ELSEVIER
Catalysis Today 46 (1998) 83–89
CATALYSIS TODAY

Methane conversion to syngas in a palladium membrane reactor

J. Galuszka[a,*], R.N. Pandey[b], S. Ahmed[b]

[a] Natural Resources Canada, CANMET Energy Technology Centre, Nepean, Ont., Canada K1A 1M1
[b] Guelph Chemical Laboratories Ltd., Guelph, Ont., Canada N1H 1E7

Abstract

Catalytic partial oxidation and dry reforming of methane to syngas have been carried out on Pd/Al_2O_3 between 350–550°C and 550–600°C, respectively. A conventional fixed-bed reactor and a membrane reactor containing dense palladium membrane prepared by electroless-plating were used. The CH_4 conversion, and CO and H_2 yield were considerably enhanced in the membrane reactor for both processes. CH_4 conversion increased between 4–20%. The CO and H_2 yield increased between 2–20% and 8–18%, respectively. However, filamentous carbon formation on the palladium membrane and membrane swelling leading to its destruction were confirmed by SEM. Therefore, the applicability of a palladium membrane for hydrogen separation from process streams containing methane or carbon monoxide seems unlikely. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Palladium membrane; Partial oxidation; Dry reforming; Carbon deposition

1. Introduction

Conventional technology for the production of syngas is catalytic steam reforming of methane [1]. However, the process has a number of disadvantages including high endothermicity (energy-intensive), catalyst-coking propensity and requirements of high temperature (>750°C) and high pressure (>20 atm). Also, the 3:1 ratio of hydrogen and carbon monoxide in the product stream is not optimal for most applications. On the whole, steam reforming is highly capital-intensive accounting, for instance, for about 70% of total investment and operating costs in methanol production based on natural gas [2]. This fact definitely provides a substantial incentive for developing an alternative strategy for syngas production. Catalytic partial oxidation of methane may offer an alternative route for producing synthesis gas [3]. Another possible route for syngas production is catalytic CO_2 reforming of methane. Like steam-reforming reaction, CO_2 reforming of methane is also highly endothermic requiring large energy input. Despite this drawback, a resurgence of interest in CO_2/CH_4 reforming has occurred mainly due to the realization of a possible positive impact of the large-scale application of the process on global CO_2 emissions [4]. Recent advances in the development of carbide-based non-coking catalysts for methane reforming [5] will very likely solidify the industrial feasibility of this process.

During partial oxidation of natural gas to syngas CH_4 undergoes combustion producing CO_2 and H_2O. The formation of CO and H_2 is the result of secondary reversible reactions of unreacted CH_4 with H_2O and CO_2 and the water gas shift reaction [3,4]. A similar

---

*Corresponding author.

PII: S0920-5861(98)00329-0

reaction network leads to syngas during dry reforming of CH_4. The reversible nature of these reactions imposes a limit, determined by thermodynamic equilibria, on the conversion and yields of CO and H_2 that is well below commercially acceptable levels, unless the reaction temperature is very high (>800°C). However, if H_2 is selectively and continuously removed from the reaction zone the equilibrium limitations of a conventional reactor can be circumvented. Alternatively, this offers the possibility of obtaining a given level of conversion at a much lower operating temperature than that realized in a conventional reactor. Studies on syngas production by steam reforming of methane in palladium-based membrane reactors [6–8] and by partial oxidation of methane in ceramic reactors [9,10] have been reported.

The present study investigates the concept of using a hydrogen transfer reactor (comprising H_2-permeable palladium membrane wall) to enhance the conversion of CH_4 and yield of syngas during partial oxidation and CO_2 reforming of CH_4. Conversion of methane to syngas has been studied in a palladium membrane reactor as well as in a conventional reactor. The performance of the membrane reactor was evaluated by comparing the data from these two types of reactors.

