membrane reactors over a Ni/α–Al_2O_3 catalyst. For gas separation silicalite membranes inside an alumina and a porous stainless-steel matrix were synthesized and applied in the catalytic measurements. Moreover, a membrane obtained by deposition of palladium on the stainless-steel silicalite membrane was tested. The zeolite membranes were stable in the whole investigated temperature range (700<T<750°C). The Pd-membrane was not stable; palladium layer did not withstand temperatures above 650°C. In the catalytic measurements in the fixed-bed reactor and in the fluidized bed ($P_{CH_4} = 66.6$ kPa, $P_{O_2} = 33.3$ kPa, m_{cat}/V=14 gs/ml) nearly thermodynamic equilibrium was achieved. However, neither in the fixed-bed reactor nor in the fluidized-bed membrane reactor an improvement in the syngas yield by means of the integrated product separation could be achieved. In the fixed-bed membrane the unselective separation of methane was detrimental for methane conversion. In the fluidized-bed membrane reactor the amount of permeated hydrogen was not sufficient to shift significantly the equilibrium towards higher syngas yield. However, in the fluidized-bed membrane reactor significant better selectivities of separation were achieved. © 1998 Elsevier Science B.V.

1. Introduction

The catalytic partial oxidation of methane (CPOM) is a new promising route for producing synthesis gas. Membrane reactors have been proposed as reaction engineering mean for achieving at low temperatures (T<1000°C) and high pressures (P>20 bar) high conversions of methane and yields to synthesis gas. Several experimental studies confirmed that by performing the CPOM reaction with integrated product separation the thermodynamic constraints can be overcome. However, in order to eliminate high temperature spikes fixed-bed membrane reactors could be operated only with highly diluted feed. Furthermore, this reactor type suffered from the catalyst deactivation. Against this background a fluidized-bed reactors equipped with palladium or porous membranes has been proposed [1]. The simulation study performed for the fixed-bed and fluidized-bed reactor equipped with porous membranes (see Part I [2]) indicated that in the fluidized-bed reactor even higher syngas yields can be obtained than in the fixed-bed membrane

*Corresponding author. Present address: BAYER AG, ZT-TE Geb E41, D-51368 Leverkusen; fax: +214/305 0262; e-mail: LESLAW.MLECZKO.LM@bayer-ag.de

PII S0920-5861(98)00007-8

reactor. The work presented in this paper aimed at the qualitative experimental validation of the conclusions drawn from the previous simulation studies [2]. In order to achieve this goal the catalytic partial oxidation of methane over a Ni/α–Al_2O_3 catalyst was investigated in the atmospheric-pressure fixed-bed and in the fluidized-bed membrane reactors.

The experimental work in the laboratory-scale reactors was preceded by the development of suitable membranes. The membranes were investigated with respect to their thermal and mechanical stability. Furthermore, the effect of the integrated product separation on the catalytic performance was studied, focusing on gas separation selectivity by means of ceramic membranes. Membranes for application in the reactors for partial oxidation have to operate under severe reaction conditions, i.e., at temperatures from 700 to 900°C and high concentrations of water. In order to prevent carbon deposition due to the methane pyrolysis and Boudouard reaction they should not be catalytically active. Since an industrial-scale reactor for the CPOM reaction has to be operated at high pressures, the mechanical resistance of the membrane is an important factor, especially when the separation is driven by the total pressure in the reactor. Furthermore, in case of the gas separation in a fluidized-bed reactor the membrane should be resistant to pressure fluctuations. These fluctuations are known to be responsible for the vibration of buffles immersed in the bed, e.g. vibration of tubes of a heat exchanger. Finally, from the safety reasons the sealing of the membranes can be a limiting factor for scale-up of membrane reactors.

All these demands can be fulfilled when applying separation tubes made of palladium. The Pd-membranes were successfully applied by Adris et al. [3] in a steam reformer. This solution suffers, however, from the high investment costs and low permeation rates; the permeation rates decreases with thickness of the wall [1]. In several studies ceramic membranes have been proposed as promising alternative to the massive Pd-tubes. However, the selectivity of the porous membranes is significantly lower than those of the Pd-membranes. Investigations of oxidative coupling and partial oxidation of methane confirmed a high thermal stability of the membranes made of porous alumina [4,5]. Ioannides and Verykios [6] reported that when applying dense silica membranes on Vycor glass tube (d_{pore}=40 Å) in the temperature range from 500 to 700°C for dry reforming of methane and the CPOM reaction constant permeation rates as well as high selectivity of separation were achieved. However, when the membrane was exposed for several days to water the permeance of hydrogen decreased by 50%, indicating that the dense membrane was not stable at high partial pressures of water. Finally, asymmetric zeolite silicalite membranes can be used [7]. The low pore diameter (d_{pore}=5.5 Å) leads to high selectivities of hydrogen separation. However, the experience with application of zeolite membranes in high temperature processes is until now very limited. Against this background silicalite and supported palladium membranes that consisted of layer of palladium on a porous support were selected as the most promising types for application in the CPOM reaction.

