ECN-RX--05-188

Hydrogen membrane reactor for industrial hydrogen production and power generation

Y.C van Delft

L.A. Correia

J.P. Overbeek

D.F. Meyer

P.P.A.C. Pex

J.W. Dijkstra

D. Jansen

Paper presented at the Sustainable (Bio)Chemical Process Technology incorporating the 6th International Conference on Process Intensification Delft, The Netherlands: 27 – 29 September 2005

Revisions	
A	28 July 2005, draft version
B	11 November 2005, final version

Made by: Y.C. van Delft 25/11/05	Approved by: P.P.A.C. Pex 23/12/05	ECN Energy Efficiency in Industry
Checked by: H.M. van Veen 25/11/05	Issued by: P.T. Alderliesten 11/1/06	Separation technology

September 2005

Acknowledgement
The authors gratefully acknowledge the financial support of the Dutch Ministry of Economic Affairs (EZ), EDI programme (EDI03202, Senter) of the work presented.

Abstract
Hydrogen membrane reactors have been identified as a promising option for hydrogen production in future power production systems and industrial chemical production processes. This paper gives an overview of the results and current status of the hydrogen membrane reactor development at ECN for energy efficient industrial hydrogen production and power generation.
Dense tubular membranes with very thin Pd/Ag layers have been made on ceramic supports with electroless plating on a 1m2 scale. Measurements have shown that after initial activation very high hydrogen permeances can be obtained with high selectivities. Prior to actually testing the performance of the membrane reactor, different catalysts have been tested under simulated membrane reactor gas conditions. The noble catalyst did not show significant deactivation and was selected for application in the membrane reactor. It was shown that methane conversions well beyond the thermodynamic limits could be reached during steam reforming at 500-600°C and 50 bar in the membrane reactor. The membrane has been on stream for more than 100 days using different feed gases and is showing acceptable performance.

Contents

List of figures

1. Introduction

Combining reaction and separation using membrane reactors has shown to offer numerous advantages for hydrogen production in future power production systems and industrial chemical production processes. The application of hydrogen selective membranes for the removal of hydrogen from reforming and shift reactions gives higher conversion of these equilibrium reactions at lower temperatures while elegantly CO_2 can be captured under high pressure or chemical products can be obtained cost-effectively. In steam reforming and water gas shift processes membrane separation can be economical viable using current thin layer palladium alloy membrane technology, however a further increase in flux and/or decrease in membrane price is absolutely needed to convince the process owners of the suitability of this promising technology. Also a customized catalyst is required for reforming of methane, which should be active at low temperatures and resistant to coke formation under the carbon-rich membrane conditions. This paper gives an overview of the results and current status of the hydrogen membrane reactor development at ECN for energy efficient industrial hydrogen production and power generation.

2. Membrane development

In steam reforming and water gas shift processes membrane separation can be economical viable using current thin layer palladium alloy membrane technology, however a further increase in flux and/or decrease in membrane price is absolutely needed to convince the process owners of the suitability of this promising technology. Membrane development at ECN focuses on the development of thinner and cheaper metallic membranes with higher permeation rates. Dense Pd/Ag membranes consist of a very thin layer of alloy supported by a porous inorganic substrate. The Pd/Ag membranes are made by electroless plating. Pure (gas-tight) palladium layers can be prepared varying in thickness between 0.5 and 4 micron. Silver is deposited on top of the thin pure Pd-membrane and sintered to obtain the required alloy composition. By optimising the electroless plating technique it is possible to manufacture membrane layers (Pd/23%Ag) with a thickness of 3 to 5 micron on ceramic supports (see Figure 2.1).

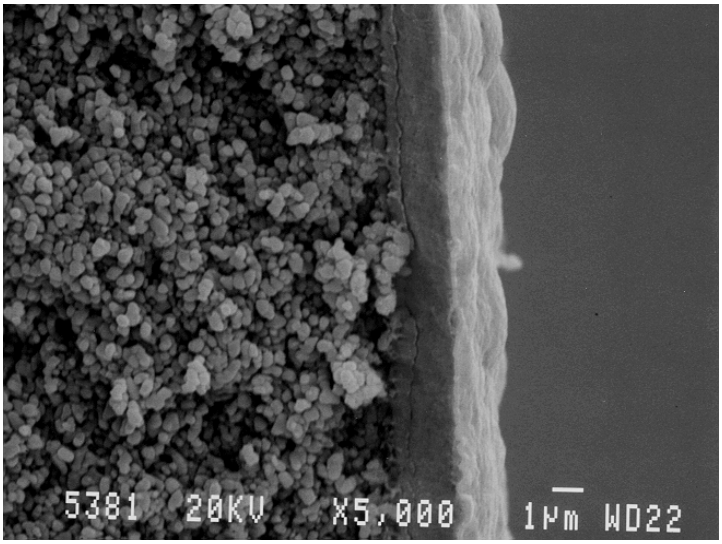

Figure 2.1 *SEM cross section of fractured sample of Pd/23%Ag membrane layer on ceramic support*

