

## Gas phase transport of gold with gold(III) oxide and carbon monoxide

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A transport reaction of gold occurs during the reaction of Au<sub>2</sub>O<sub>3</sub> with CO at temperatures around 400 °C. The reaction proceeds through a short-lived gas phase species of Au; analysis of quartz powder substrates placed downstream of the Au<sub>2</sub>O<sub>3</sub> indicates volatilisation yields of a few wt% Au<sub>2</sub>O<sub>3</sub>.

During a recent study of the heterogeneously catalysed oxidation of CO by gold we noticed that the reduction of Au<sub>2</sub>O<sub>3</sub> in gas streams containing CO was sometimes accompanied by the deposition of metallic Au downstream of the reaction zone.<sup>1</sup> Further experiments established that the addition of O<sub>2</sub> to the gas stream as a 1 : 1 mixture with CO increased the efficiency of the deposition process. Metallic Au powders were not transport-active. Likewise, Au transport was never observed after heating Au<sub>2</sub>O<sub>3</sub> to temperatures where the thermal decomposition to well-ordered metallic Au is known to occur.<sup>2,3</sup> Here, we report further results that establish gas phase transport by unidentified, short-lived Au species formed around 400 °C as the mechanism of the deposition process.

We constructed a reactor for the deposition of Au onto SiO<sub>2</sub> (quartz) powder samples placed downstream of a Au<sub>2</sub>O<sub>3</sub> supply. Physical contact between Au<sub>2</sub>O<sub>3</sub> and quartz as well as diffusion of Au over the surfaces of the reactor interior was prevented by using a tubular gas-flow system containing two concentric quartz tubes with different diameters (Fig. 1). Samples of 20 mg quartz powder (Strem Chemicals, 325 mesh, 99.5%) were embedded between two plugs of quartz wool in the centre of the larger reactor tube (4 mm ID). The tube with a smaller diameter (2 mm ID) was loaded with 10 mg of Au<sub>2</sub>O<sub>3</sub> (Aldrich Specpure 99.99%) and carefully inserted into the main reactor tube so that the Au<sub>2</sub>O<sub>3</sub> supply was located upstream of the quartz powder. This assembly was mounted in a vertical furnace. The gold supply tube was always positioned below the quartz substrate to prevent adventitious contamination of the quartz by dropping

Au<sub>2</sub>O<sub>3</sub> particles. The inlet of the Au<sub>2</sub>O<sub>3</sub> supply tube was connected to mass-flow controllers for CO, O<sub>2</sub> and He. The temperature in the reactor was regulated to within ±5 K using a thermocouple inserted into the quartz bed. Throughout all experiments the concentrations of He, CO, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> in the reactor effluent were continually monitored by means of a quadrupole mass spectrometer (QMS).<sup>†</sup>

Before every deposition run, the reactor was purged with He at 30 ml min<sup>-1</sup>.<sup>‡</sup> When the QMS analysis indicated less than 100 ppm residual N<sub>2</sub> in the effluent the flow was switched to the reaction mixture of CO, O<sub>2</sub> and He. After the room-temperature reduction of Au<sub>2</sub>O<sub>3</sub> by CO had subsided (this reaction is not accompanied by Au transport, see below), the temperature of the reactor was raised as quickly as possible (several min) to a final reaction temperature, at which it was held for 4 h. After cooling down, the efficiency of Au deposition was evaluated *ex situ* by powder X-ray diffraction (XRD)<sup>§</sup> analysis of the quartz powder.