2. Experimental

Palladium membrane supported on Membralox T-170 α-alumina tube (O.D. 10 mm, 250 mm long, 20 mm length of each end glazed with a high temperature sealant) supplied by U.S. Filter was prepared by electroless-plating of the inside layer having a mean pore diameter of 0.2 μm using a method developed by Rhoda in 1959 [11]. The procedure involved contacting the inside surface of the support tube with an electroplating solution for several hours, with replenishment of the solution every hour. The plating solution consisted of $Pd(NH_3)_4Cl_2$, hydrazine, Na_2EDTA and ammonium hydroxide. Plating was carried out at 55–60°C. Before plating, the inner surface of the porous alumina tube was activated by subjecting the sensitization and activation treatment using $SnCl_2$ and $PdCl_2$ solutions. The thickness of the deposited film as estimated from weight gain was 10–15 μm.

Partial oxidation and dry reforming of methane to syngas were carried out in a fixed-bed membrane reactor. The reactor was a double tubular-type and the inner tube was the palladium hydrogen-permselective membrane. The inner tube (membrane tube) of the reactor was charged with 1.0 g of 5.0 wt.% Pd/γ-Al_2O_3 catalyst which was placed centrally forming about a 40 mm bed rested on quartz wool. The catalyst was prepared by incipient wetness impregnation of the γ-Al_2O_3 support with a solution of $PdCl_2$ salt. For partial oxidation the feed stream consisting of a 3:1 mixture of CH_4 and O_2 diluted in 50% N_2 was passed at 87 ml min^{-1} through the inner membrane tube. The excess of methane was used to simulate the practical necessity to carry out the process outside the explosive limits for $CH_4\backslash O_2$ mixtures when N_2 diluent would not be present in the feed stream. Sweep gas (Ar) was passed through the outer shell tube at 40 ml min^{-1}. The catalyst bed was maintained between 350–550°C as measured with a thermocouple located inside the catalyst bed. For dry reforming the feed stream consisting of a 1.2:1 mixture of CH_4 and CO_2 diluted in 40% of N_2 was passed at 95 ml min^{-1} through the inner membrane tube. Sweep gas (Ar) was passed through the outer shell tube at 40 ml min^{-1}. The catalyst bed temperature was between 550–650°C. The inner and outer streams were analyzed separately for products and reactants by on-line TCD-gas chromatography. Methane conversion and selectivity to the products were determined.

Similar experiments were also conducted in a fixed bed conventional flow reactor to compare and evaluate the performance of the membrane reactor. For this purpose, the membrane reactor in the flow apparatus was replaced with a quartz reactor and the reactor effluent was analyzed for products and reactants.

Fresh and exposed to product stream membranes were examined by a Jeol JSM-5300 scanning electron microscope (SEM) combined with EDX.

3. Results and discussion

3.1. Palladium membrane

A fresh Pd membrane supported on Membralox T-170 tube showed H_2 permeance of about 12.7 cm^3-(STP)/cm^2 min atm between 550–625°C with about 100% selectivity to H_2 separation from N_2.

