

# COKING IN STEAM REFORMING OF NATURAL GAS OVER RHODIUM: TOWARDS A MICROSCOPIC PICTURE

Claudia Essmann, Benjamin Schädel, Martin Seipenbusch, Thomas Schimmel, Olaf Deutschmann  
Karlsruhe Institute of Technology, Germany

## *Summary*

Coking of catalysts in conversion of hydrocarbon fuels in high temperature processes is a significant problem in industrial applications leading to deactivation of the catalyst. Here we present the first investigations of coke depositions during steam reforming of natural gas by the recently developed Oscillating Friction Microscopy. This mode is based on an AFM-technique and allows to measure friction differences of a sample surface with high resolution.

Due to the high resolution of the OFM it was possible to distinguish between coke depositions, alumina support and rhodium particles and to locate the initial carbon deposition in the process.

## *Keywords*

Steam Reforming, Coking, Rhodium, Natural Gas

## **Introduction**

In conversion of hydrocarbon fuels in high temperature processes coking is a significant process leading to deactivation of the catalyst [1]. The carbon deposition occurs by chemisorption or physisorption of hydrocarbon intermediates from the gas phase and decomposition on the catalyst surface, which may lead to formation of carbonaceous over layers and even encapsulation of the catalyst particles. In order to minimize and even avoid coking, the hydrocarbon conversion and carbon deposition have to be understood in detail. The final objective is the development of coking models than can be coupled with elementary step reaction mechanisms describing hydrocarbon conversion [2-5] to numerically simulate the reactor behavior at a wide range of varying operating conditions. To reach this goal, several new efforts have been started to investigate coking in hydrocarbon conversion in detail. One step in this direction consists in a better understanding of the roles and interaction of support and catalyst during carbon deposition. In this study we exemplarily focused on hydrocarbon conversion over rhodium, because Rh is a very active but expensive catalyst widely used in reduction of pollutant emissions, fuel reformers, and chemical reactors, for instance for the production of NO from ammonia, and hydrogen from fossil and alternative feed stocks.

## **Experimental**

For our investigations we used Rh/alumina coated monoliths and thin alumina discs covered with rhodium nano particles as a model catalyst. The catalysts were coked in flow reactors heated by a furnace for steam-reforming of the fuel. The following conditions were chosen:

- i) Undiluted steam reforming of natural gas “Nordsee H” (Airliquide) was carried at GHSV of 17.000 h<sup>-1</sup> and steam-to-carbon (S/C) ratio of unity.
- ii) Additionally, selective coking of the same catalyst was performed by pyrolysis of different hydrocarbons such as propylene and methane.

The product composition during the coking experiments was analyzed by mass spectroscopy, gas-chromatography, and Fourier-transformed infra-red spectroscopy (FT-IR). The coked catalysts were burned off by temperature programmed oxidation in a flow of 20 Vol% O<sub>2</sub> and 80 Vol% N<sub>2</sub>; maximum temperature was 700°C. The amount of deposited carbon was determined by analyzing the product gas flow concerning the concentration of CO<sub>2</sub> by FT-IR. The coked Rh/alumina discs were additionally analyzed by Atomic Forced Microscopy (AFM) as well as SEM and EDX.

## Results and Discussion

In steam reforming of natural gas, formation of coke on the catalyst was detected depending on S/C ratio and temperatures [5]. Three different deposition rates were identified depending on temperature. At temperatures above 800°C, gas-phase reactions become significant accelerating catalyst deactivation, which can be described by a recently published mechanism [6].

Microscopic measurements were carried out using thin  $\alpha$ -alumina discs covered with well-defined rhodium particles after steam reforming of natural gas over that disc. The samples were analyzed by the recently developed Oscillating Friction Microscopy [7], to determine the location of the initial carbon deposition by friction measurements. This mode is based on AFM-technique and allows to measure friction differences of a sample surface with high resolution.

Due to the high resolution of the OFM it was possible to distinguish between coke depositions, alumina support and rhodium particles and to locate the initial carbon deposition in the process.

The model catalyst was investigated by OFM before and after steam reforming of natural gas at 650°C, S/C of unity and a time on stream of 30 min. Before steam reforming the rhodium particles exhibited a higher friction contrast to the AFM-tip compared to the surrounding  $\alpha$ -alumina (OFM images not shown here).

After steam reforming, this friction contrast was inverted: Figure 1 shows an OFM image of the model catalyst after steam reforming. The friction contrast between the AFM-tip and the island structures is reduced compared to the surrounding material (Figures 1 and 2a).

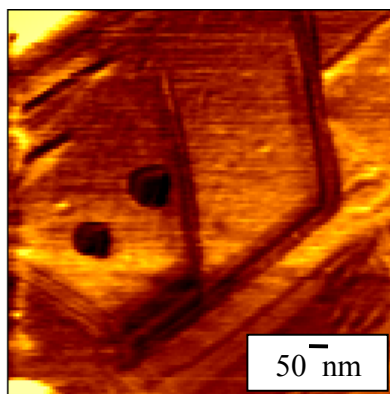


Figure 1: OFM image of the model catalyst (Rh-particles on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disc) after steam reforming of natural gas for 30 min, island structures show reduced friction contrast compared to the surrounding material

After multiple scanning of this sample the friction contrast is inverted again (Figure 2b). Now the particles show a higher friction contrast to the AFM-tip versus the alumina support again, the same friction contrast like before steam reforming. Additionally the diameter of the structures decreases during multiple scanning.

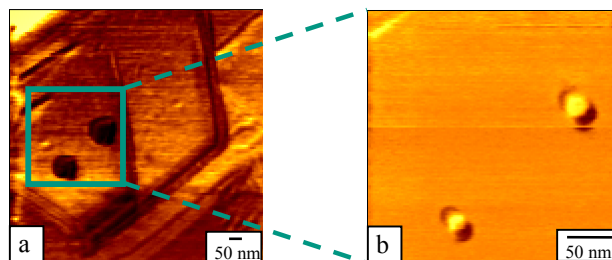


Figure 2: OFM images of Rh-particles on a  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disc after steam reforming of natural gas: a) friction contrast directly after steam reforming, b) friction contrast of the same sample after multiple scanning  $\rightarrow$  inversion of the friction, corresponding to removal of coke depositions by the AFM-tip

The OFM results obtained in this survey indicate that during the steam reforming process, for a period of time of 30 minutes, in low temperature regime at S/C of unity, coke was deposited upon and around the Rh particles. These coke depositions were removed during multiple scanning by the AFM-tip.

## References

- [1] Bartholomew, C. Mechanisms of Catalyst Deactivation, *Applied Catalysis A: General* **2001**, 212, 25.
- [2] Schwiedernoch, R.; Tischer, S.; Correa, C.; Deutschmann, O. *Chemical Engineering Science* **2003**, 58, 633.
- [3] Hartmann, M.; Kaltschmitt, T.; Deutschmann, O. *Catalysis Today* **2009**, 147, 204
- [4] Hartmann, M.; Maier, L.; Minh, H.D.; Deutschmann, O. *Combustion and Flame*, submitted
- [5] Schädel, B.T.; Deutschmann, O. *Studies in Surface Science and Catalysis* **2007**, 167, 207.
- [6] Li, A.; Deutschmann, O. *Chemical Engineering Science* **2007**, 62, 4976.
- [7] Pfrang, A.; Müller, M.; Schimmel, Th. *Photonik* **2008**, 2, 87.