In Situ Quick XAFS Studies of the Thermal Decomposition of Gold(III) Oxide

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Oxidic gold(III) species are important intermediates in many synthesis routes leading to supported gold-catalysts for the low-temperature oxidation of carbon monoxide and the selective oxidation of propylene. Relatively little is known about the thermal decomposition of gold(III) oxide, of related nonstoichiometric oxides and of hydroxidic Au(III) compounds [1]. The laboratory synthesis of ordered gold(III) oxide is highly laborious and safety requirements for the synthesis are currently not met in our laboratory. We have therefore performed studies of gold(III) oxide with commercial samples of the highest available purity (Alfa Aesar, Premion, purity of metal content > 99.99%). Synthesis details for this gold(III) oxide were not disclosed by the manufacturer, but XRD analysis revealed that the material was highly amorphous, as no diffraction lines were observed. The appearance of the material (dark brown, fine powder) and the fact that the manufacturer quoted an erroneous decomposition temperature of 423 K suggests that the synthesis was by thermal dehydration of an amorphous gold(III) hydroxide precipitate at temperatures around 423 K, which is the standard synthesis procedure quoted in the older literature. A combination of temperature-programmed reduction mass spectroscopy and thermogravimetric analysis (TGA) revealed the presence of a considerable degree of hydrate in the gold(III) oxide (fig. 1, left), which was estimated to be approximately 1.5 water molecules per Au$_2$O$_3$-unit. It is expected that this high degree of hydration interrupts the integrity of the Au$_2$O$_3$ crystal structure. In fact, the presence of hydroxidic Au, likely the precursor to the sample investigated here, cannot be excluded. Unfortunately, crystalline Au(OH)$_3$ has never been synthesized, so that no detailed crystal structure data are available for comparison. However, it appears reasonable to expect that the local coordination geometry of Au(OH)$_3$ will almost be the same as in Au$_2$O$_3$, i.e., a square planar coordination shell of 4 OH-groups around the central gold atom, which might be arranged at similar distances as the oxygen ligands in gold(III) oxide.

Figure 1: Left: Thermogravimetric analysis of commercial gold(III) oxide compared to a temperature-programmed reduction mass spectroscopy analysis at a heating rate of 0.083 K/s. Right: result of a fitting analysis of the gold(III) oxide EXAFS, as performed with FEFFIT/FEFF8, the moduli of the Fourier-transformed $k^1$-weighted EXAFS are shown. Note the absence of spectral contributions from coordination shells beyond the four nearest-neighbour oxygen ligands.
Figure 2: Left: Au L\textsubscript{3} XANES spectra obtained during reduction of gold(III) oxide in a He-stream using a new plug-flow reactor for transmission measurements [2]. The phase composition of the material was determined from a 2-component linear combination analysis (dotted spectra), based on XANES spectra of final state of the material after reaction (metallic gold) and of its initial state (gold oxide). The thus determined temporal development of the phase composition is plotted on the right hand side, together with the simultaneously measured quadrupole mass spectrometer signal of O\textsubscript{2} developed during the decomposition. Spectra were taken in quick EXAFS mode at beamline X1 of HASYLAB.

The decomposition of this gold(III) oxide sample at a heating rate of 0.033 K/s was investigated by \textit{in situ} XAFS measurements (figure 2). The phase composition at each state of decomposition was determined using a linear combination of XANES spectra from the starting material and the final reaction product, metallic Au. Within the detection limit of the linear combination method (approximately 1%), no evidence for the formation of an intermediate phase such as Au\textsubscript{2}O or a suboxide of Au was obtained: as can be seen in figure 2, all spectra obtained during the decomposition are very well reproduced by linear combinations of the canonical spectra of the Au metal formed in the reaction and the untreated gold(III) oxide sample. The XANES data reveal that the decomposition to metallic gold and dioxygen occurs between 522 K and 550 K, with a maximum decomposition rate at 540 K. The accompanying oxygen release occurred in the temperature range from 514 K to 558 K, with the maximum at 545 K. Thus, oxygen release and the structural changes proceed simultaneously. Furthermore, the data show that at the onset of the oxygen evolution reaction, i.e., at 515 K, 20% of the gold(II) content had already decomposed. This loss of Au(III) is likely to be related to water loss of the sample during heating (note that the TGA analysis the release of approximately 1.5 molecules H\textsubscript{2}O per Au\textsubscript{2}O\textsubscript{3} formula unit, cf. figure 1) and the formation of metallic gold suggests that gold hydroxide is more likely to be the major contaminant in the untreated sample than hydrated Au\textsubscript{2}O\textsubscript{3}.

References