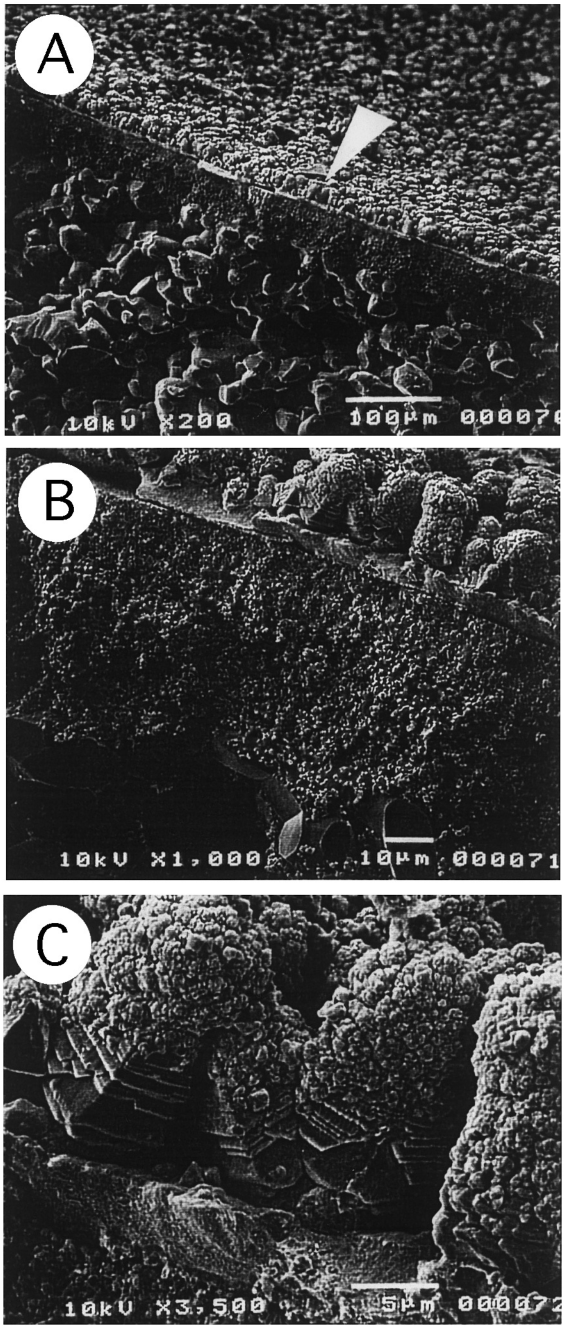

Fig. 1. SEM micrographs of cross-section of 'fresh' Pd membrane supported on Membralox porous α-alumina tube shown with increasing magnification from A to C: arrow points the specific spot magnified 1000 (B) and 3500 (C) times.

Fig. 1(A)–(C) shows a cross-sectional SEM of a fresh Pd membrane at a magnification of 200X, 1000X and 3500X, respectively. Morphological examination indicated a continuous layer of approximately 5 μm of Pd and three layers of α-alumina of successively larger particles at the inner surface of the Membralox tube. A 10 μm layer of crystalline Pd nodules resides on top of the continuous layer of palladium. The overall thickness agrees well with the Pd layer thickness estimated from the weight gain during electroplating. The Pd layer was mechanically strong with good adherence to the supporting tube.

3.2. *Partial oxidation of methane*

Results obtained for partial oxidation of methane to syngas in a conventional fixed-bed reactor indicated that the process reached equilibrium limitation between 550–700°C in the presence of 5.0 wt.% Pd/Al_2O_3 catalyst. The values of the equilibrium constants calculated from the reactor outlet gas composition for the reversible secondary reactions of unreacted CH_4 with H_2O and CO_2 and the water gas shift reaction agreed reasonably well with the respective theoretical values as shown in Table 1.

Consequently, there is a scope to obtain conversions beyond equilibrium values by selectively and continuously withdrawing product H_2 from the reaction zone by conducting the process in a H_2-permeable membrane reactor. However, it should be realized that establishing equilibrium is not absolutely essential for taking advantage of a membrane reactor. The fact that secondary reactions of unreacted CH_4 with H_2O and CO_2 and the water gas shift reaction are reversible is sufficient to obtain, in principle, a conversion in a membrane reactor that is not achievable in a conventional closed reactor under otherwise similar conditions.

Table 2 gives the results of partial oxidation of CH_4 carried out in a fixed-bed double tubular Pd membrane reactor between 350–550°C. Also included are the results of duplicate experiments conducted in a fixed-bed conventional flow reactor for comparison with the results of the membrane reactor.

Clearly, CH_4 conversion and selectivity and yield of CO and H_2 are considerably enhanced in the case of the membrane reactor. For example, at 500°C, CH_4 conversion increased from 26% in the conventional

Table 1
Comparison of experimental and theoretical equilibrium constants of secondary reactions during partial oxidation and dry reforming of methane to syngas

