

# Thermal Stability and Decomposition Kinetics of Crystalline Gold(III) Oxide and Disordered Gold(III) Oxides/Hydroxides

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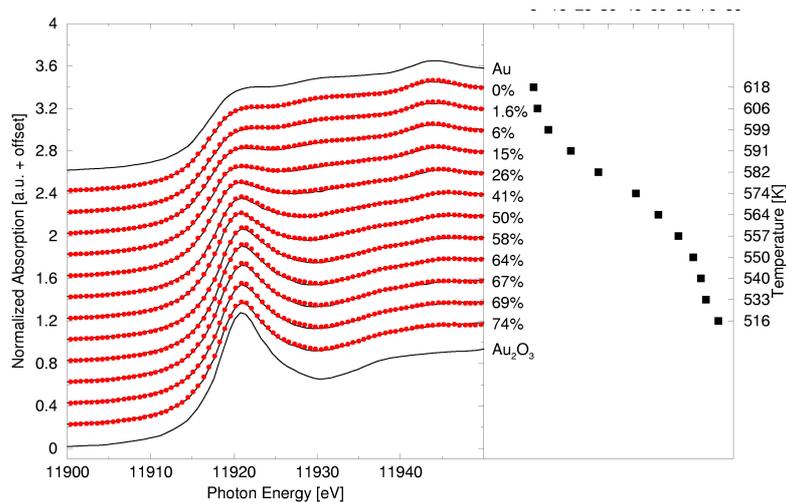
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Preparation routes leading to heterogeneous gold catalysts for oxidation reactions often involve the deposition of gold(III) oxide/hydroxide from aqueous solutions [1-3]. The strong impact on catalytic activity of subsequent preparation parameters such as calcination temperature and duration, residual water/hydroxide content or reductive pre-treatment in hydrogen has attracted much interest and speculation in the recent literature [4]. To obtain more insight into the thermal stability of crystalline and disordered Au(III) oxide/hydroxide compounds we have studied the thermal decomposition of several oxidic gold(III) samples by thermogravimetry (TGA), temperature programmed decomposition/desorption (TPD) and *in situ* X-ray absorption fine-structure spectroscopy (XAFS) coupled with TPD in a plug-flow reactor.

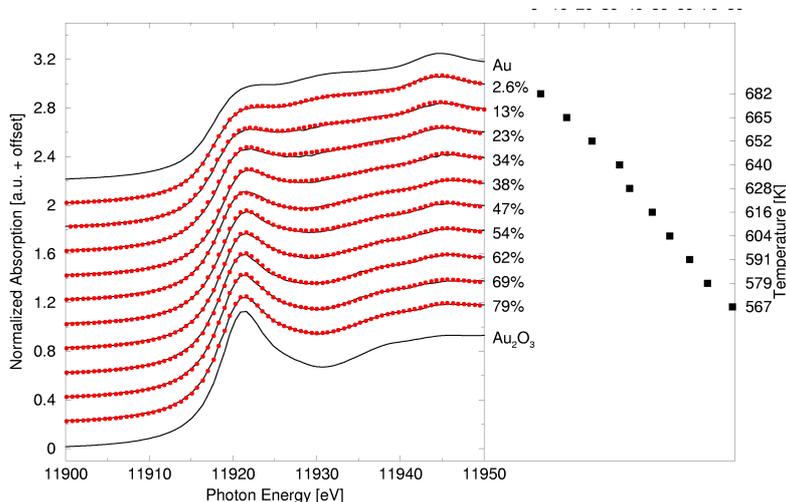
Crystalline Au<sub>2</sub>O<sub>3</sub> was synthesised by hydrothermal treatment of an amorphous Au(OH)<sub>3</sub> precipitate at 573 K and 3000 atm for several weeks. X-ray diffraction (XRD) confirmed the crystallinity of the Au<sub>2</sub>O<sub>3</sub> content, but also revealed the presence of a significant amount of metallic gold. Strongly hydrated gold oxide/hydroxide films were prepared by anodic oxidation of polycrystalline gold electrodes in dilute perchloric acid [5]. Additionally, a sample of “gold(III) oxide” was obtained commercially (Premion 99.99%, Alfa Aesar). XRD and XAFS confirmed that this substance had no significant long-range order. Combined TGA/TPR measurements also indicated that it contained approximately 1.5 hydrate molecules per nominal Au<sub>2</sub>O<sub>3</sub> formula unit.

