

## Catalytic steam reforming of methane in presence of H<sub>2</sub>S on Ni-based SOFC anodes

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### Introduction

Methane steam reforming (MSR) is one of the most common methods used for H<sub>2</sub> production. The produced CO can also react with water via the water-gas-shift (WGS) reaction to further produce hydrogen. When a methane-steam mixture is supplied directly to the anode of a Solid Oxide Fuel Cell (SOFC), these reactions take place and the produced CO and H<sub>2</sub> are electrochemically converted for electricity production. A typical problem of the direct natural gas reforming process is the effect of sulphur impurities. Small concentrations of H<sub>2</sub>S are present in natural gas, thus during direct internal reforming of natural gas, the SOFC anode suffers from severe poisoning (1-2). This study investigates the sulphur tolerance during catalytic methane steam reforming using commercial and modified (by adding Au or Mo dopants) Ni/GDC powders.

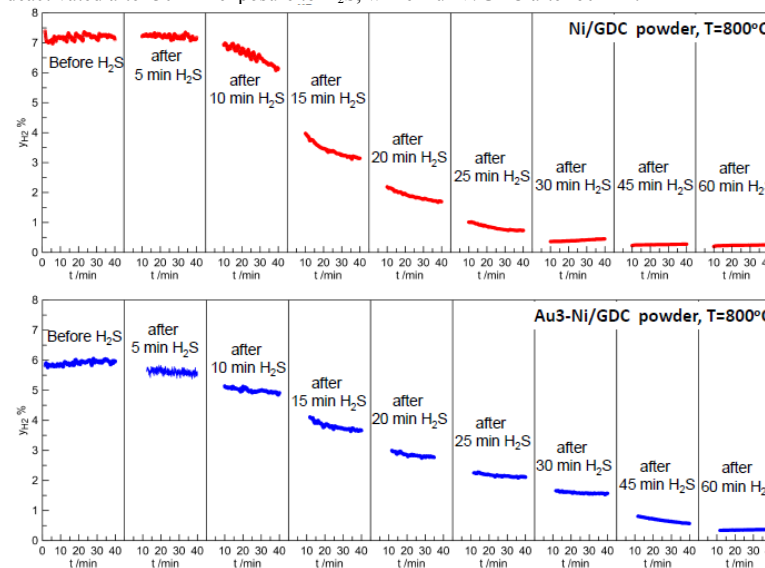
### Materials and Methods

We used commercial NiO/GDC (Marion Technologies, 65 wt% NiO) and modified powders prepared by adding Au and Mo via the Deposition-Precipitation method as described elsewhere (3). Catalyst quantities of 300 mg were introduced in a U-shaped quartz reactor with an inner diameter of 1.7 cm. Prior to the experiments, the catalysts were reduced under pure H<sub>2</sub> at 800°C for 150 min. The experiments took place at 800°C supplying H<sub>2</sub>S containing CH<sub>4</sub>-H<sub>2</sub>O gas mixtures with a total gas flow rate of 200 cc/min (He was used as vector gas). The products of the reaction were analyzed by using a Hiden Analytical HPR20 quadrupole mass spectrometer.

### Results and Discussion

The catalytic performances of the powders towards the MSR reaction in absence of H<sub>2</sub>S were stable for a period of 20 hours. TPO experiment carried out afterwards showed excellent resistance to C deposition under the specific reaction conditions. An example of sulphur tolerance investigation is given in **Figure 1** for the Ni/GDC catalyst (up) and Au 3wt%-Ni/GDC (down), where the H<sub>2</sub> concentration is plotted as a function of time. The steps followed during this experiment are: (a) Catalytic activity was measured for 40 min under 2%CH<sub>4</sub>-5%H<sub>2</sub>O, (b) 10 ppm of H<sub>2</sub>S were added to the reaction mixture for 5 min (during the poisoning step the catalytic activity was not followed by the mass spectrometer), (c) Post-poisoning catalytic activity was measured for 40 min under 2%CH<sub>4</sub>-5%H<sub>2</sub>O. The steps (b) and (c) were repeated for various cumulative times under H<sub>2</sub>S.

Full methane conversion was obtained with Ni/GDC prior to H<sub>2</sub>S poisoning, while for the Au-modified powder the initial conversion of methane was only 83%. However, the performance of Ni/GDC was deteriorated faster when H<sub>2</sub>S was added in the feed. Ni/GDC was fully deactivated after 30 min exposure to H<sub>2</sub>S, while Au-Ni/GDC after 60 min.



**Figure 1.** H<sub>2</sub> production during MSR in presence of H<sub>2</sub>S for Ni/GDC (up) and Au 3wt%-Ni/GDC catalysts (T=800°C, RM=2%CH<sub>4</sub>-5%H<sub>2</sub>O)

### Significance

H<sub>2</sub>S has a strong poisoning effect on the catalytic performances for methane steam reforming on all the investigated catalysts. The S-tolerance of Ni/GDC powders was improved by doping with Au. Post-mortem analysis (DRIFTS, XPS, XRD, TEM) were performed in order to elucidate the role of the dopant (Au or Mo).

### Acknowledgements

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### References

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