Temperature (°C)	Equilibrium constant					
	Calculated from reactor outlet gas composition			Theoretical		
	ϕ_2	ϕ_3	ϕ_4	K_2	K_3	K_4
500	3.3×10^{-3}	3.8×10^{-4}	8.7	9.65×10^{-3}	1.97×10^{-3}	4.90
550	6.5×10^{-2} (3.6×10^{-2})	1.3×10^{-2} (0.32×10^{-2})	5.0 (11.5)	7.86×10^{-2}	2.28×10^{-2}	3.46
600	0.70 (0.66)	0.20 (0.19)	3.5 (3.5)	0.51	0.20	2.56
650	3.8	1.70	2.2	2.91	1.50	1.93
675	11.7	5.2	2.3	6.34	3.71	1.76
700	19.3	8.63	2.2	13.1	8.65	1.52

Calculated ϕ_2, ϕ_3, ϕ_4 and theoretical K_2, K_3, K_4 equilibrium constants are for the following reversible reactions: $CH_4+H_2O\rightleftarrows CO+3H_2$ (2); $CH_4+CO_2\rightleftarrows 2CO+2H_2$ (3); $CO+H_2O\rightleftarrows CO_2+H_2$ (4). The Boudouard reaction is not considered. Values in parentheses are for dry reforming of methane.

Table 2
Enhancement in catalytic conversion of methane to syngas by partial oxidation in hydrogen transfer membrane reactor over 5.0 wt.% Pd/γ-Al_2O_3

Temperature (°C)	Reactor-type	Conversion (%)		Selectivity (mole %)		Yield (mole %)		H_2/CO mole ratio
		CH_4	O_2	CO	H_2	CO	H_2	
350	Conventional	18.4	~100	Trace	24.0	Trace	4.4	–
	Membrane	22.9	~100	10.5	55.0	2.3	13.8	11.9
500	Conventional	26.7	~100	20.0	68.5	5.3	18.3	7
	Membrane	40.3	~100	63.0	85.5	25.4	35.5	2.8
550	Conventional	34.7	~100	50.9	83.5	17.7	29.0	3.3
	Membrane	45.7	~100	76.3	87.0	34.9	40.5	2.3

reactor to 40% in the membrane reactor. Concomitantly, selectivity to CO increased from 20% to 63%, and to H_2 from 68% to 85%. The CO yield increased from 5% to 25% and that of H_2 from 18% to 36%.

3.3. Dry reforming of methane to syngas

The dry reforming of methane to syngas in a conventional fixed-bed reactor was carried out on 5.0 wt.% Pd/Al_2O_3 catalyst between 550–675°C. Starting from 600°C the process was equilibrated as indicated by the agreement of the calculated and theoretical equilibrium constants given in Table 1 for the reversible reactions of CH_4 with CO_2 and H_2O and the water gas shift reaction.

Table 3 gives the results of dry reforming of CH_4 with CO_2 carried out at 550°C and 600°C in a fixed-bed double tubular Pd membrane reactor.

Table 3
Enhancement in catalytic dry reforming of methane to syngas in hydrogen transfer membrane reactor over 5.0 wt.% Pd/γ-Al_2O_3

Temperature (°C)	Reactor-type	Conversion (%)		Selectivity (mole %)	Yield (mole %)		H_2/CO mole ratio
		CH_4	CO_2	H_2	CO	H_2	
550	Conventional	17.2	24.6	87.5	21.5	15.8	0.81
	Membrane	37.5	51.0	87.5	42.0	33.0	0.85
600	Conventional	40.9	56.6	89.8	50.3	38.1	0.84
	Membrane	48.6	63.0	91.0	54.5	46.5	0.94