2. Experimental

2.1. Catalyst and reactors

2.1.1. Catalyst

In both fixed-bed and fluidized-bed reactors the CPOM reaction was studied over Ni/α–Al_2O_3 catalysts. The catalysts were prepared by incipient wetness method. The support (γ-Al_2O_3)was calcined in air (T=1300°C) to get α-Al_2O_3, treated with $NiCO_3$-solution and calcined at 900°C. Directly before the reaction the catalyst was reduced in a mixture of nitrogen and hydrogen (1:1, $\dot{V}_{STP} = 1.61/min$). The temperature for the reduction was increased in four steps from 100 to 400°C, followed by 4 h at 400°C. In the fixed bed, a catalyst with a Ni loading of 17% was applied after sieving from 200 to 300 μm. In the fluidized bed, a catalyst with a Ni loading of 5% sieved to particles with a diameter ranging from 160 to 255 μm was used. The BET-area (N_2 ads. at 77 K) amounted for both catalysts to approx. 1 m^2/g.

2.1.2. Fixed-bed membrane reactor

The laboratory-scale (i.d.=2.5 cm, L=25 cm) fixed-bed reactor was made of Inconel (see Fig. 1(a)). The temperature was controlled by heating the reactor walls from outside. The ceramic silicalite membrane

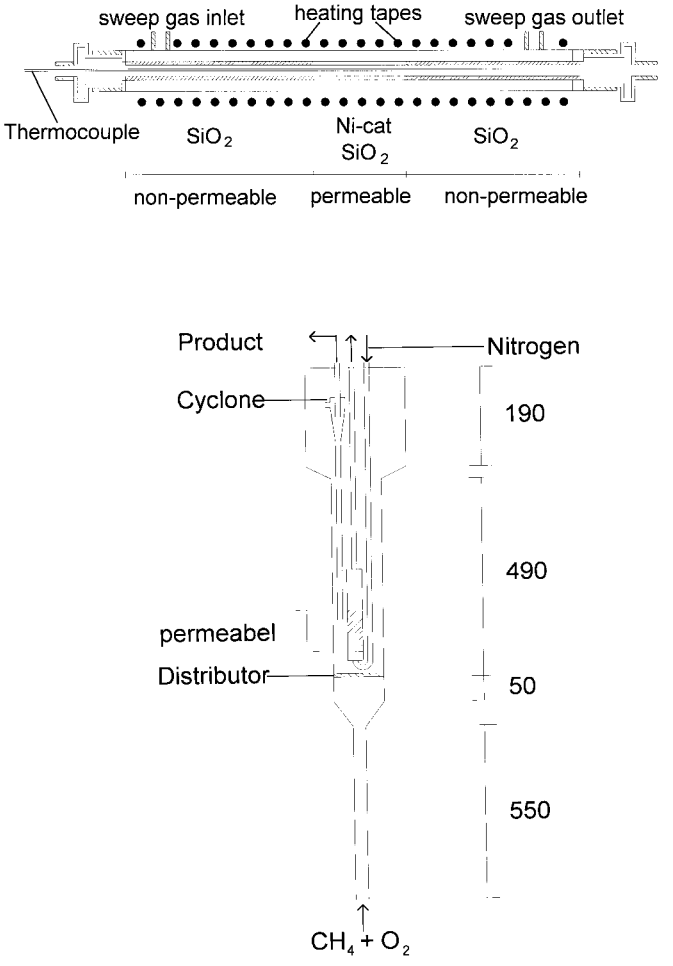

Fig. 1. Design of the (a) fixed-bed membrane reactor and (b) the fluidized-bed membrane reactor.

(i.d.=7 mm, L=25 cm) was placed inside the reactor and sealed by means of graphite rings. The membrane was permeable only in a window that was 5 cm long; the other parts of the membrane were kept impermeable by enamel. The catalyst (0.86 g, diluted 1:2 with quartz) was placed inside the membrane at the position of the permeation window. Helium was used as the sweep gas through the shell side of the membrane in co-current direction. Gas flow rates of reactants CH_4 and O_2 were stabilized by means of mass-flow controllers. For measuring the temperature profiles, a thermocouple was placed in a stainless-steel tube inside the internal compartment. The details of the reactor design are presented elsewhere [8].

2.1.3. *Fluidized-bed membrane reactor*

The fluidized-bed reactor with the inner diametere of 5 cm was made of quartz. In the preheating section, the mixed feed gases CH_4 and O_2 were heated to 300°C before distributing them through a porous quartz plate distributor (d_{pore}=40–90 μm). The temperature in the bed was controlled by heating the catalytic section from outside. In order to reduce particle loss a disengaging section and an internal cyclone were located at the top of the reaction zone. For measuring the temperature profiles, thermocouples within a quartz tube were located in two axial positions of the fluidized-bed. The details of the reactor design and of the measurements system are presented elsewhere [9]. The stainless-steel silicalite

membrane (o.d.=1.6 cm, L=10 cm, see Fig. 1(b)) was connected to stainless-steel tubes by means of welding. The membrane was placed directly above the gas distributor in the catalyst bed (H_{mf}=15 cm). The membrane immersed in the fluidized bed was swept with nitrogen in co-current mode.

