Experiment Report Form

	Experiment title: **Structure and Activity of Flame Made Ceria Supported Rh Water Gas Shift Catalysts**	Experiment number: CH/4199
Beamline: BM01B (SNBL)	**Date of experiment**: from: 12.11.14 to: 17.11.14	**Date of report**: 25.02.15
Shifts: 13	**Local contact(s)**: Herman Emerich	*Received at ESRF:*

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1. Introduction

Hydrogen is a feedstock used for diverse industrial applications, but also a clean fuel for fuel cells and a key element for chemical storage of renewable energy. The water gas shift (WGS) reaction is important for Hydrogen production and purification and an important step in many industrial processes. For this project, ceria supported noble metal catalysts for high temperature WGS reactions were prepared by flame spray pyrolysis (FSP) and characterized by *in situ* X-ray absorption spectroscopy (XAS). Noble metals supported on ceria (CeO_2) catalysts exhibit high activity, also due to the redox properties of ceria. FSP is considered a promising method for preparation of catalysts with highly dispersed active centers and high stability in a single step.

2. Experimental

During this beamtime several catalysts were investigated. Furthermore, a WGS microreactor prototype was tested. This report is focused on a 3.1 wt.% Rh/CeO_2 catalyst.

Catalyst Preparation: Rh/CeO_2 nanoparticles were prepared by FSP at Karlsruhe Institute of Technology (KIT) using solutions of the corresponding initial precursor in xylene (VWR chemicals). Precursor solutions were prepared by dissolving specified amounts of metal acetylacetonate ($Rh(acac)_3$,

26.36%, Chempur Strem chemicals) and cerium (III) 2-ethylhexanoate 49% 2-ethylhexanoic acid (12%Ce, Strem chemicals). The concentration of the noble metal precursor was 1 mol/L. The precursor solutions were fed through a capillary into a methane/oxygen flame (750 mL/min CH_4, 1600 mL/min O_2) at 5 mL/min using a syringe pump (World Precision Instruments) and dispersed by oxygen (5 L/min). The produced particles were collected on a glass fiber filter.

Ex situ and in situ X-Ray Absorption Spectroscopy (XAS): X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at the Rh K-edge (23220 eV) were performed at the Swiss Norwegian Beamline (SNBL) at ESRF in transmission mode using a Si(111) double crystal monochromator. Higher harmonics were rejected by a gold-coated mirror. Two ionization chambers were used to measure the intensity of the incident and transmitted X-ray beam, and a third ionization chamber was used for energy calibration with a Rhodium foil as a standard.

For temperature programmed reduction (TPR) with H_2 a 100-200 μm sieve fraction of catalyst powder was fixed in a quartz capillary between two quartz wool plugs. During heating from room temperature to 450 °C at 5 °C/min with a gas blower (FMB Oxford) [1] the sample was reduced in 5% H_2/He (flow 50 mL/min), and XANES spectra were recorded in rapid continuously scanning mode (Quick- EXAFS [2]). Under steady state conditions before and after reduction long EXAFS spectra were acquired in step scanning mode. Another fraction of catalyst powder was reduced in 10% H_2/N_2 (total flow 1 L/min) during heating up to 450 °C at 5 °C/min. This reduced catalyst powder and the catalyst after preparation (as prepared) were pressed into pellets with cellulose and measured *ex situ*. Additionally, EXAFS spectra of Rh_2O_3 and metallic Rh foil were recorded as reference spectra.

For XAS data analysis (energy calibration, normalization, background-subtraction, linear combination analysis (LCA) in the energy range from 20 eV below to 50 eV above the Rh-K edge) the Athena and Artemis interfaces of the IFEFFIT software package (version 0.8.056, [3]) were used.

