# Bridging the Material Gap between Model and Practical Au/$TiO_x$ Catalysts Using X-ray Spectroscopies

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## Introduction

The physical basis for the low-temperature activity of supported Au catalysts remains controversial [1-3]. The oxide support influences both morphology and electronic structure of the Au particles [4,5], and hence their catalytic activity [6,7]. We have probed the electronic structure of a highly active Au/$TiO_2$ powder catalyst *in situ* under reaction conditions by synchrotron X-ray spectroscopies (XAFS, XPS) and found that the electronic structure of the Au component is dynamically responding to environmental conditions.

## Methods and Materials

The Au/$TiO_2$ catalyst with low gold loading was prepared by deposition-precipitation [8] from $HAuCl_4$. CO-oxidation turnover frequencies per Au atom at 353 K (space velocities of 20,000 $h^{-1}$) were approximately 1 $s^{-1}$. After characterisation by standard techniques (XRD, TEM, XPS) and reaction rate measurements we measured *in situ* fluorescence-yield XAFS (X1, Hasylab, Germany; 9.2, SRS Daresbury, UK) at the Au L-edge at 1 atm, and by *in situ* synchrotron XPS (U49/2-PGM1, BESSY, Germany) at 1 mbar [9].

## Results and Discussion

XANES and EXAFS indicate that only very small, metallic Au particles are catalytically active towards low-temperature CO oxidation. For example, as catalytic activity increased at elevated temperatures, near-edge features of *in situ* XA spectra associated with lower-coordinated Au species became more pronounced (fig. 1). *In situ* XP spectra of the Au/$TiO_2$ catalyst additionally revealed reversible electronic structure changes as a function of the composition of the gaseous environment (fig. 2) [9]. We found that CO and $O_2$ appear to cooperatively influence the electronic structure of Au and likely also its morphology. Higher oxidation activity may thus be associated with the formation of raft-like Au particles (schematic fig. 2) An influence on adjacent sites of the $TiO_2$ support was not detectable by Ti photoemission. CO and $O_2$ have been found to disrupt and re-disperse Au clusters on planar model systems [4, 10]. The influence of the gas-phase environment on the XA and XP spectra of the Au particles is reminiscent of these observations and suggests that the origins of activity in planar model systems and practical Au catalysts might be similar. The results underline the dynamic nature of supported Au, and the importance of *in situ* experimentation for the elucidation of gas/surface reaction mechanisms.

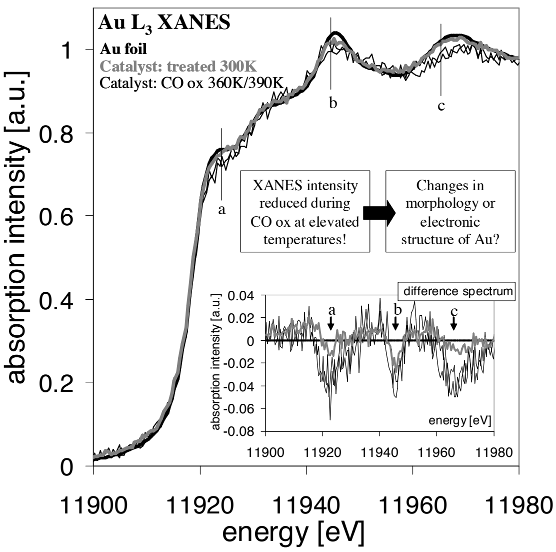


Fig. 1 *In-situ* XA near-edge spectra of the 0.5 wt% Au/$TiO_2$ catalyst exhibit reduced intensities at points a,b, and c associated with low-coorinated Au species.

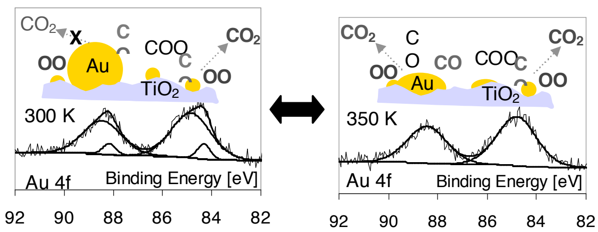


Fig. 2 Features in the broad synchrotron X-ray PE spectra of Au are characteristic of disordered Au species and change reversibly as a function of temperature during CO oxidation.[9]

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