2.1.4. Gases and Gas Analyses

Methane (99.95%), oxygen (99%), helium (99.999%) and nitrogen (99.99%) were supplied from commercial cylinders. The gases were mixed and fed to the different reactor types without further purification. Product gas composition was analyzed by gas chromatography after water was removed by cooling traps. Additionally, volumetric flows at both reactor exits, i.e. reactor side and sweep side, were measured. Water was calculated based on the hydrogen balance. Both reactors were operated in the co-current mode. Three analyses were taken for each reaction condition and reactor outlet. The accuracy of the carbon and oxygen balance amounted to 3 and 5%, respectively.

2.2. Experimental procedure and reaction conditions

2.2.1. Experimental procedure

In the first stage of the experiments the reactors were heated in helium (fixed-bed) and nitrogen (fluidized-bed), respectively. When reaction temperature had been reached, the flow of the inert gas was reduced and methane was added. After 2 min, oxygen was added and the bed temperature was controlled. In the fluidized-bed reactor nitrogen was switched off. In the first series of experiments the compositions of the product gas was analyzed by performing the reaction without using the membranes for product separation (closed membrane outlets). In the final stage of the experiments the membranes were opened, sweep gas (helium or nitrogen) was switched on and the gas composition at the reactor outlet, the composition of the permeate as well as the volumetric flows of both gas stream were measured.

For the membrane reactors the selectivity of separation was calculated by setting the concentration of hydrogen in the sweep gas equal to one and the concentrations of the other components in relation to the hydrogen concentration.

2.2.2. Reaction conditions

The CPOM was carried out at 700 and 750°C. In the fluidized-bed reactor the partial pressures of methane and oxygen amounted to 66.6 and 33.3 kPa, respectively. In the fixed-bed reactor the feed gas contained methane, oxygen and helium. The partial pressures amounted to 42.2, 21.1 and 36.7 kPa, respectively. The catalyst in the fixed-bed reactor was diluted with quartz (1:2) to minimize temperature spikes.

3. Synthesis and characterization of the membranes

3.1. Membrane preparation

3.1.1. Silicalite membranes

For the supported zeolite membranes two different supports were applied, i.e. an alumina support and a porous stainless-steel support. The alumina support (o.d.=1 cm, L=25 cm) was provided by the SCT company. The membrane on this support was applied in the fixed bed. The stainless-steel membrane (o.d.=1.6 cm, L=10 cm) was developed for achieving mechanical stability and good sealing ability.

Before the synthesis, the stainless-steel membrane support was first treated for 15 h in air at 800°C. The preparation of the silicalite structure inside the ceramic and stainless steel support is a three step process. In the first step, oligomeric Si-species were obtained in an alkaline solution. This solution was aged for several days. In the second step the supports made of alumina and stainless-steel, respectively, were hydrothermally treated with the solution for several days at 180°C. The third step is the removal of the organic template. These steps were described in details by Giroir-Fendler et al. [10].

3.1.2. Palladium membrane

In this membrane, palladium was deposited on the porous silicalite stainless-steel tube. In order to prevent erosion effect in the fluidized bed, palladium was deposited inside the membrane tube. For palladium deposition a modified technique of Shu et al. [11] was applied. It consists of (i) activating the support and (ii) deposing and reducing auto-catalytically the palladium on the activated surface. The amount of deposited palladium was calculated based on the mass difference before and after the palladium deposition.

3.2. Characterization and testing of membranes

3.2.1. Characterization of membranes

For testing, if the silicalite structure was fully developed the permeance of nitrogen (ΔP_{N_2}=2 bar) was measured. The macroporous stainless-steel support as well as the silicalite stainless-steel membrane with and without palladium deposition were further characterized by SEM-photographs. The SEM-photograph of the stainless-steel support (Fig. 2(a)) shows pores with the equivalent diameter between 5 and 40 μm. The surface of the membrane after the first stage of silicalite deposition on the support (Fig. 2(b)) illustrates the process of support covering with silicalite. The zeolite layer exhibits a narrow pore-size distribution with the average pore diameter of 5.5 Å (see [10]). The SEM photograph for silicalite membrane with palladium deposition (Fig. 2(c)) showed that small palladium clusters (average diameter: 5–10 μm) are deposited onto the silicalite structure. The thickness of the palladium layer, calculated from the mass difference before and after synthesis and the density of palladium, amounted to 2.6 Å.

3.2.2. Stability of membranes

The silicalite membranes exhibited high thermal and mechanical stability. After more than 100 h of operation in the fluidized-bed membrane reactor at temperatures between 700 and 750°C a constant selectivity of separation was measured. In spite of different thermal expansion of steel and zeolite the layer of silicalite was not apparently damaged. Also, carbon deposition in the membrane which can result in pore blockage was not detected. However, a slow deposition of carbon cannot be excluded.