3. Results and Discussion

Figure 1(a) shows Rh K-edge XANES spectra recorded *in situ* during the activation of the 3.1 wt.% Rh/CeO_2 catalyst (TPR in 5% H_2/He). The relative concentrations of oxidized and reduced species were determined by LCA of the XANES data using the first and last spectrum of the TPR series as reference spectra. The results in Figure 1(b) show a steep increase in the reduction rate at 50 °C and indicate that at ca. 100 °C almost 70% of the Rh atoms are in a reduced state. Above this temperature no significant changes in the XANES spectra (Figure 1(a)) occur, although the linear combination fitting results (Figure 1(b)) suggest that reduction still continues at a low rate. Compared to catalysts prepared by conventional methods the reduction temperature of this flame made Rh/CeO_2 catalyst is lower [4, 5].
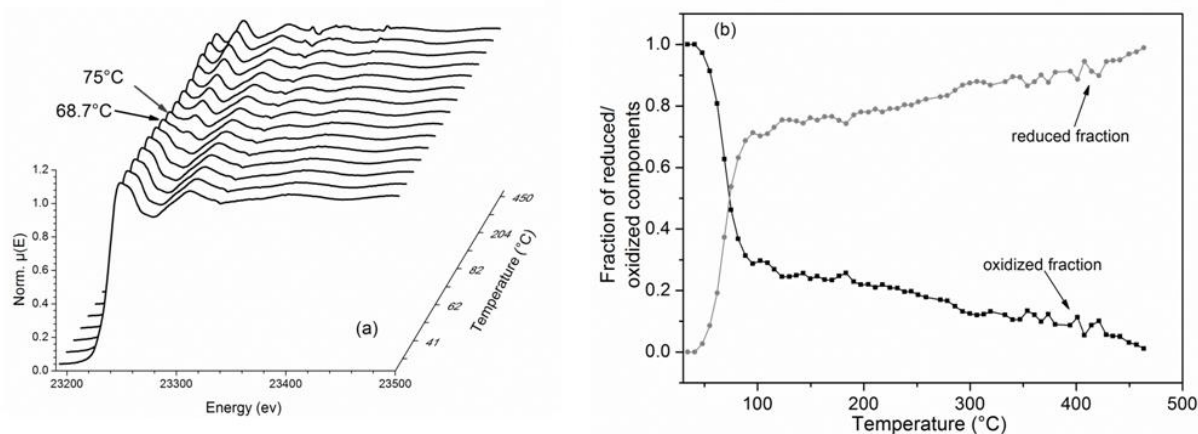

Figure 1: (a) Rh K-edge XANES spectra of the 3.1 wt.% Rh/CeO_2 catalyst recorded during temperature programmed reduction (TPR), (b) changes in relative concentrations of oxidized and reduced Rh species during TPR obtained from linear combination fitting

Fourier transformed k^2–weighted EXAFS data of as prepared, *ex situ* and *in situ* reduced Rh/CeO$_2$ catalysts are shown in Figure 2, and quantitative information obtained from fitting this data is presented in Table 1. The coordination numbers for the Rh foil, the Rh precursor, Rh$_2$O$_3$ and the first shell of the as prepared catalyst were set (fixed values from database), while all other parameters were fitted.

The Fourier transformed EXAFS data of the Rh precursor (Rhodium (III) acetylacetonate), Rhodium (III) oxide (Rh$_2$O$_3$), Rh foil and as prepared Rh/CeO$_2$ (after FSP, without treatment) are shown in Figure 2 (a). In both Rh$_2$O$_3$ and the precursor Rh is hexacoordinated by oxygen atoms in the first coordination shell. However, for the precursor a significantly lower value was obtained from EXAFS fitting for the Debye-Waller-Factor σ^2, representing the mean square deviation of atomic distance, which is related to the atomic disorder. This could be due to the rigid bidentate chelate structure of the precursor. Further coordination shells in the precursor data could not be fitted due to the low amplitude of the corresponding peaks. The Rh$_2$O$_3$ data could be fitted with one and four Rh atoms in the second and third coordination shells, at 2.69 Å and 3.06 Å respectively, and the Rh foil with 12 Rh atoms in the first (2.68 Å), and 6 in the second shell (3.79 Å).

Table 1: Structural parameters for the atomic environment around the Rh absorber atom obtained from refined EXAFS data.

Sample	Shell	Atom	N	r [Å]	$\sigma^2 \cdot 10^{-3}$ [Å^2]
Rh precursor	1st	O	6	1.99	2.5±0.1
Rh foil	1st	Rh	12	2.68	3.7±2.6
	2nd	Rh	6	3.79	6.0±1.1
Rh$_2$O$_3$	1st	O	6	2.01	4.9±0.7
	2nd	Rh	1	2.69	12.3±4.2
	3rd	Rh	4	3.06	9.9±0.1
Rh/CeO$_2$ as prepared	1st	O	6	2.03	3.8±1.0
	2nd	Rh	2.7±1.0	2.72	5.5±2.4
Rh/CeO$_2$ *ex situ* reduced	1st	O	4.2±0.3	2.03	3.8±1.0
	2nd	Rh	3.9±0.7	2.68	4.7±1.1
Rh/CeO$_2$ *in situ* reduced	1st	Rh	8.7±0.7	2.67	5.5±0.4

