



In situ X-ray photoelectron spectroscopy on supported powder and model Au/TiO₂ catalysts – influence of the material gap

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Oxide supported Au catalysts with finely dispersed small Au nanoparticles have attracted considerable interest in recent decades because of their high activity for numerous reaction, e.g., the low-temperature CO oxidation. The question of oxygen activation and the role of ionic Au^{δ+} or Au⁰ species in the reaction mechanism are still controversially discussed [1-4]. To investigate the influence of the reaction atmosphere on the support and on the chemical /electronic state of the Au surface atoms in more detail, we performed a comparative *in-situ* high pressure XPS study on the interaction of different reactive gases, O₂, CO and CO/O₂ mixtures, with dispersed Au/TiO₂ catalysts and planar Au/TiO₂(110) model catalysts. These two catalyst systems differ by their density of surface defects. The dispersed catalysts consist of a highly defective support material, while the model catalysts, on the other hand, are supported on almost ideal surfaces of fully oxidized and atomically smooth TiO₂(110) substrates. The two catalysts used in this study have comparable Au particle sizes (~3 nm₀) and they were pre-conditioned in the same way prior to the exposure, with only metallic Au⁰ species being detectable after conditioning [5,6].

First, the Au/TiO₂(110) model catalyst was exposed to 0.3 mbar O₂ at increasing temperatures up to 400°C, in order to study the extent of surface oxidation of the Au particles. All Au 4f spectra (fig. 1, left panel) exhibit the same characteristics, almost symmetric peak shapes and a constant peak width (FWHM 0.8 eV), indicating that the spectra are dominated by a single Au species. A small shift of about 0.5 eV to higher BEs in the Au 4f signal, from RT to 400°C, remaining after calibration to a constant Ti 2p peak BE (459.2 eV), indicates that both temperature as well as the ambient atmosphere (vacuum or O₂ at 400°C) affect the

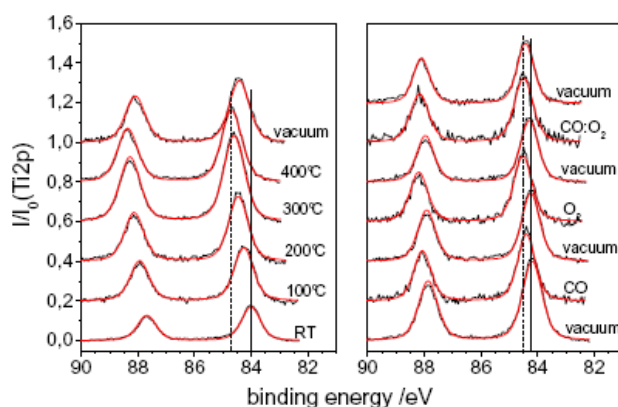


Fig. 1: *Left panel:* Sequence of Au 4f spectra recorded on a Au/TiO₂ model catalyst in vacuum at RT, in 0.3 mbar O₂ at temperatures up to 400°C and in vacuum at 400°C; *right panel:* Sequence of Au 4f spectra recorded at 80°C on a Au/TiO₂ model catalyst in vacuum, 0.3 mbar CO, vacuum, 0.3 mbar O₂, vacuum, 0.3 mbar O₂/CO (1:1) and vacuum.

electronic/chemical state of the Au particles. The origin of this shift is not yet clear, but based on the constant peak shape it can not be related to surface oxide formation, which should show up as a high BE shoulder on the Au 4f peak (larger FWHM and different peak shape). Additionally, during the whole experiment the O 1s/Ti 2p intensity ratio remains constant, indicating that oxygen adsorption on the well ordered TiO₂(110) support is insignificant. In the second part of this experiment (fig. 1, right panel), we stepwise approached the situation during the CO oxidation reaction by exposing the model catalyst first

to CO (0.3 mbar), then to O₂ (0.3 mbar), and finally to a 1:1 O₂/CO gas mixture (0.3 mbar total pressure) at 80°C, which represents a typical reaction temperature [7]. In between the measurements, the reaction cell was pumped off, and additional XPS measurements were performed under vacuum conditions to identify permanent changes of the model catalyst surface after the different stages of this sequence. Analogously to the data in the first sequence (O₂ exposure up to 400°C, cf. fig. 1, left panel), the Au 4f peak shapes and FWHMs remain constant, indicating that also under these conditions significant surface oxidation can be ruled out.