The observed stability of the membranes is in line with results obtained with stainless-steel silicalite membranes at low temperatures. Bakker et al. [12] found that at T<350°C the permeation rate did not change significantly with time, i.e., less than 10% in 1.5 year. Casanave et al. [7] applied the same type of silicalite ceramic membrane than used in this study for the dehydrogenation of *i*-butane at temperatures up to 450°C and constant reactor performance was reported. Since the membrane applied in this study was used up to 750°C, it is difficult to compare its stability with low temperature systems.

After palladium deposition, the separation selectivity applying the same conditions was found similar to the selectivity of the silicalite membrane, i.e. no preference for hydrogen permeation was detected during the CPOM reaction (Fig. 3). This result suggests either that the Pd impregnation within the zeolite pores was only partial, leaving numerous pores free from metal particles, or that the palladium film on the surface of the stainless-steel silicalite membrane was not stable. The latter effect could be due to the detachment of the palladium film from the silicalite layer inside the stainless-steel tube at high temperatures. Literature analysis showed that composite palladium membranes were always used at temperatures significantly below 600°C [13–15]. Against this background only porous membranes were used for the catalytic measurements.

4. Catalytic measurements

4.1. Fixed bed reactor

4.1.1. Long time stability

No deactivation of catalyst was detected for more than 100 h on stream. This stability could be due to the large amount of catalyst (overcapacity) compared to the low partial pressure of reactants applied in the fixed-bed experiments.

4.1.2. Temperature profiles

In the fixed-bed reactor steep temperature gradients were observed (see Fig. 4). The profiles were independent from the flow rate of the sweep gas. For an inlet temperature of 700°C the temperature in the bed increased to maximum value of 716°C. Since the reactor was operated in the polytropic mode the increase of the temperature was lower than the adiabatic temperature rise that amounted to 237 K for an inlet temperature of 700°C. Down-stream to this hot spot that was measured at z/L=0.25 the temperature dropped to 675°C, i.e. below the inlet value. In the back end of the reactor (z/L>0.41) no further change of the temperature occurred. The temperature profile for 744°C gas inlet temperature was similar to the previously described one. In both cases, the temperature down-stream to the hot spot was lower than the temperature of the heating elements.

