

# Nature of the active Au species during the low-temperature water-gas shift reaction on Au/CeO<sub>2</sub> catalysts

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**1. Background:** Purification of hydrogen-rich feed gases by the removal of residual CO is achieved most commonly using a combination of several catalytic processes including the preferential CO oxidation (PROX), the selective methanation of CO (SelMeth), and the water gas shift (WGS) reaction [1]. Among these, the WGS reaction is important as an initial step to decrease the level of CO from about 10 %, after steam reforming, down to < 1 %, where either PROX or SelMeth can be used to further reduce the CO concentration in the feed gas to levels necessary for the application in low-temperature fuel cells ( $\leq 10$  ppm). Commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts are the traditional catalysts for the WGS reaction, but these are not very attractive in fuel cell applications due to their sensitivity to temperature excursions, air exposure (pyrophoric), and water condensation during reactor shutdown [2]. Gold nanoparticles (NPs) supported on reducible oxides, such as ceria and titania, were found to be highly active catalysts for different catalytic processes already at rather low temperatures, including the (preferential) CO oxidation and the WGS reaction. Focusing on the WGS reaction, a key question refers to the nature of the active gold species present on the surface of highly active Au/CeO<sub>2</sub> catalysts under working conditions. Some groups claimed that gold in ionic form is the predominant species responsible for the activity of the Au/CeO<sub>2</sub> catalysts [3,4], whereas other groups suggested that metallic Au NPs represent the active species during the WGS reaction [5-7]. In this aspect, we showed that a Au<sup>3+</sup> enriched Au/CeO<sub>2</sub> sample, generated by leaching metallic Au from the catalyst with cyanide, has a significantly lower activity compared to the reductively pre-treated leached/unleached catalysts, indicating that metallic Au NPs are predominantly the active species [6]. These conclusions, however, were based on results from *ex-situ* XPS measurements. To unravel the nature of gold species responsible for the high activity of this catalytic system under reaction conditions and to clarify the above mentioned contradictions, *in-situ* XAS measurements were conducted during activation as well as during reaction.

**2. Experimental:** A 5.6 wt.% Au/CeO<sub>2</sub> catalyst prepared by the deposition precipitation method was studied by *in-situ* XAS measurements. The measurements were carried out in a flow reactor especially designed for such type of investigation. The high catalytic activity of the Au/CeO<sub>2</sub> catalyst used in this study for the WGS reaction has already been demonstrated in previous studies in our group [8]. Firstly, the fresh Au/CeO<sub>2</sub> catalyst was heated up to 200°C in a flow of N<sub>2</sub> and was kept at this temperature for 30 minutes. Afterwards the catalyst was pre-treated, also at 200°C, by exposure to a reducing atmosphere (10% H<sub>2</sub>/N<sub>2</sub>) for 45 min. Finally, the catalyst was cooled down to reaction temperature (180°C) in a flow of N<sub>2</sub>. The WGS reaction was performed at 180°C in an idealized gas mixture (1% CO, 2% H<sub>2</sub>O, rest N<sub>2</sub>). During all these individual steps (heating, pre-treatment, reaction) the oxidation state of the Au species was determined by recording *in-situ* XAS spectra of the Au L<sub>3</sub>-edge. The X-ray absorption spectra were collected in fluorescence mode using PIPS (Passivated Implanted Planar silicon) diode detector.

