

Steam Reforming in Membrane Reactors using Nickel Catalysts

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1 Introduction

Hydrogen membrane reactors are being studied for power production with pre-combustion carbon capture. The membrane reactor produces hydrogen from natural gas at a low pressure and a stream rich in CO₂ and steam at high pressure. Condensation of the steam leaves a concentrated CO₂ stream at high pressure for underground storage. The hydrogen separated will be used as fuel in a gas-turbine combined-cycle plant to generate electricity at high efficiency. Due to the in situ removal of reaction products, the reaction equilibriums of the reforming and shift reactions are shifted to higher conversions in the membrane reactor. Therefore, relatively low temperatures can be used. Compared to conventional schemes for pre-combustion CO₂ capture the need for multiple shift reaction stages and a CO₂ absorber is avoided, CO₂ scrubbing and the compression requirement for the captured CO₂ is minimized. Unlike conventional reforming, membrane reforming benefits from high operation pressure due to the increased H₂ partial pressure differential across the membrane, which acts as the driving force for hydrogen permeation. Palladium (Pd) or Pd-alloy membranes exist that selectively permeate hydrogen between 573 and 873 K with a significant permeance. Higher temperatures should be avoided due to membrane disintegration problems.

The catalyst used in membrane reactors should be 1) sufficiently active for both the reforming and water-gas shift at relatively low temperatures (673-873K), 2) resistant to deactivation under the hydrogen-lean conditions in membrane reactors. The present study aims at obtaining insight in the potential of Nickel-based catalysts for steam reforming of methane in steam reformer membrane reactors (SRMR). Several ECN-made and pre-commercial or commercial catalysts based on Nickel and Rhodium has been studied for their methane conversion stability under conditions that approach the conditions in the membrane reactor. From this catalyst evaluation study a promising catalyst was selected and tested in an experimental membrane reactor test rig at 873K and a feed pressure of 30 bars.

2 Experimental

Stability testing of (commercial and ECN-made) Ni and Rh catalysts was conducted at 873 K. Gas compositions varied from 7.5% CH₄, 22.5% H₂O (H/C=10) to 1.3% CH₄, 3% H₂, 16% H₂O, 0.14% CO, 11.8% CO₂ (H/C=2.5), in 5%Ar/N₂, denoted reference condition, "REF" and (simulated) membrane condition "MR" respectively. Ni (and Lanthanum) was deposited onto MgAl₂O₄ (MA) by impregnation ((wt%)20 and

(wt%)40NiMa) of the nitrate salts and Homogenous deposition precipitation (HDP). Catalysts were diluted with α -alumina (alfa aesar) at 1:27 except for NiLa-MgAl₂O₄ that was diluted at 1:10. TEM, Temperature programmed analysis, Chemisorption and RAMAN were used to characterize the catalyst before and after reaction. A Ni-based catalyst was tested in an experimental membrane reactor test rig with a Pd membrane at high pressure.

A Process Development Unit (DPU) for membrane reactor tests (8-tube membrane reformer) is recently brought into use for bench-scale testing of membranes and catalysts. The reactor was conceived from a concept developed for full scale application. The reactor can hold a maximum of 8 reactor tubes that contain 50 cm Pd-alloy membranes, with catalyst in an annular zone outside the tube.

3 Results

The kinetics described by Xu (Nickel)[1] and that of Wei (Rhodium)[2] have been combined in a 1-D model together with the hydrogen permeation calculated from $J_{H_2}(\text{mol/m}^2\cdot\text{s}) = k_{\text{mem}}(P_{H_2, \text{reform}}^n - P_{H_2, \text{permeate}}^n)$ with $n=1$ [3]. It follows that as the membrane permeance increased, all catalysts reach a point where they are no longer able to maintain chemical equilibrium. However, both Rh and Ni maintain equilibrium conversion at a representative high permeance of $10^{-6} \text{ mol/m}^2\cdot\text{s}\cdot\text{Pa}$. Although the activity of Nickel catalysts for steam reforming is lower than rhodium, its activity appears to be high enough for use in membrane reactors.

Figure 1 shows the immediate onset of enhanced deactivation upon exposure of commercial Precious Metal steam reforming catalyst (PM-SR) and Rhodium supported MgAl₂O₄ (05RhMA) after changing from conventional steam reforming (REF) to the simulated membrane reactor feed side (MR) composition. Such behavior is not observed with Ni based catalysts (see Figure 2). RAMAN and CO-uptake analysis indicate that the deactivation at low H/C goes hand in hand with a change in size and presumably the nature of the Rh sites. Carbon deposition on Rh catalysts becomes less of an issue going towards lower H/C. HDP synthesized catalysts with 20 to 30 wt% of Ni showed less deactivation, the severity of which was comparable to the commercial Ni pre-reforming catalyst (Ni-PR). RAMAN and chemisorption analysis together with mass balances and H₂/CO ratios obtained during reaction indicate that the better stability is accompanied with smaller Ni particles and less carbon (graphite) deposition. The better stability obtained with HDP synthesized Ni catalysts as compared to impregnated catalysts is at the cost of a lower turn over frequency (Table 1). HDP synthesized cata-

lysts with a Ni loading of smaller or equal to 15wt% show sintering-related deactivation. Lanthanum stabilizes the Ni-MgAl₂O₄ steam reforming conversion at high H/C. The mechanism of which La stabilizes Ni-MgAl₂O₄ is currently being studied.