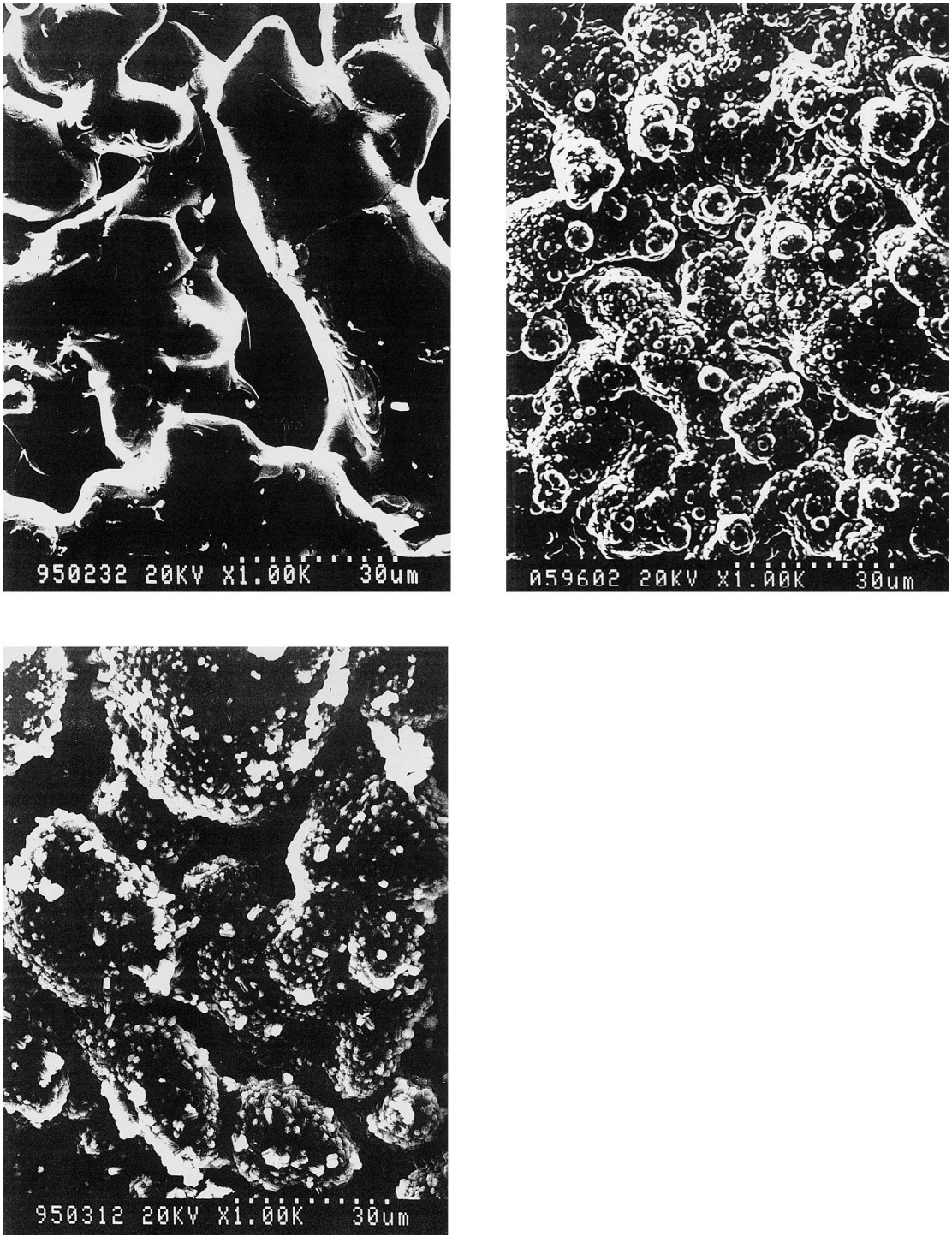

Fig. 2. SEM-photographs of the (a) stainless-steel support, (b) the stainless-steel support after the first deposition of silicalite and (c) the palladium deposited stainless-steel silicalite membrane.

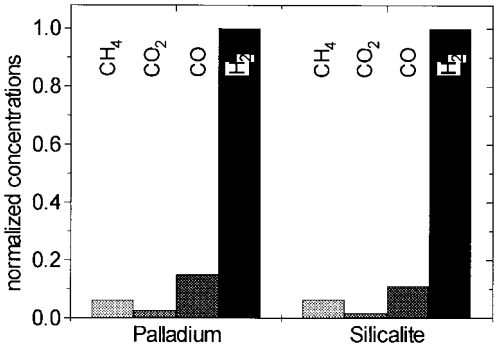

Fig. 3. Separation selectivity of the silicalite membrane and the palladium-silicalite membrane at 700°C.

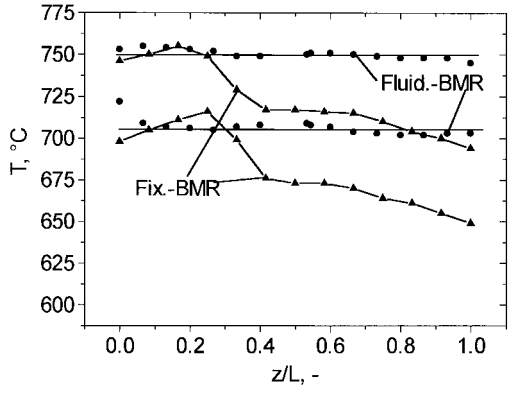

Fig. 4. Temperature profiles measured in the fixed-bed and the fluidized-bed membrane reactors at 700 and 750°C (Fix -BMR: fixed-bed membrane reactor; Fluid. -BMR: fluidized-bed membrane reactor).

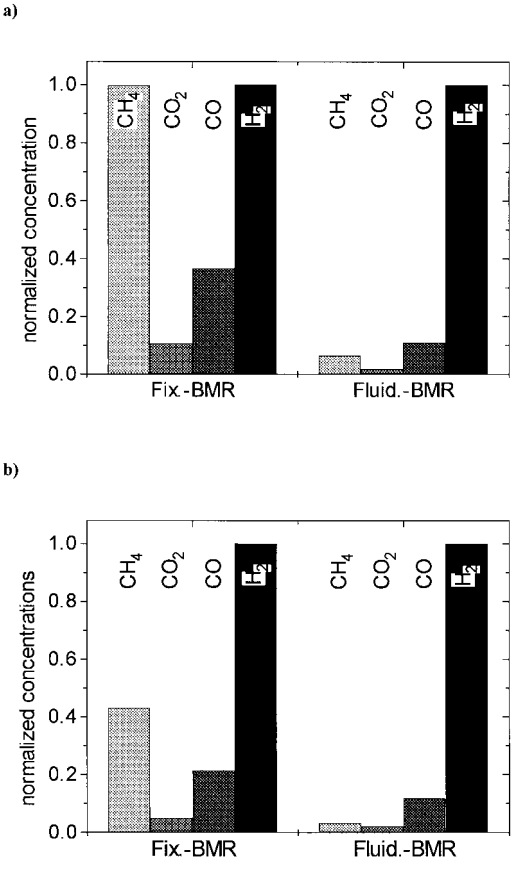

Fig. 5. Separation selectivity of the silicalite membranes installed in the fixed-bed and the fluidized-bed membrane reactor at (a) 700 and (b) 750°C (Fix-BMR: fixed-bed membrane reactor; Fluid.-BMR: fluidized-bed membrane reactor).