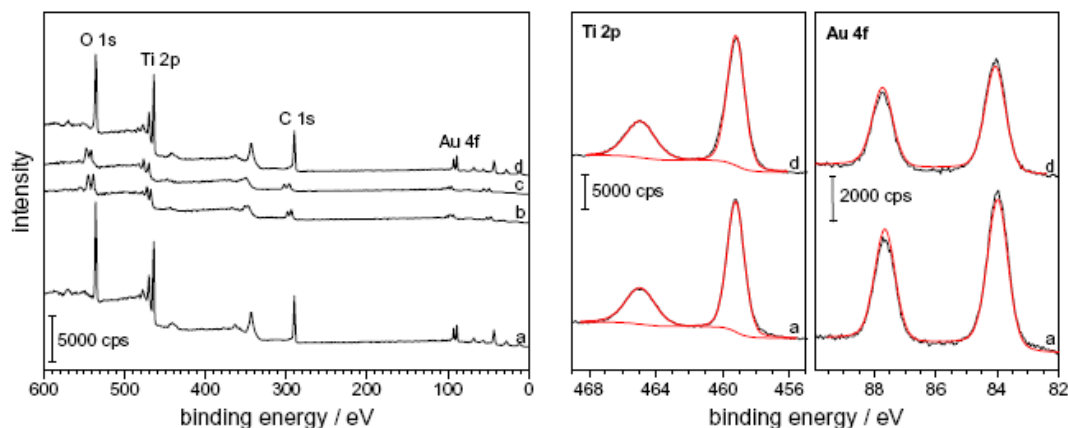


Fig. 2: XP spectra of the Au/TiO₂ powder catalyst at 80°C recorded (a) in vacuum after conditioning in O₂, (b and c) during O₂ exposure after 2 and 9 min, respectively, as well as (d) after O₂ exposure in vacuum. Left part: survey scans ($h\nu = 850$ eV), right part: Ti 2p ($h\nu = 619$ eV) and Au 4f ($h\nu = 234$ eV) peaks recorded at a higher resolution.

For the powder catalyst, exposure to 0.3 mbar O₂ leads to a shift in the BE of all peaks compared to the measurements under vacuum conditions due to sample charging (fig. 2). The energy shift is inhomogeneous and results in broadened peaks of each signal. The charging effects could be removed by quantitative comparison with a C 1s contamination peak, which is assumed to be constant in shape and BE under the present conditions. (It should be noted that for O₂ exposure at 400°C an additional charging was not observed.) The resulting Au 4f and Ti 2p spectra closely resemble those obtained before O₂ exposure, indicating that also on the dispersed catalyst significant Au oxidation can be ruled. In addition, the O 1s/Ti 2p intensity ratio increases during O₂ exposure, indicative of oxygen adsorption. This increase in intensity ratio is reversible, i.e., the adsorbed oxygen can be pumped off again (fig. 2d); the oxygen must be weakly adsorbed, most likely in a molecular state.

In a series of experiments displayed in fig. 3, we investigated the effect of exposing a fresh Au/TiO₂ powder catalyst to a CO/O₂ mixture under reaction conditions (1:1 mixture, 80°C, 0.3 mbar total pressure). During exposure, a significant shift in the BEs occurred (fig. 3b-d), increasing with the reaction time. After subsequent evacuation, the energy shift is reduced but not completely removed. All signals are broadened again and show the typical features of inhomogeneous charging. Removal of the charging effects (see above) leads to Au 4f and Ti 2p peaks very similar to those obtained before exposure to the

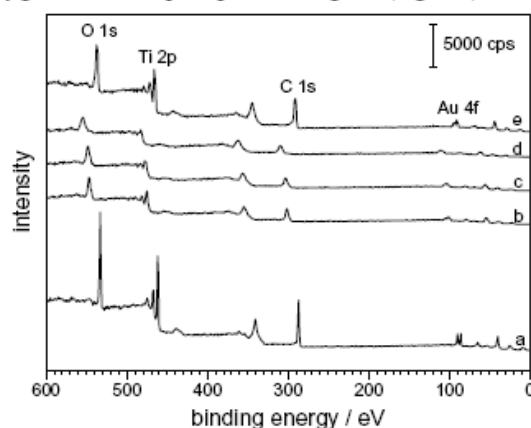


Fig. 3: XP survey spectra of the Au/TiO₂ powder catalyst recorded (a) in vacuum after heating in O₂, during CO oxidation at 80°C after (b) 4 min, (c) 9 min and (d) 45 min as well as (e) in vacuum.

reaction gas mixture (fig. 3a). Hence, the metallic character of the Au particles is maintained also under reaction conditions.

For both systems, the model catalyst as well as the dispersed catalyst, we found no detectable Au oxide formation upon exposure to O₂, CO or to a CO:O₂ (1:1) reaction mixture at 80°C. This result apparently contrasts recent findings in an *in-situ* high pressure XPS data on a dispersed Au/TiO₂ catalyst [4], where the authors reported an increasing intensity of a 0.9 eV up-shifted component, which they related to a final-state shifted signal (small Au particles). The discrepancy to our present results is almost certainly caused by the different morphology of the catalysts, due to the different pre-treatment. The unconditioned Au/TiO₂ catalyst (pre-treatment: drying in air at 50 - 80°C) contained a high content of very small (and possibly not completely reduced) Au clusters/particles, while the catalysts used in the present study were characterized by 3 nm diameter, metallic Au particles. Obviously, these larger particles are significantly more stable against oxide formation or adsorbate induced changes in the electronic structure of the Au particles.

Finally, the significant amount of adsorbed oxygen on the powder catalyst during O₂ exposure at 80°C may point to weakly bound, molecular oxygen species adsorbed on the support, most likely on defect sites, but more definite measurements are necessary for a clear assignment. In total, the experiments clearly demonstrate the potential of comparative *in-situ* studies on model systems and realistic catalysts of well defined structural characteristics and under comparable conditions.

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