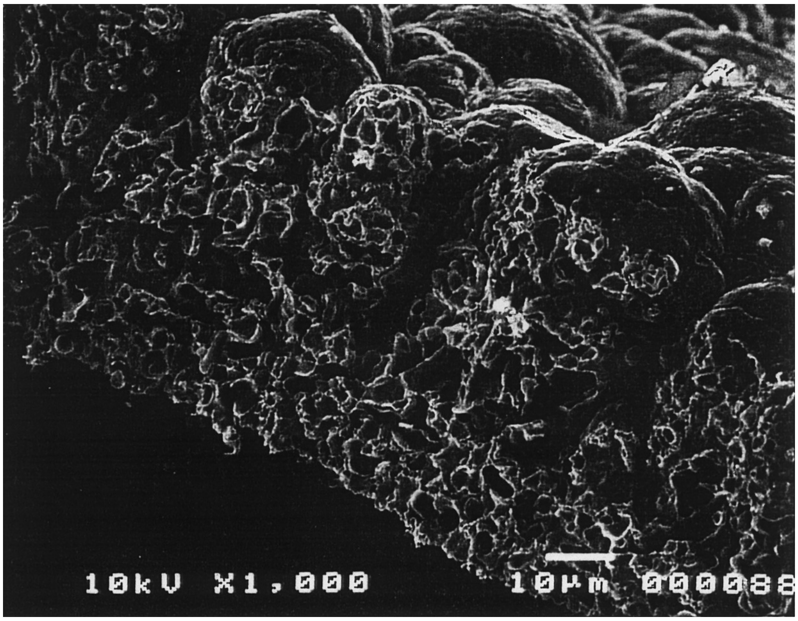

Fig. 2. Cross-section of Pd layer of used membrane separated from Membralox support.

The results of the experiments conducted in a fixed-bed conventional reactor are also included for comparison.

It is evident from Table 3 that at 550°C a remarkable increase in the conversions of CH_4 and CO_2 occurred in the membrane reactor. Concurrently, yields of CO and H_2 also increased dramatically (from 21% to 42% for CO and from 16% to 33% for H_2).

3.4. *Carbon deposition on dense Pd membranes*

Fig. 2 shows a cross-section of a Pd layer that separated easily from the supporting Membralox tube after the membrane was used in a syngas generating reactor for more than 20 h between 550–650°C. During that period, therefore, the Pd membrane was exposed to CH_4, H_2, CO, CO_2 and H_2O. Substantial swelling and development of porosity in the Pd layer of the used membrane can be easily recognized in the SEM photograph shown in Fig. 2.

Also 'corrosion' of the top layer of Pd from the same membrane by filamentous carbon formation is quite pronounced as shown in Fig. 3. This type of process combined with Pd swelling would lead eventually to metallic membrane destruction.

Assuming that the swelling of the membrane, caused mostly by hydrogen, can be controlled, these membranes have a potential for hydrogen separation from process streams that are methane- and carbon monoxide-free. For instance, a sweep stream from a syngas generating membrane module would contain mostly nitrogen and hydrogen.

Large amounts of filamentous carbon were also identified on spent Pd/Al_2O_3 catalyst by SEM. The growth of the carbon filaments occurs in a catalytic 'self-cleaning' system [12]. The rate of carbon deposition will remain almost independent of time as long as the metal particle at the tip of the filament is not encapsulated by carbon. Formation of filamentous carbon explains the relatively insignificant decrease of the catalyst activity after a long time on stream and encourages revision of some literature data [3] that claimed that equilibrium gas composition was achieved during partial oxidation of methane to syngas at high temperatures using supported metal catalysts.

4. Conclusions

Although the process was not optimized, the feasibility of achieving the enhancement of the CH_4