The measured temperature profiles are in line with the consecutive reaction scheme, i.e. exothermic combustion of methane followed by the steam- and dry reforming of methane. Similar profiles and even higher temperature spikes were reported also by other investigators. Heitnes et al. [16] measured in the fixed bed temperature spikes between 60 and 80 K. Santos et al. [5] reported for the fixed-bed membrane reactor temperature increase of 55 K. When assuming that the increase of the temperature was related to the availability of oxygen the contact time that was required for complete conversion of oxygen amounted to about 0.5 g s/ml.

4.1.3. Selectivity of separation

In the fixed-bed membrane reactor the concentration of methane in the sweep gas at 700°C was almost equal to the concentration of hydrogen (Fig. 5(a)). Oxygen was not detected. The concentration of water could not be measured directly since it was removed by cooling traps. When reaction temperature was increased to 750°C (Fig. 5(b) the concentration of methane in the sweep gas in the fixed-bed membrane reactor decreased significantly, as expected from higher reaction rate and lower equilibrium methane concentration.

4.1.4. Catalytic performance and permeation rates

In the fixed-bed reactor operated without product separation, i.e. closed sweep gas outlets, nearly equilibrium conversions were achieved. At gas inlet temperatures of 700 and 750°C methane coversions of 85 and 91%, respectively, were measured, they were

close to the equilibrium conversions which were calculated for the hot-spot temperature (716 and 755°C) and amounted to 86 and 92%, respectively. Also the experimental selectivities to carbon monoxide of 92 and 97% were close to the equilibrium ones, i.e. 91 and 95%. These results are in line with literature data, i.e. several groups reported that within experimental errors thermodynamic equilibrium was reached in similar systems (see, for instance, [17–20]).

When integrated product separation took place (with sweep gas in the external compartment), the conversion of methane in the fixed-bed reactor decreased to 71 and 81% at 700 and 750°C, respectively. The decrease of methane conversion was caused by the low selectivity of separation, i.e. large amounts of methane were removed from the catalytic bed through the membrane and therefore could not be consumed in the reforming steps (see Fig. 5). Ioannides and Verykios [6] who reported an increase in methane conversion from 72 to 95% at 700°C (CH_4:O_2:N_2=2:1:0) also observed a strong dependence of the performance of the membrane reactor on the residence time. The performance of the fixed-bed reactors equipped with porous membranes could be improved by placing the catalyst upstream to the permeable zone of the membrane; equilibrium gas composition, i.e. a low concentration of reactants and a high one of products should be reached before the separation takes place. This method was applied by Santos et al. [5] who carried out the CPOM in a fixed-bed membrane reactor (i.d.=6.6 mm, ceramic membrane); they deposited silica into the first part of the membrane and reported an increase in methane conversion from 96 to 97.8% at 800°C and from 95 to 97.7% at 775°C (CH_4:O_2N_2=2:1:1).

4.2. Fluidized-bed reactor

4.2.1. Long time stability

No deactivation of catalyst was detected for more than 100 h on stream. The constant activity of the fluidized-bed reactor system was also reported by other investigators who studied the CPOM reaction over nickel catalysts in laboratory-scale (i.d.=2.4–5 cm) fluidized-bed reactors [17,21,22]. The stable catalytic performance of the fluidized-bed reactors was explained by the solids motion in this reactor type. Circulation of solids cause that deactivated particles are transported from the upper part of the bed to the oxygen rich distributor zone where carbon deposits are combusted.

4.2.2. Temperature profiles

In contrast to the steep temperature gradients in the fixed-bed membrane reactor almost isothermal conditions were achieved in the fluidized-bed membrane reactor. However, a strong decrease of temperature was observed in the freeboard. Isothermal operation when performing the CPOM reaction in the laboratory-scale fluidized beds were also reported by other investigators [17,18,22]. The isothermicity of the catalytic bed in the reactor investigated in this work indicate that the circulation of the solids was not influenced by the membrane.

4.2.3. Bed hydrodynamics

In order to interpret results obtained in the fluidized-bed reactor its hydrodynamics should be characterized. The particles of the Ni/α–Al_2O_3 catalyst with d_p=200 μm belong to group B according to the classification of Geldart. Therefore, at gas velocities (u_0/u_{mf}=3.4) applied in the experiments bubbling bed can be expected. However, when calculating bubble diameter from the correlation of Werther [23] the diameter increases from 0.5 cm at the gas distributor to about 3.5 cm at the height of 18 cm. Since the distance between reactor wall and membrane/stainless-steel tube amounted to 1.7 cm, slugging has to be expected in the upper part of the bed (H>9 cm). This should lead to a decrease in the separation selectivity compared to the freely bubbling bed since no 'prefiltering' by the mass transfer limitation between bubble and the emulsion phase was present.

