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# ***In situ* characterization of catalysts and membranes in a microchannel under high-temperature water gas shift reaction conditions**

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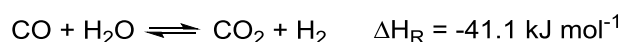
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**Abstract.** *Microreactor technology with high heat transfer in combination with stable catalysts is a very attractive approach for reactions involving major heat effects such as methane steam reforming and to some extent, also the high temperature water gas shift (WGS) reaction. For this study Rh/ceria catalysts and an ultrathin hydrogen selective membrane were characterized in situ in a microreactor specially designed for x-ray absorption spectroscopic measurements under WGS conditions. The results of these experiments can serve as a basis for further development of the catalysts and membranes.*

## **1. Introduction**

The worldwide growing demand for energy, increasing levels of harmful emissions and limited stocks of fossil fuels have led to increased efforts in the search for environmentally clean, sustainable and renewable energy sources and to a growing interest in efficient hydrogen production. Hydrogen, a feedstock used for diverse industrial applications, can be used as a clean fuel for fuel cells and is a key element for chemical storage of renewable energy. H<sub>2</sub> can be produced by the water gas shift (WGS) reaction:



Advantages of microreactor technology such as high surface to volume ratio and high heat and mass transfer coefficients have shown a high potential to intensify production efficiency [1]. Membrane reactors can shift the equilibrium limitation by continuously removing one of the reaction products from the reaction area [2]. Therefore, integration of H<sub>2</sub> selective membranes into microreactors will be highly beneficial for hydrogen production processes [3]. In order to gain a deeper understanding of such systems, both the catalysts and the membranes need to be characterized, preferentially under operating conditions [4, 5] and in a spatially resolved manner [6, 7]. For this purpose, a special microreactor, which allows to characterize catalysts and membranes under WGS conditions using X-ray absorption spectroscopy (XAS), was designed. The first results are presented here on a Rh/CeO<sub>2</sub> catalyst with an ultrathin hydrogen selective PdAg membrane.

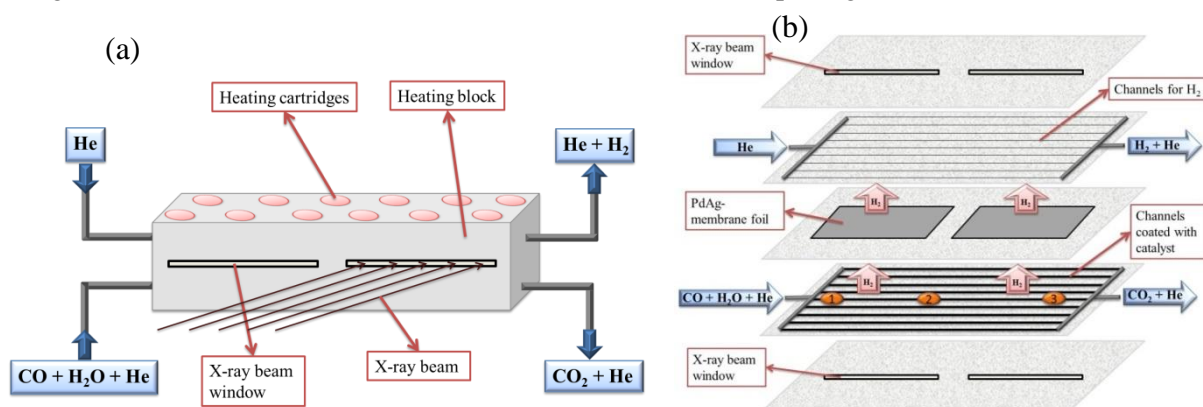


## 2. Experimental

10.5 wt.% Rh/ceria nanoparticles were prepared by flame spray pyrolysis (FSP) [8], using solutions of the corresponding initial precursor in xylene (VWR chemicals). Precursor solutions were prepared by dissolving specified amounts of metal acetylacetonate ( $\text{Rh}(\text{acac})_3$ , 99% (25% Rh), abcr GmBH & Co. KG), and cerium (III) 2-ethylhexanoate 49% 2-ethylhexanoic acid (12%Ce, Alfa Aesar). The precursor solutions (1 mol/L of the noble metal) were sprayed through a capillary into a methane/oxygen flame (750 mL/min  $\text{CH}_4$ , 1600 mL/min  $\text{O}_2$ ) at 5 mL/min using a syringe pump and dispersed by oxygen (5 L/min). A cylindrical steel vessel with a glass fiber filter (75 cm diameter, Whatman GF6) was placed above the flame. The produced particles were collected on this filter with aid of a vacuum pump using a recently established setup at KIT [8].

