

# **In-situ EXAFS/XANES study on Au/TiO<sub>2</sub> in CO adsorption and CO oxidation: presence of anionic Au species and oxygen vacancies in the support**

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With the first experimental results on the unexpected catalytic activity in the CO oxidation reaction of small Au nanoparticles (NPs) (less than 5 nm in diameter) supported on disperse TiO<sub>2</sub>, a new field of fundamental research was opened with a focus on the physical / chemical / electronic origin of catalysis by Au NPs on metal oxide (MeO<sub>x</sub>) supports and the respective reaction pathway. The huge variety of supported Au/MeO<sub>x</sub> catalysts produced by many different chemical routines and groups led to a high number of, often contradictory, findings, which are until now widely discussed in the literature. In this report, we will focus on one the presence of negatively charged Au NPs in CO adsorption, which is closely related to discussion of the presence of positively or negatively charged Au NPs on TiO<sub>2</sub> supports during the CO oxidation reaction and their importance regarding this catalytic reaction. Although there is nowadays a certain agreement that Au NPs with a size of about 3 nm are metallic and do not exhibit any significant charge in the presence of CO and O<sub>2</sub>, the situation is clearly different in pure CO. Recently, we could demonstrate that the interaction of CO with a planar Au/TiO<sub>2</sub> model catalyst at room temperature and pressures >2 kPa mbar results in the formation of negatively charged Au<sup>δ-</sup> species, which were identified by a characteristic shift of the C-O stretch frequency from ~2110 cm<sup>-1</sup> to ~2070 cm<sup>-1</sup> [1]. IR results obtained from Au NPs on disperse titania supports (P25) showed CO related IR bands can only be understood by assuming negatively charged Au particles. Comparable observations were made for highly dispersed Au/TiO<sub>2</sub> [2] and Au/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts. Besides IR spectroscopy, X-ray absorption spectroscopy (XAS) is one of the few methods that allows to investigate the size/coordination (EXAFS) and the electronic state (XANES) of nano-sized metal NPs in the presence of gases close to atmospheric pressure conditions.

The experiments related to this proposal were performed at the beamline X (HASYLAB) by recording XA spectra in transmission at the Au L<sub>3</sub> absorption edge of disperse Au/TiO<sub>2</sub> catalysts, both close to the absorption edge (XANES) and beyond this edge in the EXAFS mode. Since XANES is sensitive to charge deposited on metal NPs by showing different kinds of variation (energy shift, intensity difference, additional peaks) at the absorption edge, we used this method to investigate our catalyst regarding the presence of negatively charged Au NPs in CO. The experiments themselves were carried out in a home-made flow cell designed for in-situ measurements, details are described elsewhere. Before CO exposure, the catalysts were pretreated by different treatments (e.g., calcination in O<sub>2</sub>, heating in H<sub>2</sub>) which were tested before in our labs with DRIFTS measurements in CO.

As an example, we choose a set of XANES spectra from Au/TiO<sub>2</sub> where the catalysts were directly exposed to CO without further treatments (calcination in O<sub>2</sub>, exposure to H<sub>2</sub>). The topmost dataset in Fig. 1 represents the native Au/TiO<sub>2</sub> catalysts after Au loading, three spectra below the catalysts after exposure to CO (duration: see inset), the lowest spectrum (thick orange line) was recorded from a gold foil and represents metallic Au<sup>0</sup>. (for comparison, this spectrum has been added as a reference (thin solid line in orange) to other spectra during CO exposure (15% CO in N<sub>2</sub>). It is well known that Au is present as an oxidized Au species directly after loading. The XANES data clearly show a pronounced peak in front of the main Au L<sub>3</sub> absorption edge, which results from excitations into the partially unfilled Au 5d states for oxidized Au species. For XANES data recorded from metallic Au, this peak is still present, but much smaller in intensity. The main feature is related from excitations into the Au continuum states. Compared to the oxidized species, the inflection point (excitations into continuum states) for the metallic species shifts by 5 eV to lower photon energy, whereas the peak representing excitations into the Au 5d states is nearly constant in energy. The spectra during CO exposure look, on the first glance, quite similar to the Au reference spectra obtained from metallic Au (cf. thin solid lines). However, there are significant differences which support, after a more detailed analysis, the presence of negatively charged Au NPs. First of all, the

spectra show a steeper increasing at the Au L<sub>3</sub> edge and a higher intensity at the first maximum at the Au absorption edge. A more quantitative analysis with respect to the analysis performed by Pantelouris [3] results in a small shift of the inflection point (representing excitations into continuum states) to smaller photon energies and a suppression of excitations from Au 5d states (together with a small shift to lower photon energies). Both facts hint to the presence of negatively charged Au species as outlined in the manuscript from Pantelouris et al. [3] Depending on the magnitude of the negatively charged Au species, these authors found, that the intensity of the peak resulting from the Au 5d states decreases strongly from positively charged Au species (pronounced peak located at around 11920 eV) via metallic Au (small intensity, now at 11919.2 eV) to a very small intensity for Rb<sub>3</sub>AuO (peak at 11918 eV) before it completely vanishes for CsAu species (neg. charged Au). Along with the decrease in intensity of the Au 5d peak, the inflection point of the excitation into Au continuum states shifts from 11926 eV (Au<sup>3+</sup>) via 11921 eV (Au<sup>0</sup>) to 11918.9 - 11919.1 eV for all negatively charged Au species.

This behaviour is reflected in our data, the fits show a strong decrease in intensity (and a small energy shift) of the Au 5d related peak during CO exposure accompanied with an energy shift of the inflection point to energies below 11920 eV. For the spectra during CO exposure, the quantitative analysis has to be improved into order to narrow the error bars, but the spectra clearly show a line shape that is related to the presence of negatively charged Au species.

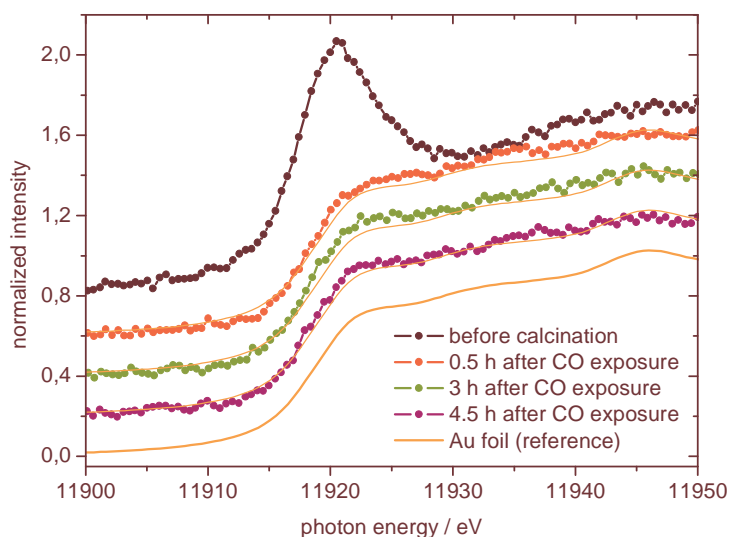


Figure 1: XANES spectra of Au/TiO<sub>2</sub> after calcination (top) and after subsequent exposure to CO. The lowest line and the thin solid lines represent the reference Au<sup>0</sup> spectra obtained from Au foil. Note that the spectra have been shifted upwards for better visibility.

## References

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