N: number of neighboring atoms at distance r (±0.01 Å), σ^2: mean-square disorder in the atomic distance (Debye-Waller factor)
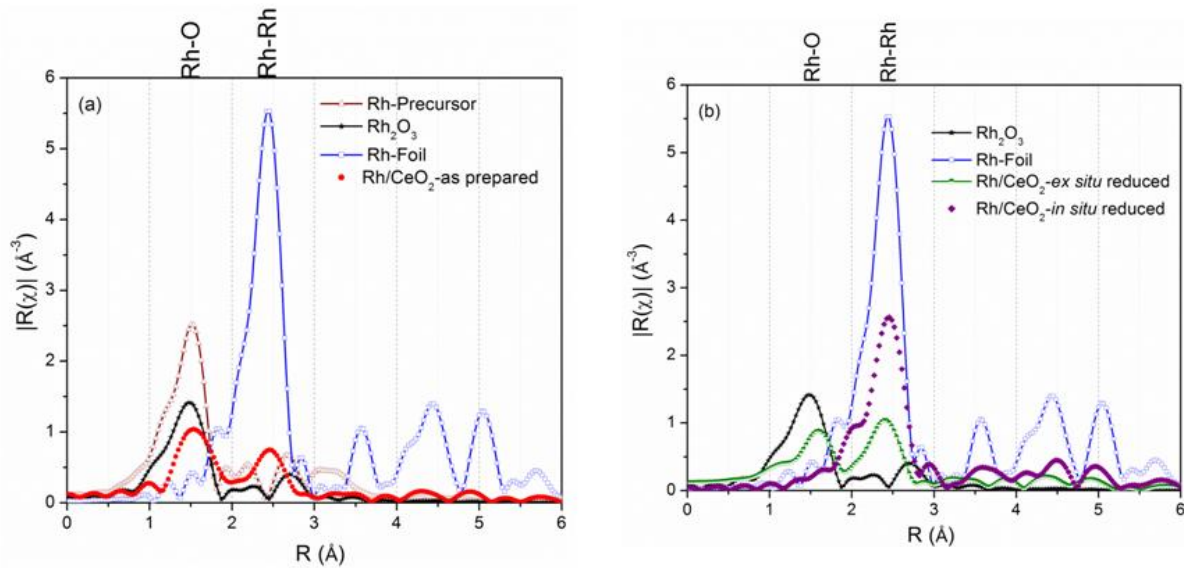

Figure 2: k^2-weighted Fourier transformed EXAFS data (a) comparison of Rh precursor, rhodium oxide, metallic Rh foil and Rh/CeO$_2$ catalysts after preparation (b) comparison of rhodium oxide, metallic Rh foil and Rh/CeO$_2$ catalysts after reduction with and without exposure to air

The first shell (between 1 and 2 Å in Figure 2(a)) in the as prepared Rh/CeO$_2$ can be attributed to oxygen atoms. According to Table 1, the values for the Rh-O bond length (and Debye-Waller-Factor) obtained

from the as prepared Rh/CeO_2 catalyst are higher than those for the precursor. This suggests a shift towards oxide-like Rh-O bonds and thus indicates that during preparation the precursor was at least partly incorporated into CeO_2, resulting in a rhodium oxide-like structure.

The bond length obtained for the second shell in the as prepared sample (2.72 Å) could in principle correspond to either metallic or oxide backscattering (cf bond lengths Table 1). The white line intensity and edge energy in the spectra of the as prepared Rh/CeO_2 catalyst suggest that in this sample oxidized rhodium is the dominating Rh species. On the other hand, the oscillations obtained from a backward Fourier transform of the second shell for the as prepared Rh/CeO_2 sample and the metallic Rh foil, are out of phase, which may be due to the significant shift in bond lengths (cf Table 1). Therefore, the structure of Rh in the as prepared Rh/CeO_2 sample can be described as a mixture of oxide-like and metallic clusters, which are smaller and more disordered than those found after reduction of the catalyst. Moreover, the low reduction temperature suggests that the Rh species are rather located on the surface of the CeO_2 particles. This indicates that the abovementioned second shell can be attributed to Rh in a metallic cluster. In the Fourier transformed EXAFS data (Figure 2(a)) the second shell peak is weak due to a shielding effect of oxygen.

The Fourier transformed EXAFS data in Figure 2(b) show that the *ex situ* Rh/CeO_2 catalyst was reoxidized in air, thus confirming the previous conclusion that the Rh oxide-like clusters are located on the surface of CeO_2. However, this sample was only partly reoxidized as shown by the lower number of oxygen neighbors in the first shell and higher number of Rh neighbors in the second shell compared to the as prepared sample. The distance between the absorbing and the neighboring atoms in both samples is comparable. On the other hand, *in situ* reduction produced metallic clusters with 8.7±0.7 Rh atoms in the first coordination shell. The cluster size estimated from this coordination number using a method developed by Jentys [6] is 1.7 nm. This shows that flame spray pyrolysis is well-suited for the production of small Rh particles as catalytically active centers.

4.   References

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