The new catalytic microreactor with hydrogen selective membranes designed for the present study is shown in Figure 1. Two channel plates, one for the catalytic bed and reactant gas flow and the other one for the produced  $\text{H}_2$ , are separated by a commercial hydrogen selective PdAg alloyed membrane. Heating cartridges in the reactor shell and gas connections allow XAS measurements at the Rh and Pd K-edge under reaction conditions. Each of the nine reactor channels is 0.1 cm wide and 20 cm long (total area 18 cm<sup>2</sup>). The channels were coated with 720 mg (total amount) of the catalyst mixed with 1 mol/L NaOH and dried overnight. The gasses were pre-mixed and the water was added using Control Evaporator Mixer (CEM) (not calibrated). Note that both the coating and the gas dosing system were preliminary and are presently improved.

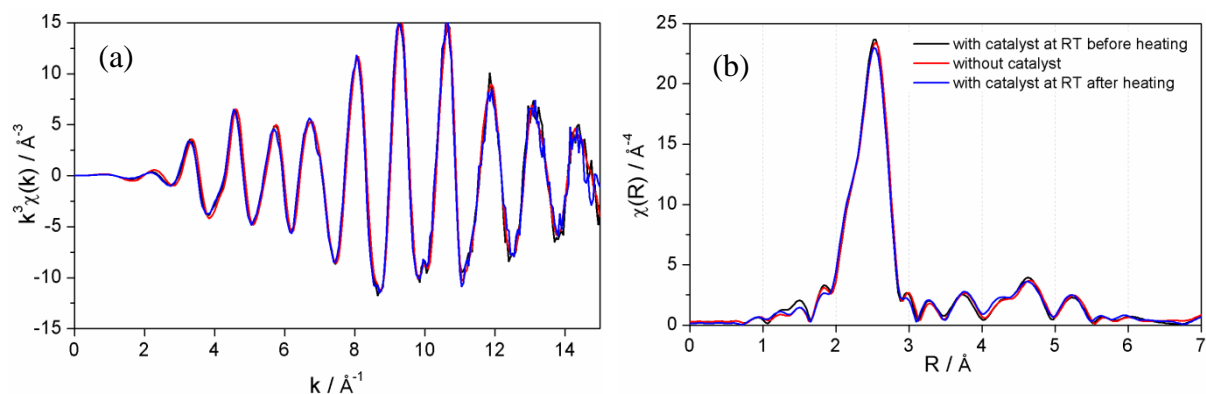
X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS, ca. 25 min/scan) spectra at the Rh K-edge (23220 eV) along the central reactor channel were recorded at the Swiss Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in transmission mode using a Si(111) double crystal monochromator (typical beam size 0.4 x 5 mm<sup>2</sup>). Two ionization chambers were used to measure the intensity of the incident and transmitted X-ray beam, and a third for energy calibration with a rhodium foil. XAS data analysis was conducted using the Athena and Artemis interfaces of the IFEFFIT software package (version 0.8.056) [9].



**Figure 1.** (a) Schematic drawing of the microreactor prototype designed by IMVT and ITCP/IKFT (KIT) and built at IMVT for *in situ* spectroscopic studies of catalysts and membranes under WGS conditions (b) Reactor window, channel plates for reactants and the produced hydrogen, and hydrogen selective PdAg membrane foil. The EXAFS analysis positions close to the reactor inlet, middle and reactor exit are indicated.

## 3. Results and Discussion

Figure 2 shows Pd K-edge EXAFS data of the PdAg foil in the microreactor at room temperature before the channels were coated, after coating with 10.5 wt.% Rh/CeO<sub>2</sub> and after applying WGS reaction conditions (gas mixture 8% CO, 32% H<sub>2</sub>O and 60% He, total flow 25 mL/min) and cooling down at position 1 close to the reactor inlet. According to EXAFS fitting results obtained from this data the distances between absorbing and neighbor atoms are 2.76 Å and 3.87 Å in the first and second shell and the numbers of nearest neighbor atoms are 12 and 6 in the first and second shell. Obviously, neither heating nor WGS reaction conditions have significant influence on the EXAFS data.

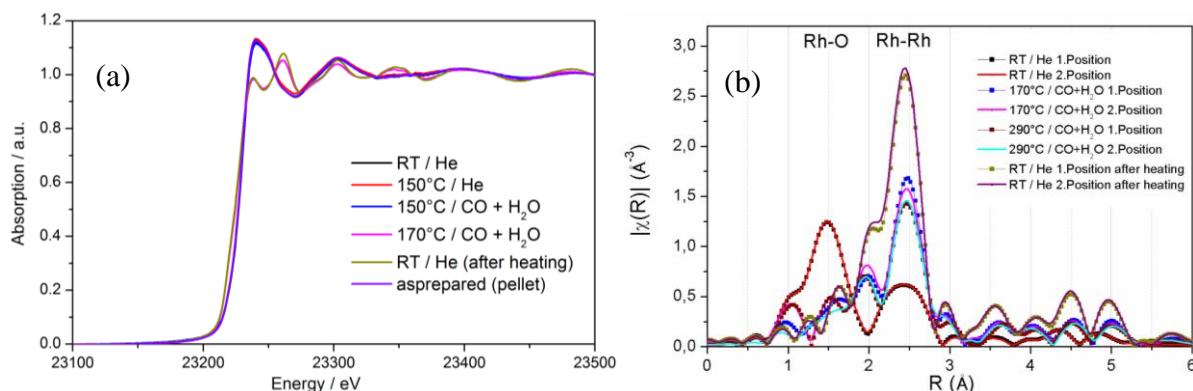


**Figure 2.** (a)  $k^3$ -weighted Pd K-edge EXAFS data (b) Fourier transformed data of the PdAg foil in the reactor without catalyst, with catalyst at room temperature and after WGS reaction at position 1.