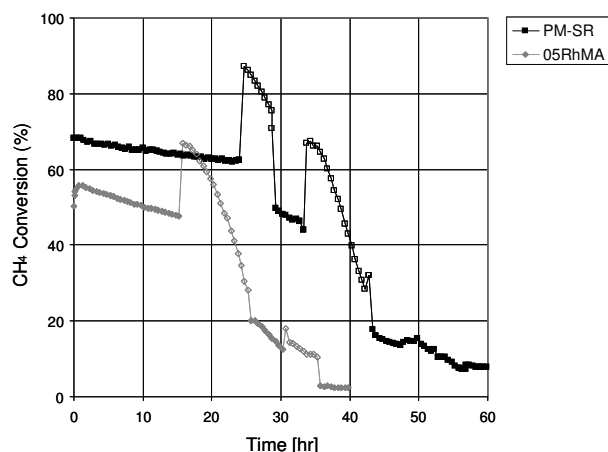


Figure 1. Methane steam reforming conversion with PM catalysts at 873K during two interchanging conditions REF and (open symbols) MR. Table 1. Turnover frequencies obtained with Ni-MgAl₂O₄: comparison of HDP synthesized and impregnated catalysts

	Dispersion (%)	Turnover Frequency (s ⁻¹)	Normalized Turnover Frequency
20 wt% Ni wet impregnated	1.7	18.5	1.00
28 wt% Ni HDP	2.2	12	0.65
20 wt% Ni HDP	3.2	10.9	0.59
15 wt% Ni HDP	10.2	4.1	0.22

The addition of (a theoretical) monolayer of La decreases the conversion with a factor 3.

From the catalytic testing it follows that Nickel catalyst can perform well in membrane reactors. Ni-PR was tested in a hydrogen selective (Pd) membrane reactor test during 3 weeks at 873 K. Stable methane conversion of 87% was obtained.

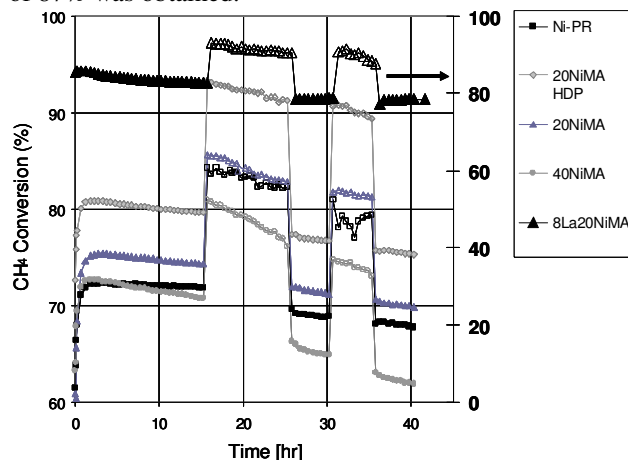


Figure 2. Methane steam reforming conversion with Ni catalysts at 873K during two interchanging conditions REF and (open symbols) MR.

The design of the process development unit features gas supply by means of a header arrangement using flanges and flexible connections, as derived in a design study for a full scale application. For the top connections flanges are used, for the bottom connection a gland

packing. This arrangement makes that reactor tubes can be individually removed and installed which eases catalyst charging without the risk of membrane damage. The reactor design is in essence equal to the full scale design, with the exception of heating which is done with an electric oven rather than with radiant burners to allow for easier operation.

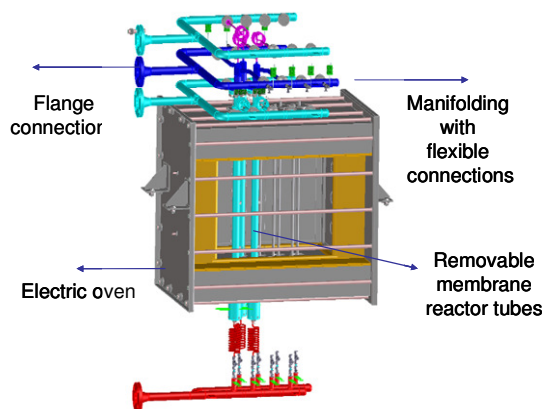


Figure 3. Reactor design for the 8-tube process development unit

The selected Ni-PR catalyst will be tested in a steam reformer experiment using 50 cm Pd/Al₂O₃ membranes in the 8-tube reactor, monitoring the overall hydrogen recovery and methane conversion as well as the gas composition of permeate and retentate of all individual tubes.

4 Conclusions

Membrane reformers can be used for power production with pre-combustion decarbonisation to meet CO₂ capture and sequestration targets. Tests of Ni and PM(Rh) based catalysts under a-typical membrane conditions favor the use of Ni in the SRMR process. Lanthanum stabilizes the Ni-MgAl₂O₄ steam reforming conversion at high H/C. This stabilization is at the cost of conversion activity. Ni-PR was tested during 3 weeks in a membrane reactor and stable methane conversion close to 90% was obtained. A process development unit has been design and constructed to assess the feasibility of the reactor concept on a multi-tube scale.

5 Acknowledgements

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