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Dynamic Electronic Structure of a Au/TiO$_2$ Catalyst under Reaction Conditions

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Considerable research effort has aimed to elucidate the physical basis for the low-temperature activity of supported Au catalysts.[1−3] Investigations of model systems have shown that the support material influences both the morphology and the electronic structure of the Au particles[4,5] and hence the catalytic activity.[6,7] We have now probed the electronic structure of a practical Au/TiO$_2$ catalyst in situ by synchrotron X-ray photoelectron spectroscopy (XPS). A strong Au4f binding energy (BE) shift indicates the presence of small Au clusters electronically different from bulk Au. Their electronic structure is dynamic; at elevated temperatures it differs significantly from what would be observed by ex situ XPS.

The powder catalyst, 0.5 wt % Au on TiO$_2$ (P25, Degussa), was prepared by deposition−precipitation[8] with dilute NH$_3$ and HAuCl$_4$. It was dried in air at 320 K and not treated further. Plug-flow reactor studies established that a few minutes of conditioning in the reaction mixture (1% CO, 20% O$_2$) at 350 K led to stable active catalysts. Very high CO turnover frequencies around 1 s^{-1} per Au atom (not per Au *surface* atom, as particle sizes were too small to determine morphologies—see later) were achieved at 350 K and space velocities of 20 000 h^{-1}. Deactivation was insignificant even after 50 h on stream. During XPS, O$_2$ and CO were dosed at pressures of 0.1 mbar. The catalytic CO oxidation rate was monitored through the CO$_2$ partial pressure in the vacuum chamber.

All Au4f XP spectra (Figure 1) were strongly broadened, with fwhms around 2 eV, suggesting a distribution of Au species with varying electronic structure. The spectra were also asymmetric, with two components to which we shall refer as Au1 and Au2. The BE and fwhm of the Au1 component is close to that of the Au4f emission from Au foil (Figure 1). In contrast, the component Au2 has a fwhm of 1.9 eV (±0.1 eV) and is BE-shifted by +0.9 eV (±0.1 eV) relative to Au1. A linear relationship between BE and valency in Au compounds[9] may suggest that Au2 represents an oxidation state close to Au$^+$.[10] However, BE shifts similar to that of Au2 have previously been reported for small metallic clusters**,** in which reduced screening of the core hole decreases the kinetic energy of the final-state electron.[4,11,12] BE shifts of +0.7 eV (clusters with 1−6 Au atoms),[13] +0.8 eV (20% of a monolayer, approximately 2 nm Au particles)[14] and +1.1 eV[15] have been observed in planar Au/TiO$_2$(110) model catalysts. TEM images of our powder catalyst confirm that most of the Au is “invisible”, i.e., present in particles below the resolution limit (∼1 nm) of the TEM instrument. The Au2 component thus likely represents Au in aggregates with very small (i.e., subnanometer) size parameters.

To condition the catalyst, it was initially heated to 350 K (spectrum 2, also note the higher reaction rate at 300 K after conditioning), and XPS data was taken at different temperatures and gas compositions (Figure 1). The Au1 component was entirely absent in CO + O$_2$ at 350 K (spectra 2, 4) but reappeared after cooling to 300 K (spectra 3, 5). At 300 K it was evident regardless of gas composition, that is, not only under CO-oxidation conditions but also in pure CO and O$_2$ (spectra 6, 7). Irrespective of temperature and gas composition, the Au1 emission was always BE-shifted by +0.3 (±0.1) eV relative to Au foil (Figure 1).

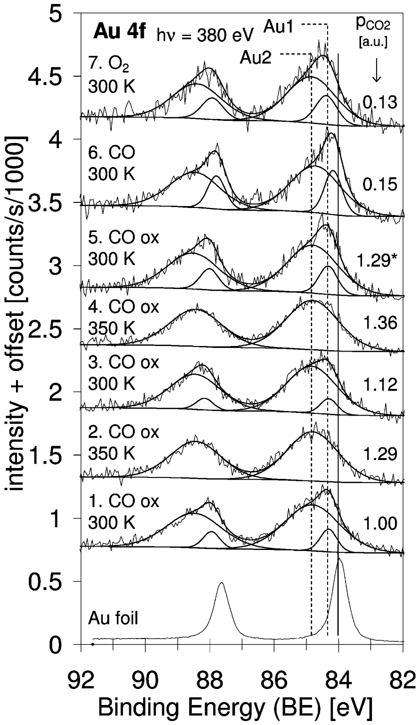

Figure 1. Synchrotron XP Au 4f spectra of the 0.5 wt % Au/TiO$_2$ catalyst. Intensities in 2−7 were scaled to the intensity of Au2 in spectrum 1. BEs are referenced to Ti 3p. On the right the relative partial pressures of CO$_2$ are noted to indicate catalytic reaction rates. The CO$_2$ pressures in 6 and 7 stem from the residual gas in the vacuum chamber. (∗)The CO$_2$ pressure associated with 5 may be an overestimate because of slowly increasing CO and O$_2$ pressures (cf. Supporting Information.)