Using the above described procedure membrane tubes with a length of 0.8 meter and an outer diameter of 14 mm can be prepared reproducibly on a regular basis [4]. 24 of these comprise about 1 m^2 of membrane area. He leak tests show that the prepared and sintered membranes are gas-tight. In Figure 2.2 a photograph is given of these membranes. After activation the majority of the membrane samples have been used for single gas permeance tests at different temperatures and for the separation of hydrogen from reformate gas, using a bench scale test system that can operate up to 500ºC and 65 bar feed pressure with a membrane area of about 50cm^2. Before and after each test with reformate gas single gas permeance tests at 350ºC using hydrogen and nitrogen have been done in order to monitor changes in the membranes performance and to determine the issues for further improvement.

Figure 2.2 *Set of membrane tubes with a length of 0.8 meter for the separator unit*

3. Results

Results of bench scale hydrogen permeance tests at different temperatures are presented in Figure 3.1. Hydrogen permeation measurements have shown that after initial activation very high hydrogen permeances of 50-100 $m^3/m^2hbar^{0.5}$ can be obtained with high permselectivities.

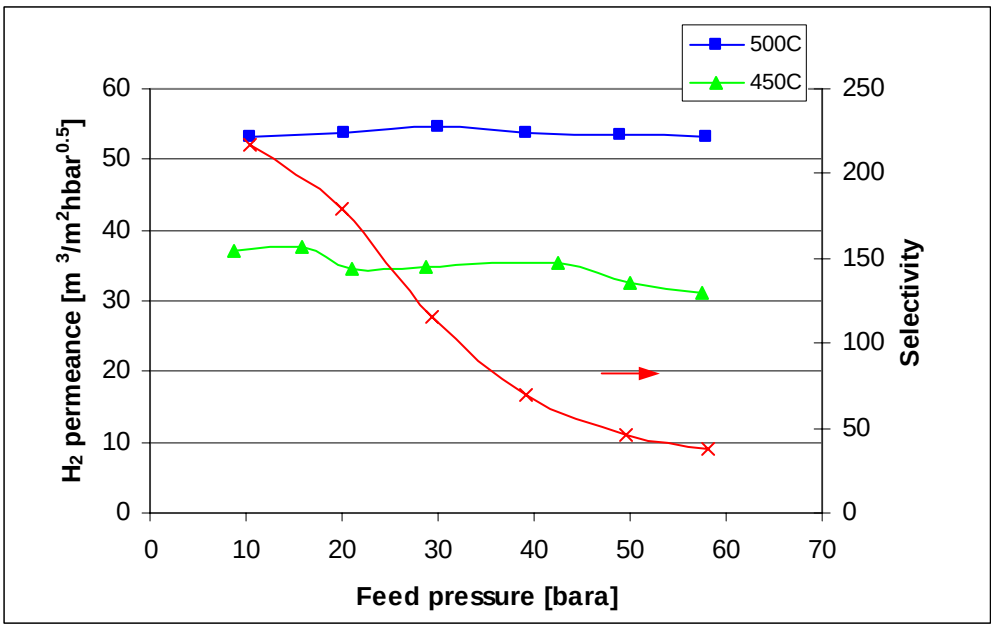

Figure 3.1 *Hydrogen permeance and selectivity vs feed pressure at different temperatures*

Tests with simulated reformate gas at 500ºC gave lower selectivities due to lower hydrogen permeances caused by the poisonous CO in the reformate gas. With the Pd/Ag membrane the hydrogen concentration was increased from 10% in the simulated reformate gas to 90% in the permeate. A shift in equilibrium was observed and extra hydrogen was produced without the use of a catalyst (see Figure 3.2).