4.2.4. Selectivity of separation

The separation selectivities of the silicalite membrane in the fluidized-bed membrane reactor are presented in Fig. 5 for 700 and 750°C, respectively. For all temperatures the measured selectivities of separation in the fluidized-bed membrane reactor were higher than in the fixed-bed membrane reactor. Like in the fixed-bed the concentration of methane decreased with increasing temperature due to the change of the equilibrium concentration.

In order to elucidate the mechanism of gas permeation the measured selectivities of separation were

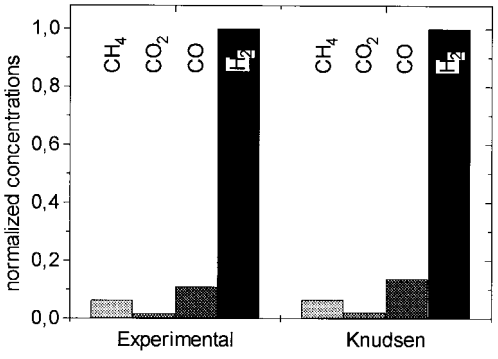

Fig. 6. Comparison of measured separation selectivities in the fluidized-bed membranes reactor and the calculated selectivities assuming Knudsen diffusion for 700°C.

compared with those calculated by applying correlations proposed for the Knudsen diffusion [24]. For calculating permeation rates the experimentally measured concentration profiles were used. For a temperature of 700°C the calculated selectivities of separation are presented in Fig. 6. For all temperatures the measured selectivities of separation in the fluidized-bed membrane reactor correlated well with the calculated values. This indicates that the transport of gas in the membrane was mainly controlled by Knudsen diffusion. The Knudsen-like transport mechanism in the supported silicalite membranes at high temperatures (T>400°C) was also reported by Giroir-Fendler et al. [10].

4.2.5. Catalytic performance and permeation rates

In the fluidized-bed reactor, methane conversions amounted to 76 and 87%, respectively, for 700 and 750°C. The corresponding equilibrium conversions amounted to 79 and 88%. The experimental hydrogen selectivities were determined to 88 and 92% for 700 and 750°C, respectively. The equilibrium ones were calculated to 92 and 95%. Carbon monoxide selectivities were also close to equilibrium values, i.e. 82 and 88% experimental values compared to 88 and 94% equilibrium ones for both temperatures.

Due to the low permeation rates compared to the total flow rate of gas no significant effect of product separation in the fluidized bed on syngas yield was detected. The permeation rates of the stainless-steel silicalite membranes of hydrogen estimated from concentrations in the emulsion phase and in the sweep gas amounted to $1.16 \cdot 10^{-7}$ and $1.20 \cdot 10^{-7}$ mol $(m^2\ s\ Pa)^{-1}$ at 700 and 750°C, respectively. For methane, values of $2.82 \cdot 10^{-7}$ and $2.33 \cdot 10^{-7}$ mol $(m^2\ s\ Pa)^{-1}$, respectively, were calculated for both temperatures. Permeation rates of same order were reported by Giroir-Fendler et al. [10] for silicalite membranes on an alumina support, e.g. for hydrogen at 400°C a permeability of $8.2 \cdot 10^{-7}$ mol $(m^2\ s\ Pa)^{-1}$ was determined. The permeation rates determined in this work and the ones reported by Giroir-Fendler et al. are even closer when taking into account that with increasing temperature the permeability of hydrogen decreases.

4.2.6. Target permeation rates

In order to estimate the permeation rates that are necessary for achieving a marked improvement of the syngas yield simulations of a laboratory-scale reactor applying the previously developed model (see Part I [2]) were performed. Furthermore, the Peclet number (see [25]) which is given by the ratio of the molar flow rate at the reactor inlet and the permeation rate was calculated.

In the investigated fluidized-bed membrane reactor the Peclet number amounted to 34. This value is very high compared to the value of 1.4 that was applied in the previous simulations (see Part I [2]). In the fluidized-bed, the low Peclet numbers have to be achieved by increasing the amount of permeated gas; the other possibility, the reduction of gas flow, is limited due to the fact that the gas velocity has to be higher than the minimum fluidization velocity. Also the results of simulations indicate that for the reaction conditions used in this work the separation rate had to be significantly increased, e.g. at 700°C by factor 35 in order to achieve an increase in methane conversion form 80 to 87%.

Similar problems can be deduced from the results reported by steam reforming in a fluidized-bed membrane reactor. Low Peclet numbers (Pe=2.2–4) assumed in simulations resulted in the significantly increase of methane conversion, e.g. from 67 to 88% at 22.5 bar and 763°C [3]. However, in the 9.7 cm i.d. fluidized-bed reactor equipped with 12 palladium tubes conversions for methane at 7 bar and 652°C was increased by means of the integrated product separation only from 69 to 70.3% [3]. The Peclet number estimated from data presented in their paper amounted to 81.

