

# On the potential of Nickel Catalysts for Steam Reforming in Membrane Reactors

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## Introduction

Hydrogen membrane reactors are being studied for power production with pre-combustion decarbonisation. The membrane reactor produces hydrogen from natural gas at a low pressure and a steam and CO<sub>2</sub> rich stream at high pressure. Condensation of the steam leaves a concentrated CO<sub>2</sub> stream at high pressure for disposal. 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 equilibria of the reforming and shift reactions are shifted to higher conversions in the membrane reactor. Therefore, relatively low temperatures can be used. The need for multiple shift reaction stages is avoided, CO<sub>2</sub> scrubbing becomes much easier and the compression requirement for the captured CO<sub>2</sub> is minimized. Unlike conventional reforming, membrane reforming benefits from high operation pressure due to the increased H<sub>2</sub> partial pressure differential across the membrane, which acts as the driving force for hydrogen permeation. Membranes exist that selectively permeate hydrogen between 773 and 873 K with high flux. Higher temperatures should be avoided due to membrane or membrane-support 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, 2) resistant to deactivation under the hydrogen-lean conditions in separation-enhanced reformers. The present study aims at obtaining insight in the potential of Nickel-based catalysts for steam reforming of methane in membrane reactors (SRMR). A modeling study was carried out to compare catalyst activity of Ni and precious metal (PM) based catalysts together with hydrogen permeance in a palladium membrane reformer. Several ECN-made and pre-commercial or commercial catalysts based on Nickel and Rhodium have 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 high pressure.

## Materials and Methods

The system is modeled in a 1-D rectangular geometry, consisting of six coupled differential equations solved in Matlab. Hydrogen permeation is calculated from the eq. 1 below with  $n=1$  [1]. Kinetic expressions for Ni- and Rh-based catalysts are obtained in literature [2-5]. Stability testing of (commercial and ECN-made) Ni and Rh catalysts was conducted at 873 K. Gas compositions varied from 7.5% CH<sub>4</sub>, 22.5% H<sub>2</sub>O (H/C=10) to 1.3% CH<sub>4</sub>, 3% H<sub>2</sub>, 16% H<sub>2</sub>O, 0.14% CO, 11.8% CO<sub>2</sub> (H/C=2.5), in 5%Ar/N<sub>2</sub>, denoted reference condition, "REF" and membrane condition "MR" respectively. TEM, Chemisorption, FTIR 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 PdAg membrane at high pressure.

$$J_{H_2} = k_{mem} (p_{H_2, reformate} - p_{H_2, permeate}) \quad [\text{mol/m}^2\text{s}] \quad (1)$$

## Results and Discussion

From the modeling it follows that as the membrane permeance increased, all catalysts reach a point where they are no longer able to maintain chemical equilibrium. The kinetics of Xu (Nickel)[3] predicts an activity similar to that of Wei (Rhodium)[2]; both maintain equilibrium conversion at a representative high permeance of 10<sup>-6</sup> mol/m<sup>2</sup>.s.Pa. Figure 1 shows the immediate onset of enhanced deactivation upon exposure of commercial steam reforming catalyst (PM-SR) and Rhodium supported MgAl<sub>2</sub>O<sub>4</sub> (05RhMA) to the membrane feed composition. Such behavior is not observed with Ni based catalysts (see Figure 2). Ni was deposited onto MgAl<sub>2</sub>O<sub>4</sub> by impregnation (18 and 40NiMa) and Homogenous deposition precipitation (HDP). HDP synthesized catalysts showed less deactivation similar to the commercial Ni pre-reforming catalyst (Ni-PR). Preliminary characterization studies indicate that the deactivation may be caused by carbon formation with Ni while sintering may dominate the deactivation of PM-based catalysts. This first evaluation of Ni and PM based catalysts favors the use of Ni in SRMR. Ni-PR was used in a membrane reactor test during 3 weeks at 873 K for which a constant methane conversion close to 90% was obtained.

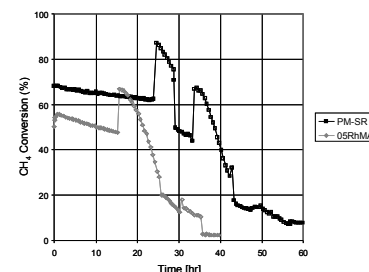


Figure 1. Methane steam reforming conversion with PM catalysts at 873K during two interchanging conditions REF and MR. (open marker symbols represents data collected while the catalyst was operated under MR conditions).

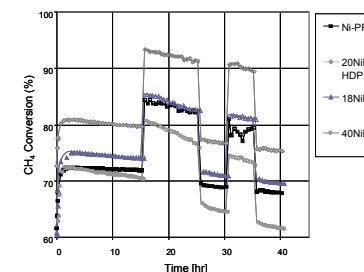


Figure 2. Methane steam reforming conversion with Ni catalysts at 873K during two interchanging conditions REF and MR. (open marker symbols represents data collected while the catalyst was operated under MR conditions).

## Significance

Membrane reformers may be used for power production with pre-combustion decarbonisation, which is an important technological approach to meet CO<sub>2</sub> capture and sequestration targets. The use of relative cheap Ni-catalysts in membrane reformers may boost the general acceptance of this pre-combustion CO<sub>2</sub> capture technology.

## References

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