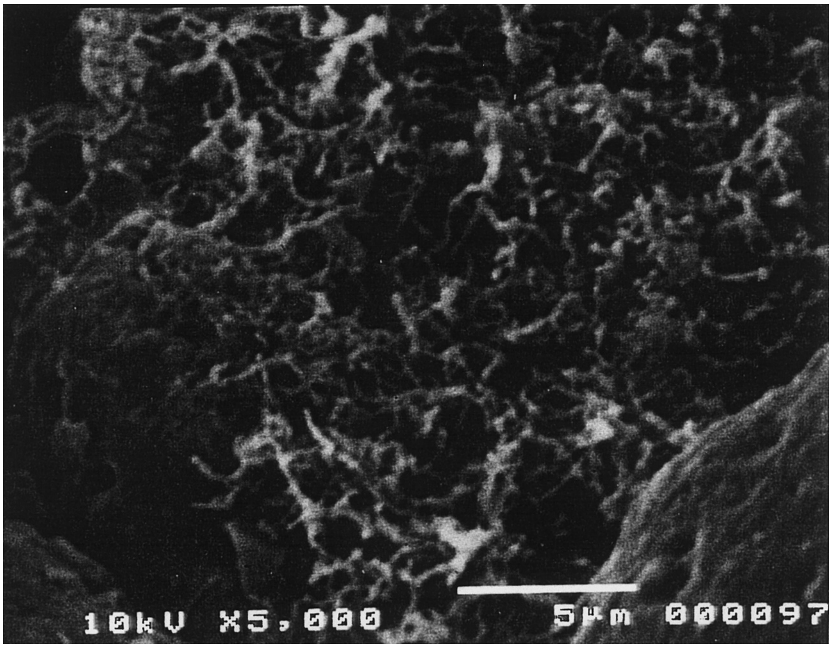

Fig. 3. Top Pd layer of used membrane. Corrosion of the metal by filamentous carbon is clearly visible.

conversion and CO and H_2 selectivity beyond the limits stipulated by thermodynamic equilibrium during catalytic partial oxidation or dry reforming of methane to syngas has been convincingly demonstrated by the use of a palladium membrane reactor. The direct practical consequence of this development is the possibility of improving the economics of syngas generation by using a membrane reactor [13]. However, the metallic membranes are likely to have no application for hydrogen separation from the process streams containing methane and carbon monoxide due to carbon deposition and filamentous carbon formation that inevitably leads to membrane destruction. This aspect was apparently overlooked in a recent report [14] about the use of a palladium membrane reactor for dry reforming of methane. It is obvious, as already observed by Saracco et al. [15], that further success of any membrane reactor mainly depends on whether a high temperature, sufficiently permeable and stable membrane becomes available. However, the problem of carbon deposition on the methane partial oxidation and dry reforming catalysts must also be addressed for further development of these processes.

Acknowledgements

The authors wish to thank Mr. G. Pleizier, National Research Council of Canada for SEM analysis. Financial support provided by the Consortium on Conversion of Natural Gas (CCNG) and the federal Program on Energy Research and Development (PERD) is gratefully acknowledged.

References

[1] Development in Syngas Production, Chem. Systems, Report No. 92S6, July 1994.
[2] D.L. Trimm, M.S. Wainwright, Catal. Today 18 (1993) 305.
[3] S.C. Tsang, J.B. Claridge, M.L.H. Green, Catal. Today 23 (1995) 3.
[4] J.H. Edwards, Catal. Today 23 (1995) 59.
[5] A.P.E. York, J.B. Claridge, A.J. Brungs, S.C. Tsang, M.L.H. Green, Chem. Comm. (1997) 39.
[6] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 67 (1991) 223.
[7] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Appl. Catal. A 119 (1994) 305.
[8] M. Chai, M. Machida, K. Eguchi, H. Arai, Appl. Catal. A 110 (1994) 239.

[9] A. Santos, J. Coronas, M. Menendez, J. Santamaria, Catal. Lett. 30 (1995) 189.
[10] T. Ioannides, X.E. Verykios, Catal. Lett. 36 (1996) 165.
[11] R.N. Rhoda, Trans Inst. Met. Finesh. 36 (1959) 82.
[12] J. Galuszka, M. Back, Carbon 22 (1984) 141.
[13] J. Sogge, T. Strom, Studies in Surface Science and Catalysis, in: M. de Pontes, R.L. Espinoza, C.P. Nicolaides, J.H. Schultz, M.S. Scurrell (Eds.), vol. 107, Natural Gas Conversion IV, Elsevier, Amsterdam, The Netherlands, 1997, p. 561.
[14] E. Kikuchi, Y. Chen, Studies in Surface Science and Catalysis, in: M. de Pontes, R.L. Espinoza, C.P. Nicolaides, J.H. Schultz, M.S. Scurrell (Eds.), vol. 107, Natural Gas Conversion IV, Elsevier, Amsterdam, The Netherlands, 1997, p. 547.
[15] G. Saracco, G.F. Versteeg, W.P.M. van Swaaij, J. Mem. Sci. 95 (1994) 105.