

# Investigation of a Rh/CeO<sub>2</sub> Catalyst and a Pd Membrane in a Micro-Structured Membrane Reactor

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In the past decade hydrogen production, purification and separation technologies have become a globally significant subject of research for sustainable energy development. An essential process for hydrogen production and purification is the water gas shift (WGS) reaction. For such applications micro reactors are very attractive due to large surface area to volume ratios and high heat and/or mass transfer [1]. Since membrane reactors can shift the equilibrium limitation of chemical reactions by continuously removing one of the reaction products from the reaction area [2], integration of H<sub>2</sub> selective membranes into micro reactors can be highly beneficial for hydrogen production processes. For this study, a novel micro-structured membrane reactor was specially designed for *in situ* spectroscopic characterization of catalysts and membranes under WGS conditions.

The membrane reactor consists of two channel plates, one for the catalytic bed and reactant gas flow (retentate side) and the other one for the produced H<sub>2</sub> (permeate side), separated by a commercial hydrogen selective PdAg alloyed membrane [3]. Heating cartridges in the reactor shell and gas connections allow X-ray absorption spectroscopy (XAS) measurements under reaction conditions. The reactor channels were coated with 100 mg of a flame made 10.5 wt.% Rh/CeO<sub>2</sub> catalyst. X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Rh and Pd K-edge were performed at the BM25A beamline at ESRF (Grenoble) using fluorescence detection mode.

Rh K-edge XAS spectra of the catalyst were recorded along the central retentate channel in He and under WGS reaction conditions. Comparison of spectra recorded at RT and at 350 °C in He showed that the Rh species underwent a transition from an oxidized state to a reduced state. After re-oxidation in 5% O<sub>2</sub>/He at 350 °C the catalyst was exposed to WGS reaction gas mixtures (steam/carbon ratios of 1.5/1 and 1/1.5). XANES spectra recorded at the reactor inlet and outlet indicated that under both WGS reaction conditions the catalyst was reduced to the same extent. More detailed information about the atomic environment of the absorbing Rh atoms under different reaction conditions was obtained from fitting the corresponding EXAFS data in R-space. Comparison of the k<sup>2</sup>-weighted EXAFS data at both positions unraveled the same catalyst structure (oxidation state) along the channel. Since with this set-up H<sub>2</sub> extraction could be monitored *in situ* during the synchrotron based XAS measurements, Pd K-edge spectra were also recorded under the same WGS reaction conditions as during the Rh K-edge experiments. The Pd species did not show any change under various WGS reaction conditions. This implies that the Pd membrane foil shows a high degree of stability.

In conclusion, a new *in situ* micro membrane reactor was designed that allows simultaneous XAS characterization of the catalyst or membrane and gas analysis on the retentate

and permeate side. In the future more advanced materials can be studied for further development of membranes.

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