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Experiment Report Form

	Experiment title: Local and electronic structure changes of active sites on Au/CeO2 catalysts during the CO oxidation: Insights into the origin of the high activity and of the deactivation	**Experiment number:** CH 4095
Beamline: BM26A	**Date of experiment:** from: 11 Apr 2014 to: 15 Apr 2014	**Date of report:** 19.09.2017 *Received at ESRF:*
Shifts: 18	**Local contact(s):** Dr. Alessandro Longo	

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Report:

The proposal was related to investigate a correlation between the deactivation of Au/CeO_2 powder catalysts during the CO oxidation reaction after oxidative or reductive pretreaments and their electronic structure . In order analyze this, we have performed XANES and EXAFS measurements after such pretreatment with in O_2, CO_2, and H_2 (each 10% in N_2 at 400°C, 30 min, atmospheric pressure) and during the subsequent CO oxidation reaction (1% O_2 , 1% CO, balance N_2 at 80°C, atmospheric pressure). All investigations have been performed in our home-made flow cell under in operando conditions.

In Figure 1, we show XANES spectra of Au/CeO_2 powder catalysts (i) before (fresh) and (ii) directly after calcination in different atmospheres together with two references (metallic Au foil and oxidic Au_2O_3 powder) are added for comparison.

The data clearly display the different electronic states (based on XANES data) before and after the different pre-treatment procedures, ranging from a strongly oxidized state (fresh catalyst) via a slightly oxidized state after an oxidative treatment in O_2 to a metallic state after reductive treatment in H_2. The treatment in CO_2 results in an electronic state close to the metallic state with only a small contribution of the Au L_3 white line which is indicative for the presence of oxidized Au species. Please note that the spectrum of the Au_2O_3 powder has not been corrected for saturation effects up to now, which might explaining the somehow smaller white line as compared to the “fresh” catalyst (before treatment).

Only the oxidatively pre-treated sample (calcination in 10% O_2 /N_2) shows a moderate peak at the position of the white line,whereas this feature is not visible in a reductive atmosphere (H_2). The experimental data recorded at the Au L_3 edge were, for a more detailed analysis, compared to reference XANES data available in the literature for Au being present in different oxidation states [1].

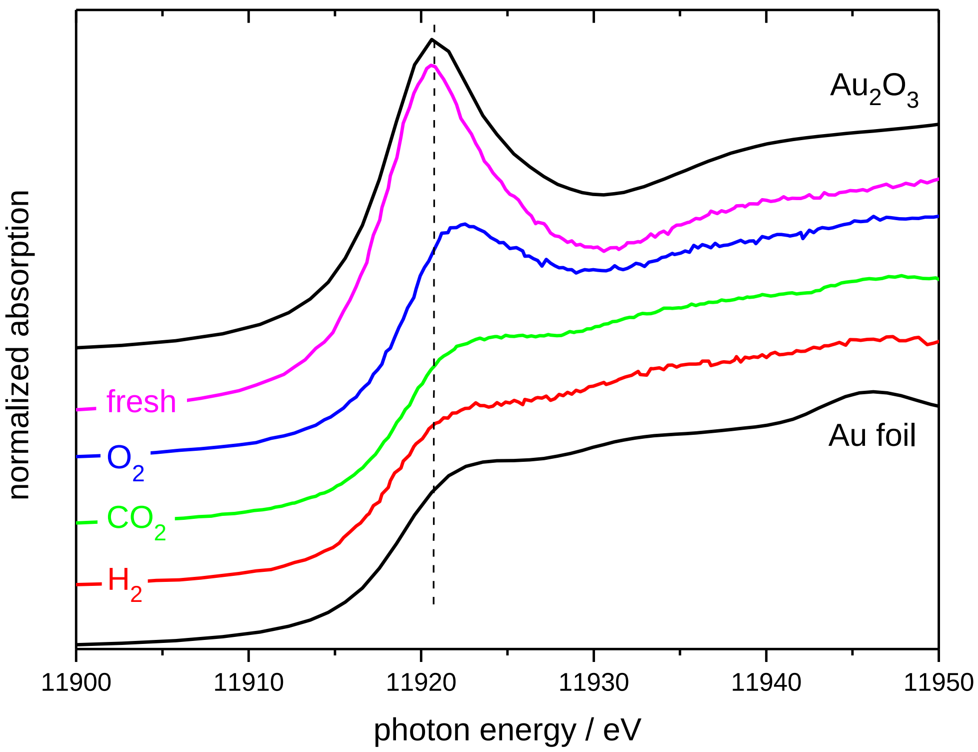

Fig. 1: normalized XAS spectra recorded at the Au L_3 edge: black curves: Au reference (metal foil and Au_2O_3 powder, lila: fresh Au/CeO_2 catalyst; blue, green and red curves: after pretreatments in 10 % O_2, CO_2, or H_2, respectively; for details, see text.

EXAFS analysis of data recorded at the Au L_3 edge confirm the results obtained from the XANES data evaluation: After H_2 treatment, there are solely Au-Au scattering events (coordination number CN: 4.7, R=2.83Å), while for the O_2 treated sample there are mainly Au-Au, but also a small amount of Au-O scattering events (Au-Au: CN: 6.3, R=2.84Å, and Au-O: CN: 0.5, R=1.96Å). The Au-Au bond lengths correspond to very small Au particles with diameters of 12-16Å [2]. The rather unstructured XANES data of the differently pretreated Au/CeO_2 samples (compared to Au reference) also hint at the presence of small particles, as it is seen by the EXAFS analysis of the data.

During / after CO oxidation, the XANES data show similar characteristics for all pre-treatments: the Au nanoparticles of all samples are in a metallic state after reaction, independent of the pre-treatment. Even for the oxidatively pretreated Au /CeO2 particles, the change to a metallic state happens on a short time scale after only a few minutes during time on stream. The size of the particles increases during time on stream: for the oxidative treatment, EXAFS data show an increase of the (mean) particle size to about 20-25 Å as indicated by the higher coordination number (CN: ~7.5-8), cf. [2]. For the sample after reductive pre-treatment (H_2), the EXAFS data recorded during time on stream lead to the presence of smaller particle when compared to the O_2 treated sample.

References:

1. A. Pantelouris et al., J. Am. Chem. Soc. 117 (1995) 11749.
2. J.T. Miller et al., Catal. 240 (2006) 222