

## Catalyst Deactivation in Autothermal Reforming of Natural Gas Feedstocks at Elevated Pressure

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### Introduction.

Autothermal reforming, Combined reforming and Gas Heated reforming [1] are leading technologies for the production of synthesis gas from natural gas for large scale methanol and gas to liquids plants. In each of these technologies, a hydrocarbon feedstock, or a partially reformed hydrocarbon feedstock is mixed with an oxidant via a burner, in a refractory lined vessel containing a combustion and mixing zone and a catalyst zone. This process step is called autothermal reforming or secondary reforming. In technology for the production of ammonia, air rather than oxygen is used as the oxidant. Combustion, steam reforming and the water gas shift reactions occur simultaneously in the flame region. Whilst peak flame temperatures of over 2500°C are predicted, the temperature of the gas entering the catalyst bed is typically 1250-1300°C, where further reforming reactions take place to achieve equilibrated gas temperatures of 900-1050°C. In this paper we investigate the deactivation of Ni/ Al<sub>2</sub>O<sub>3</sub> catalysts currently used in autothermal reformers and examine the performance of alternative catalyst systems at elevated pressure. During deactivation we observed sublimation of alumina from the catalyst as well as Ni volatilization. Rh/Al<sub>2</sub>O<sub>3</sub> catalysts offer better stability. We will describe the impact of various process feed parameters.

### Experimental

Alpha alumina honeycomb catalyst supports were prepared by extrusion and fired at 1500c. Sections of honeycombs 8 mm in length were dipped in metal salt solutions, dried and calcined at 475°C in air. Activity measurements were carried at atmospheric pressure in a 10mm recrystallised alumina tube mounted inside an electric furnace. A flow of 1.0 m<sup>3</sup>hr<sup>-1</sup> of nitrogen, 0.05 m<sup>3</sup>hr<sup>-1</sup> of desulphurised natural gas and 0.15 m<sup>3</sup>hr<sup>-1</sup> of de-ionised water vapor (steam: natural gas 3:1) was established over the catalyst and the exit the methane content of the dry gas determined using an IR analyzer.

The catalyst was installed in an ATR operating on an ammonia plant at 38 bar for periods of 20-100 days. Catalyst temperatures were calculated at different operating conditions using Johnson Matthey software.

### Results/Discussion

The percentage conversion of methane when the reaction temperature of the catalyst reached 1200°C in the laboratory ATR experiments is shown in Fig 1. The performance of the Ni catalyst fell rapidly with time, whilst the performance of the Rh catalyst was essentially constant. SEM analysis of the discharged catalyst confirmed that the surface of the Ni catalyst was denuded in Ni particles compared to the core of the honeycomb webs, and large Ni crystallites were detected downstream. In Table 1 the mass loss of alumina from catalysts operating in an ATR is reported. The implications of the observed behavior on the performance of operating plants are discussed. The results from the catalysts in the laboratory experiment and the operating plant are rationalized in terms of a mechanism involving the

formation of H<sub>2</sub>NiO<sub>2</sub> and AlH<sub>3</sub>O<sub>3</sub> in the vapor phase; the performance of alternative catalysts are predicted and further experimental observations will be reported.

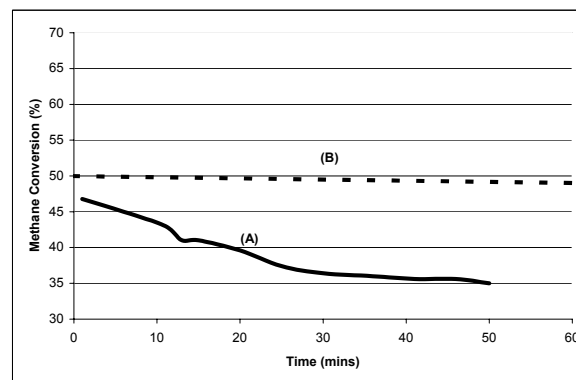


Figure 1 Catalyst Activity at 1200c during laboratory ATR experiments - (A) 8% Ni/ Al<sub>2</sub>O<sub>3</sub>, (B) 1% Rh/ Al<sub>2</sub>O<sub>3</sub>

Table 1 Rate of Alumina Loss from ATR Catalysts

Catalyst type	Loss rate g/m <sup>2</sup> day	Calculated Temperature (°C)
Alpha Al <sub>2</sub> O <sub>3</sub>	31.4	1245
Alpha Al <sub>2</sub> O <sub>3</sub>	16.9	1220
0.4% Rh/ Alpha Al <sub>2</sub> O <sub>3</sub>	9.5	1180
8% Ni/ Alpha Al <sub>2</sub> O <sub>3</sub>	7.0	1150

### Significance

Degradation and deactivation of catalysts in ATR results in pressure drop build-up in the ATR bed, fouling of downstream heat exchangers and carry-over of Ni, which is a potential poison for downstream catalysts. All have significant implications on operation of the plant. Understanding the mechanisms of the processes occurring allows new catalysts to be developed.

### References

1 Appl M. in " Ammonia Methanol Hydrogen Carbon Monoxide Modern Production Technologies" ( A. More Ed), CRU Publishing Ltd, 1997