Figure 3(a) shows Rh K edge XANES spectra of the catalyst recorded at the same position (close to the reactor inlet) at different temperatures and in different gas atmospheres: The first 2 spectra in Figure 3(a) were measured at room temperature and after heating to 150 °C in Helium. At this temperature, the gas feed was switched from He to a WGS reaction gas mixture (8% CO, 32% H<sub>2</sub>O and 60% He, total flow 25 mL/min). Up to this point, no changes in the XANES spectra occurred; the catalyst was obviously in an oxidized state. Afterwards, the reactor was heated further up to 170 °C. This leads to a decrease in white line intensity which indicates reduction of Rh oxide to metallic particles.

In Figure 3(b) Fourier transformed  $k^2$ -weighted EXAFS data of the catalyst recorded at two different positions (close to the reactor inlet and close to the middle) are compared. Data measured at a third position near the reactor exit show a high noise level at  $k > 5 \text{ \AA}^{-1}$  (probably due to sample inhomogeneities) and were therefore not included in the EXAFS analysis. The Fourier transformed EXAFS results in Figure 3(b) show that the Rh particles are in an oxidized state at room temperature, and were reduced at 170 °C under WGS reaction conditions (in accordance with the XANES results in Figure 3(a)) at both positions along the reactor channel. They stayed reduced after heating further up to 290 °C and finally cooling down to room temperature and switching the feed gas back to Helium. The similarity of the EXAFS data recorded at different positions under the same conditions (temperature, feed gas composition) indicates that the structure of the catalyst does not change along the channel. Therefore, further results are only shown for one position (close to the reactor inlet).

Structural parameters were derived from curve fitting of the  $k^3$ -weighted EXAFS data in R-space. The experimental data that aligned the model implicate two main shells, a Rh – O shell and a Rh – Rh shell. This model was used in a previous study that indicates rhodium (III) oxide (Rh<sub>2</sub>O<sub>3</sub>) at a distance of 2.01 Å for Rh – O and 2.69 Å for Rh – Rh [10]. The first peak is observed at about 2.03 Å, that is same as the Rh – O bond length in Rh<sub>2</sub>O<sub>3</sub>. The coordination number obtained for oxygen is 4.5 – 5 for this catalyst, Rh coordinates with 6 oxygen atoms in Rh<sub>2</sub>O<sub>3</sub>. According to Gayen et al. [11] the Rh ions may substitute such Ce<sup>4+</sup> sites in the surface layer of the CeO<sub>2</sub> crystallites, as surface Ce<sup>4+</sup> ions have only four O<sup>2-</sup> ions. The second backscattering peak about 2.70 Å can be attributed to Rh – Rh (second nearest neighbor distance in Rh<sub>2</sub>O<sub>3</sub> cf. ref [10]). After *in situ* reaction under WGS reaction conditions, the first shell Rh – Rh coordination number increases and no oxygen was observed anymore, indicating the formation of Rh metal particles. Rh exhibited an average coordination number of 9 in the reduced phase of the catalyst, indicating a particle size of 2 – 3 nm.



**Figure 3.** (a) X-ray absorption near edge structure data at the Rh K-edge of 10.5 wt.% Rh/CeO<sub>2</sub> in the microreactor under WGS reaction conditions, *ex situ* measurements of 10.5 wt.% Rh/CeO<sub>2</sub> as prepared (pellet). (b) k<sup>2</sup>-weighted Fourier transformed EXAFS data of the catalyst at RT under He, at 170 °C, and 290 °C under 8% CO, 32% H<sub>2</sub>O, 60% He and at RT after heating under He in microreactor at position 1 and position 2 (close to the reactor inlet and close to the middle).

#### 4. Conclusion

This feasibility study shows that the microreactor specially developed for this project is suitable for X-ray absorption spectroscopic characterization of Rh based WGS catalysts and hydrogen selective Pd alloy membranes under reaction conditions. At both absorption edges high quality XANES and EXAFS data (in a k-range up to 15 Å<sup>-1</sup>) could be acquired, and the reactor remained stable and gas tight at high temperature and in CO/H<sub>2</sub>O reaction atmosphere.

#### 5. Acknowledgement

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