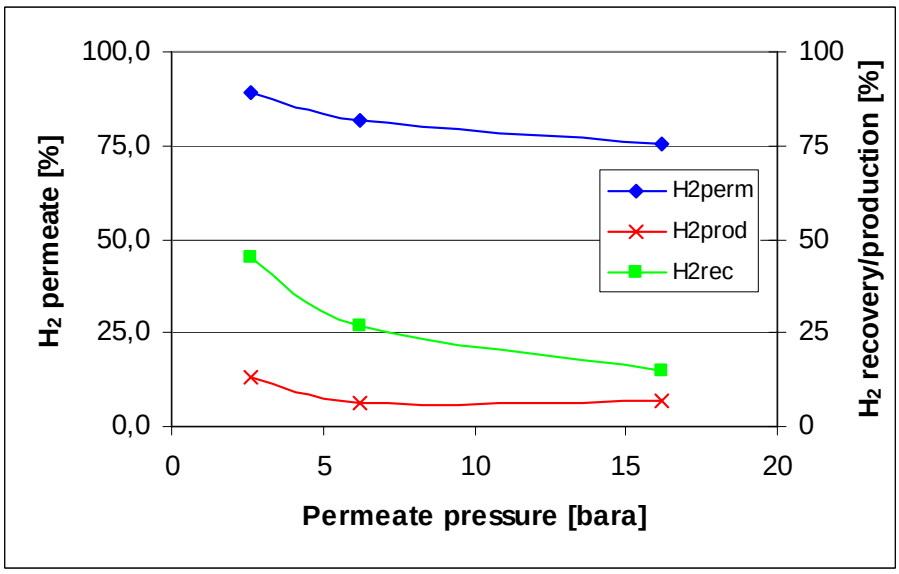

Figure 3.2 *H_2 production, recovery and permeate concentration vs permeate pressure*

The membrane has been on stream for more than 100 days using different feed gases and its performance is shown in Figure 3.3.

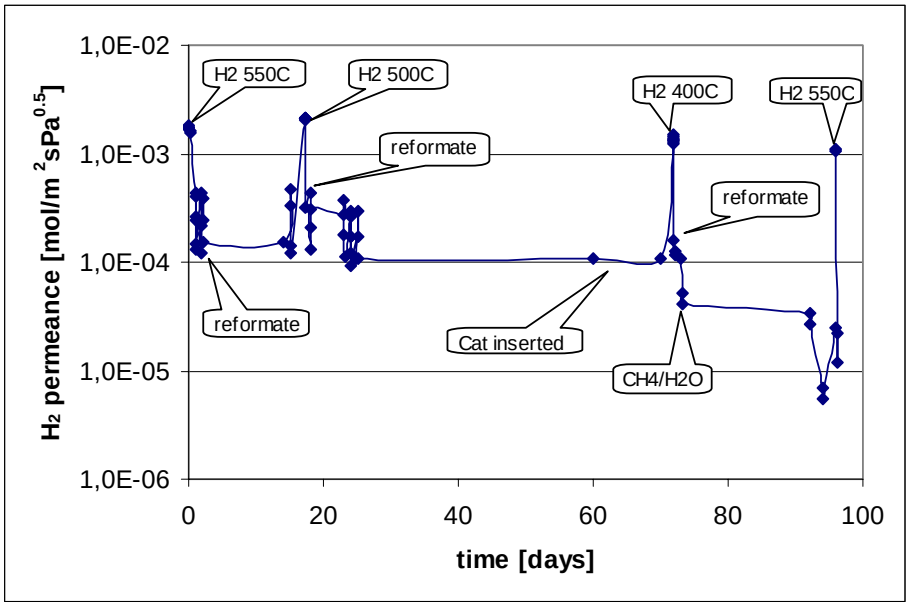

Figure 3.3 *H_2 permeance vs. time on stream (T=400-550ºC, Pfeed= 40-50 bara)*

4. Catalyst screening

Prior to actually testing the performance of the membrane reactor, different catalysts have been tested under simulated membrane reactor gas conditions. During 140h on stream at 500°C, the reference nickel catalyst showed significant deactivation under the simulated membrane reactor conditions, probably due to carbon deposition (see Figure 4.1). The noble catalyst did not show significant deactivation and was selected for application in the membrane reactor.