**3. Results:** To obtain the oxidation state of the Au species from the XANES absorption spectra, these were compared to the spectra of both metallic Au foil and Au<sub>2</sub>O<sub>3</sub> powder; the respective spectra are shown in Fig. 1. Comparison of the XANES spectra of the fresh Au/CeO<sub>2</sub> catalyst recorded in air (a) with the spectra of Au<sub>2</sub>O<sub>3</sub> standard (top) clearly shows the oxidic nature (by the presence of a pronounced peak at the absorption edge) of the Au NPs on the catalyst before the activation process. The next spectrum (b) was recorded after heating the catalyst in N<sub>2</sub> to 200°C. It can be seen that the characteristic peak for oxidic Au species has almost vanished, indicating a (partial) reduction of the Au NPs already by heat treatment in an inert atmosphere. Spectrum (c)

was recorded during the reduction process with a flow of 10% H<sub>2</sub>/N<sub>2</sub> at 200°C. On a first glance it looks similar to spectra (b), with no peak characteristic for oxidic Au species. The inflection point (IP) of the adsorption edge, however, is shifted by ~3 eV to higher photon energies, from 11916 eV to 11919 eV. For Au, such a shift reflects a further reduction of the Au NPs. This is also confirmed by the comparison with the Au<sup>0</sup> reference (metallic Au foil, spectrum at the bottom in Fig. 1), with an almost identical position of the IP (11919 eV). For guidance, the IP of the Au<sup>0</sup> reference is also drawn as dashed line in Fig. 1. Note that the XAS peak visible around 11948 eV in Au<sup>0</sup> might strongly be suppressed in Au nanoparticles [8]. From these results it is proposed that the oxidic Au<sup>3+</sup> species present on the fresh catalyst are first reduced to Au<sup>δ+</sup> species during the heating process, due to thermal decomposition, and further reduced to metallic Au<sup>0</sup> species in the presence of hydrogen. Finally, spectrum (d) was recorded during the reaction, after it was running for 4.5h. It is nearly identical to the spectrum recorded during the reductive pre-treatment (c), demonstrating that the Au NPs on the Au/CeO<sub>2</sub> catalyst stay completely reduced also during the reaction / under reaction conditions, and that no re-oxidation occurs due to the presence of H<sub>2</sub>O. Moreover, the comparison of the shape of the absorption edge and the energetic position of the inflection point with experimental data reported by Pantelouris supports the assignment of these spectra to metallic Au species. [9]

Based on *ex-situ* XPS studies before and after reaction over leached Au/CeO<sub>2</sub> catalysts we have already proposed that metallic gold species contribute predominantly to the WGS activity on Au/CeO<sub>2</sub> catalysts. This is confirmed by the results presented herein, which showed mainly metallic gold species after reductive pre-treatment as well as during the reaction. The presence of small amounts of Au<sup>3+</sup> species at the surface of the Au NPs, which have been detected by previous *ex-situ* XPS measurements, however, can not be excluded, but are below the detection limit. [6]

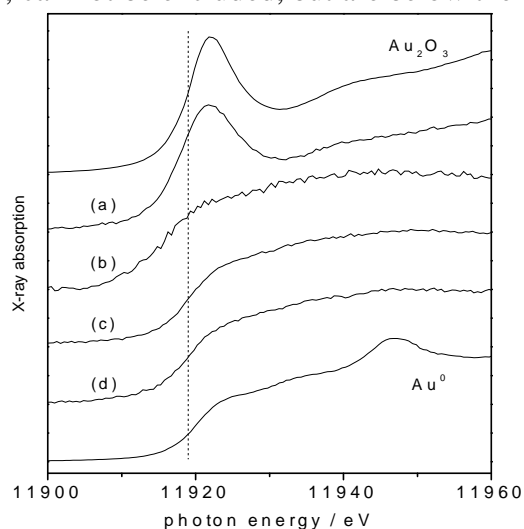


Fig.1 XANES spectra of the fresh Au/CeO<sub>2</sub> catalyst (a), during heat-treatment in N<sub>2</sub> at 200°C (b), during reduction in 10% H<sub>2</sub>/N<sub>2</sub> at 200°C (c), and during the WGS reaction at 180°C (1% CO, 2% H<sub>2</sub>O, rest N<sub>2</sub>) (d), reference spectra for oxidic Au (Au<sub>2</sub>O<sub>3</sub>, top), and metallic Au (Au foil, bottom).

## References

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