5. Conclusions

Catalytic partial oxidation of methane to synthesis gas over a Ni/α–Al_2O_3 catalyst was investigated in laboratory-scale fixed-bed and fluidized-bed membrane reactors. In the reactors operated at 700 and 750°C, and at atmospheric pressure two different membranes were tested, i.e. silicalite and Pd-membranes on a ceramic cupport. The silicalite membranes exhibited over more than 100 h of operation high thermal stability. No improvement in separation properties was obtained with Pd-membrane. Further works are in progress to improve the membrane with respect to thermal stability and the location of Pd deposits within the zeolite layer.

In the catalytic measurements either in the fixed-bed or in the fluidized-bed reactor, nearly thermodynamic equilibrium was achieved. The analysis of the separation selectivities in both types of reactor confirmed the conclusions reached in the simulation studies [1,2]: in fluidized-bed membrane reactors significant better separation selectivities to hydrogen permeation could be obtained. However, neither in the fixed-bed membrane reactor nor in the fluidized-bed membrane reactor the amount of permeated hydrogen was sufficient to shift significantly the equilibrium towards higher syngas yields. However, it can be forecast from the present study that by improving the selective permeability of the membrane a fluidized-bed membrane reactor can be considered as a promising alternative for the partial oxidation of methane.

6. Notation

CPOM	catalytic partial oxidation of methane to synthesis gas
d_{pore}	pore diameter (μm)
Fix-BMR	fixed-bed membrane reactor
Fluid-BMR	fluidized-bed membrane reactor
H	axial reactor height (m)
H_{mf}	catalyst bed height at minimum fluidization (m)
i.d.	inner diameter (m)
L	reactor length (m)
m_{cat}	catalyst mass (g, kg)
o.d.	outer diameter (m)
p_j	partial pressure of component j (Pa)
Pe	Peclet number (–)
T	temperature (°C, K)
$\dot{V}$	volumetric flow (1/min)
z/L	dimensionless reactor length (–)

References

[1] L. Mleczko, T. Ostrowski, T. Wurzel, Chem. Eng. Sci. 51 (1996) 3187.
[2] T. Ostrowski, C. Mirodatos, A. Giroir-Fendler, L. Mleczko, Catal. Today, see this issue.
[3] A.M. Adris, S.S.E.H. Elnashaie, R. Hughes, Can. J. Chem. Eng. 69 (1991) 1061.
[4] D. Lafarga, J. Santamaria, M. Menéndez, Chem. Eng. Sci. 49 (1993) 2005.
[5] A. Santos, J. Coronas, M. Menéndez, J. Santamaria, Catal. Lett. 30 (1995) 189.
[6] T. Ioannides, X.E. Verykios, Catal. Lett. 36 (1996) 165.
[7] D. Casanave, A. Giroir-Fendler, J. Sanchez, R. Loutaty, J.-A. Dalmon, Catal. Today 25 (1995) 309.
[8] J. Shu, B.P.A. Grandjean, S. Kaliaguine, P. Ciavarella, A. Giroir-Fendler, J.-A. Dalmon, submitted to J. Membr. Sci. (1996).
[9] L. Mleczko, R. Andorf, M. Baerns, Chem. -Ing. -Tech. 62 (1990) 762.
[10] A. Giroir-Fendler, J. Peureux, H. Mozzanega, J.-A. Dalmon, Stud. Surf. Sci. Catal. 101 (1996) 127.
[11] J. Shu, B.P.A. Grandjean, E. Ghali, S. Kaliaguine, J. Membr. Sci. 77 (1993) 181.
[12] W.J.W. Bakker, F. Kapteijn, J. Poppe, J.A. Moulijn, J. Membr. Sci. 117 (1996) 57.
[13] E. Kikuchi, S. Uemiya, N. Sato, H. Inoue, H. Ando, T. Matsuda, Chem. Lett., (1989) 489.
[14] E. Kikuchi, Catal. Today 25 (1995) 333.
[15] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1995) 325.
[16] K. Heitnes, S. Lindberg, O.A. Rokstad, A. Holmen, Catal. Today 21 (1994) 471.
[17] L. Mleczko, T. Wurzel, J. Chem. Eng. 66 (1997) 193.
[18] A. Santos, M. Menéndez, J. Santamaria, Catal. Today 21 (1994) 481.
[19] S.S. Bharadwaj, L.D. Schmidt, J. Catal. 146 (1994) 11.
[20] M. Prettre, C. Eichner, M. Perrin, Trans. Faraday Soc. 43 (1946) 335.
[21] A. Santos, M. Menéndez, A. Monzón, J. Santamaria, E.E. Miró, E.A. Lombardo, J. Catal. 158 (1996) 83.
[22] U. Olsbye, E. Tangstad, I.M. Dahl, Natural Gas Conversion II, in: H.E. Curry-Hyde, R.F. Howe (Eds.), Elsevier Science B.V., 1994.
[23] J. Werther, Chem. Eng. Sci. 47 (1992) 2457.
[24] J.C.S. Wu, P.K.T. Liu, Ind. Eng. Chem. Res. 31 (1992) 322.
[25] S. Agarwalla, C.R.F. Lund, J. Membr. Sci. 70 (1992) 129.