The kinetics of oxygen evolution at atmospheric pressure were studied by TPD in a He stream (20 ml/min), with heating rates between 0.033 K/s and 0.333 K/s. It was observed that some hydrate water and/or hydroxide groups were stable up to the temperature for oxygen evolution (see below). However, most water and hydroxide groups were loosely bound and were released at temperatures below 420 K. The temperatures of maximal oxygen evolution from the crystalline Au<sub>2</sub>O<sub>3</sub> were found to be consistently approx. 50 K above those for amorphous Au<sub>2</sub>O<sub>3</sub>. Thermogravimetric analysis (TGA) confirmed these results. A heating rate analysis of the temperature-programmed decomposition data for crystalline Au<sub>2</sub>O<sub>3</sub> provided an activation energy for oxygen evolution of 204 kJ/mol and pre-exponential factors of 8.08·10<sup>14</sup> (assuming 1<sup>st</sup> order O<sub>2</sub> evolution kinetics) and 1.10·10<sup>13</sup> (assuming 2<sup>nd</sup> order O<sub>2</sub> evolution kinetics). The same analysis for the commercial “Au<sub>2</sub>O<sub>3</sub>” sample yielded an activation energy of 165 kJ/mol and pre-exponential factors of 5.70·10<sup>12</sup> (1<sup>st</sup> order) and 7.75·10<sup>10</sup> (2<sup>nd</sup> order). *In situ* XAFS data (figs. 1 and 2) of the Au L<sub>3</sub>-edge were taken at beamline X1 of the HASYLAB synchrotron facility in Hamburg, Germany. A linear combination analysis of the spectra taken during the thermal decomposition of amorphous and crystalline samples (figs. 1 and 2) indicated that the oxygen release occurred in one step from Au(III) to Au(0), with no evidence for the existence of a sufficiently long-lived compound with an intermediate oxidation state of gold, e.g. Au<sub>2</sub>O or AuO. The linear combination analysis of near-edge spectra also provided the relative decomposition rates of amorphous, crystalline and hydrous electrochemical gold(III) oxides. The temperature of 50% decomposition (T<sub>50%</sub>) increased as the samples became more ordered and less hydrated. For strongly hydrated (electrochemically generated), amorphous and crystalline gold(III) oxide T<sub>50%</sub> was approx. 425 K [6], 560 K (fig. 1) and 610 K (fig. 2), respectively. The temperature increase indicates that low order and strong hydration decrease the activation energy needed to overcome the kinetic barrier to oxygen evolution, likely because of the additional energy required to overcome the lattice energy of the crystalline sample.

The high activation energy for O<sub>2</sub> evolution from crystalline Au<sub>2</sub>O<sub>3</sub> is at 204 kJ/mol higher than all previously reported values for bulk oxides or adsorbed oxygen layers on surfaces. This high activation energy and the corresponding O<sub>2</sub> desorption temperature thus provide indicators for the stability of gold-oxygen bonds that should be considered an upper limit in microkinetic models of the reaction mechanisms underlying oxidation reactions over gold catalysts. At temperatures below 600 K, atomic oxygen species bound to gold (e.g., at defect sites) can be expected to have sufficient lifetimes to be active for the oxidation of more short-lived co-adsorbates, e.g. carbon monoxide, olefin and alcohol molecules. However, hydroxide



**Figure 1: In situ XANES spectra (black lines) taken in transmission during the thermal decomposition of XRD-amorphous, hydrated  $\text{Au}_2\text{O}_3$ ; the temperature of the sample was raised with a linear rate of 0.033 K/s. The dotted spectra were calculated by linear combination of the spectra of pure Au and the untreated  $\text{Au}_2\text{O}_3$  sample.**



**Figure 2: In situ XANES spectra (black lines) taken in transmission during the thermal decomposition of crystalline  $\text{Au}_2\text{O}_3$ ; the temperature of the sample was raised with a linear rate of 0.06 K/s. The dotted spectra were calculated by linear combination of the spectra of pure Au and the untreated  $\text{Au}_2\text{O}_3$  sample.**

groups and/or hydrate molecules on gold also appear to be stable up to the temperature of oxygen evolution, opening up the complicating possibility that these species might be involved in the oxidation reactions.

## References

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