CO and O$_2$ are known to chemically modify TiO$_2$ surfaces[16] and may cause some of the variations in the Au4f emission. Partially reduced Ti sites on TiO$_2$ surfaces stabilize small Au particles[17,18] and can also be involved in surface reactions.[19−21] Reactive adsorption near the Au/TiO$_2$ interface could influence the Au particles, but no significant chemical changes of the TiO$_2$ support were evident in the Ti2p or the Ti3p emission from the catalyst, despite tuning the X-ray energy to optimum surface sensitivity. Such chemical inertness of the TiO$_2$ substrate may be due to OH-

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termination, which appears plausible given the aqueous acid/base treatments during the catalyst preparation. However, it should also be noted that changes at the Au/TiO_2 interface of our catalyst are difficult to detect by Ti photoemission because Au covers at best 2% of the total TiO_2 surface area.

The Au1/Au2 intensity variations may alternatively be due to the interaction of Au with adsorbed molecules and/or reaction intermediates. Electronegative adsorbates are expected to withdraw electron density from the Au particles, resulting in an initial-state increase of the BE of the Au core electrons, and possibly also in reduced screening (and thus an additional BE increase) of the photoinduced core hole in the final state. CO adsorbs on Au much more strongly[22] than O_2.[23−25] Adsorption energies on Au single crystals[22,23] suggest that any Au in the catalyst should be predominantly covered with CO under the conditions during which spectra 2−6 were acquired. In fact, adsorbed CO on Au(110) is known to cause a broad Au4f feature with a positive BE shift of +0.5 eV relative to metallic Au.[26,27] It is unlikely, however, that the Au1/Au2 intensity redistributions in Figure 1 are related to the presence of adsorbed CO only, as they are most pronounced at higher temperatures, where the concentration of adsorbed CO should actually be lower. Note also that the Au1 feature is strongest, and its BE shift lowest, in a CO-only environment at 300 K (spectrum 6)—just where the coverage with CO must be highest. After subsequent exposure to O_2 (spectrum 7) the spectrum resembled those in the CO/O_2 mixture (spectra 3, 5). Clearly the Au particles are also influenced by interaction with O_2.

Interestingly, the Au1 emission also reappears upon cooling in CO/O_2, during which any adsorbed electron-withdrawing species should be retained at the surface. A recent XPS study of Au clusters on TiO_2(110)[4] reported that CO mediated the redispersion of Au, resulting in Au4f intensity changes and BE-shifts reminiscent of those observed here. Mobile Au species were also identified by STM during exposure of Au clusters on FeO(111) to CO/O_2 mixtures.[28] Evidence has been reported that the reduction of oxidized Au with CO is accompanied by a mobile gas-phase Au species.[29] The reversible changes in the Au1/Au2 ratio may thus reflect a dynamic equilibrium between Au in a more bulklike metallic state (Au1) and a phase (Au2) formed by heating, by adsorbed intermediates, or through a transport reaction. Possibly, only morphological changes of the particles take place. Note in this context that the Au2 emission was dominant throughout, suggesting the absence of Au sintering in the temperature range studied here. Coalescence to bulklike, bigger Au particles appears negligible. Any Au transport would thus be short-range relative to the average distance between individual particles.

In conclusion, the in situ XPS results underline the dynamic nature of supported Au, and the importance of in situ studies for the elucidation of gas/surface mechanisms. Au4f XP spectra taken ex situ would almost certainly not be representative for the state of the catalyst under reaction conditions. The electronic and quite likely also the morphological structure of subnanometer Au particles was found to be sensitive to changes in temperature under reaction conditions. High CO_2-formation rates coincided with the absence of bulklike metallic Au. CO-oxidation by Au/TiO_2 does not seem to require the presence of comparatively large particles commonly found in these materials.[1−3] Evidence that such particles alone may not be responsible for the activity of Au/TiO_2 has been reported before.[30,31] The catalytic oxidation of CO over Au/TiO_2 may in this respect be more similar to the water-gas shift reaction over ceria-supported Au[10] than hitherto appreciated.

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Supporting Information Available: Sample preparation, XPS acquisition and analysis, MS data, surface coverage calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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