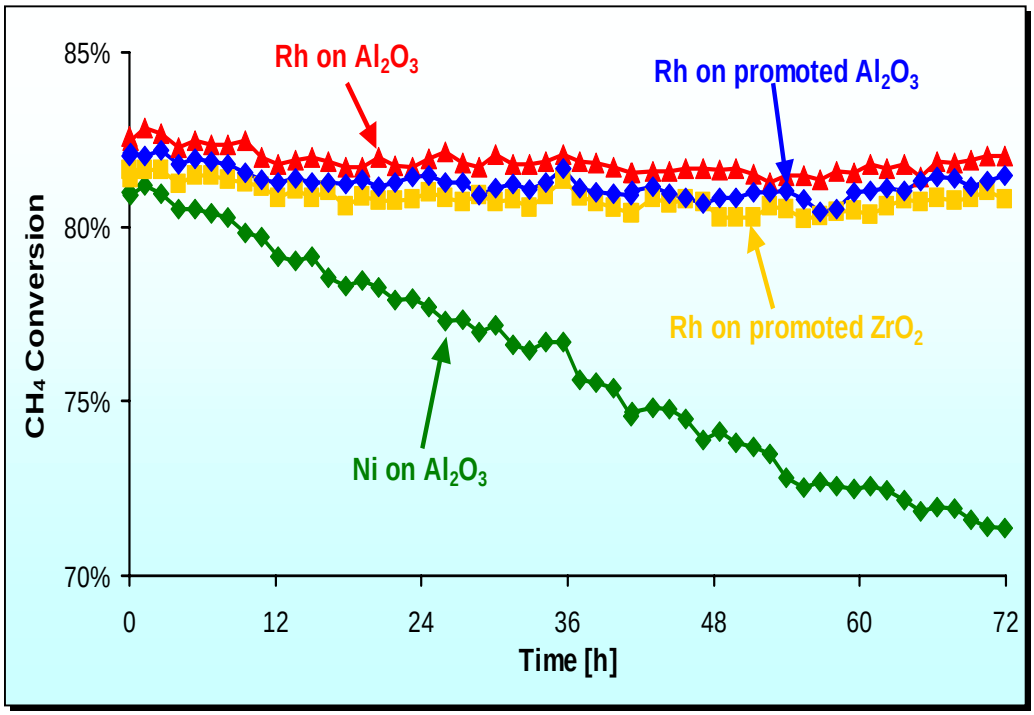

Figure 4.1 *Catalyst stability under simulated membrane reformer conditions*

It was shown that methane conversions well beyond the thermodynamic limits could be reached during steam reforming at 650°C and 12 bar in the membrane reactor.

5. Conclusions

Membrane reactors with hydrogen selective Pd/Ag membranes have been identified as a promising option for power production with CO_2 capture. Dense tubular membranes with very thin Pd/Ag layers have been made on ceramic supports with electroless plating on a $1m^2$ scale. Measurements have shown that after initial activation very high hydrogen permeances can be obtained with high selectivities. Prior to actually testing the performance of the membrane reactor, different catalysts have been tested under simulated membrane reactor gas conditions. The noble catalyst did not show significant deactivation and was selected for application in the membrane reactor. It was shown that methane conversions well beyond the thermodynamic limits could be reached during steam reforming at 650°C and 12 bar in the membrane reactor. The membrane has been on stream for more than 100 days using different feed gases and is showing acceptable performance.

References

[1] Dijkstra, J.W. and D. Jansen (2002): *Novel concepts for CO_2 capture with SOFC.* Proceedings of the 6th conference on greenhouse gas control technologies GHGT-6, Kyoto, Japan, 30 September-4 October.

[2] Jansen, D. and J.W. Dijkstra (2003): *CO_2 Capture in SOFC-GT Systems.* Second Annual Conference on Carbon Sequestration, Alexandria, VA, USA, 5-8 May.

[3] Jansen, D., P.P.A.C. Pex, J.W. Dijkstra and S.C.A. Kluiters (2004): *Membrane reactors: Key technology for production of de-carbonised energy carriers.* Proceedings of the 7th conference on greenhouse gas control technologies GHGT-7, Vancouver, Canada, September 5-9.

[4] Delft, Y.C. van and P.P.A.C. Pex (2003): *Membranes for hydrogen production.* Proceedings of the 1st European Hydrogen Energy Conference, Grenoble, France, September 2-5.

[5] Pex, P.P.A.C., Y.C. van Delft, L.A. Correia, H.M. van Veen, D. Jansen and J.W. Dijkstra (2004): *Palladium alloy membranes for energy efficient membrane reactors.* Proceedings of the 8th International Conference on Inorganic Membranes ICIM8, Cincinnati, Ohio, USA, July 18-22.