Fig. 2 contains relevant sections from XRD patterns of untreated quartz powder (bottom) and several samples treated under different conditions. The pattern at the top of the figure (marked 'best') represents the most efficient deposition conditions so far achieved in our trials. It was obtained with a mixture of 35% CO and 35% O<sub>2</sub> (balance: He) at a total mass flow rate of 30 ml min<sup>-1</sup> and a final reaction temperature of 400 °C; the distance between the Au<sub>2</sub>O<sub>3</sub> supply and the quartz powder was approximately 5 mm. Au deposition is immediately evident from the presence of strong diffraction lines corresponding to the (111) and (200) planes of Au metal. Quantitative analysis of the pattern reveals a Au content of approximately 1 wt%, indicating that at least a few wt% of the Au<sub>2</sub>O<sub>3</sub> supply can be volatilised by the treatment with CO. The width of the Au(111) line was broadened by approximately  $\Delta(2\theta) = 0.2^\circ$  relative to a Au standard; Scherrer's equation  $0.9\lambda/\Delta(2\theta)\cos\theta^2$  thus suggests mean crystallite sizes around 500 Å. The method of

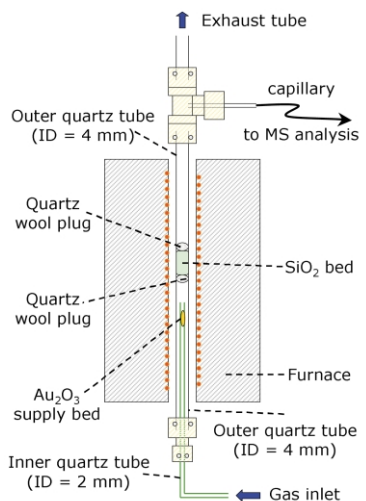


Fig. 1 Schematic drawing of the Swagelok<sup>®</sup>-sealed reactor used for the deposition of gold on quartz powder by the gas phase transport reaction.

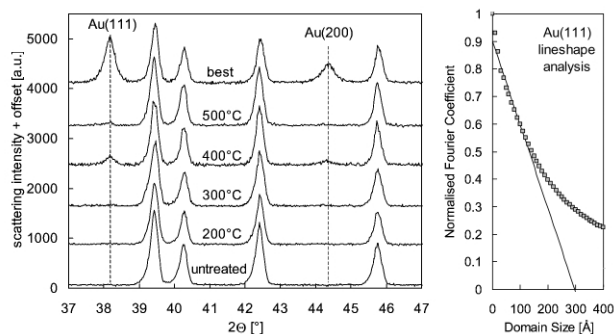


Fig. 2 XRD diagrams with Au(111) and Au(200) lines marked by vertical bars. From bottom to top: untreated quartz; quartz treated as a function of the final heating temperatures 200 °C, 300 °C, 400 °C, 500 °C at 30 ml min<sup>-1</sup> of a gas stream containing 20% CO, 20% O<sub>2</sub>, 60% He. At the top is the pattern of a sample treated with 35% CO, 35% O<sub>2</sub>, 30% He at 30 ml/min, with a shorter distance between the Au supply and the quartz powder bed. The diagram on the right contains the results of a single line variance analysis of the Au(111) line in the topmost pattern (see text).

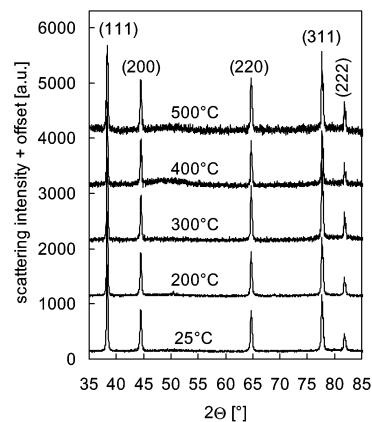
Dehlez *et al.*<sup>5</sup> yielded a value of 370 Å. A full lineshape analysis using the single line approach implemented by Krumm<sup>6,7</sup> yielded domain sizes of approximately 300 Å (Fig. 1).

The remaining diffraction data represent a series taken as a function of the final reaction temperature, using 20% CO and 20% O<sub>2</sub> in He at a total mass flow of 30 ml min<sup>-1</sup> and a Au<sub>2</sub>O<sub>3</sub> supply positioned 20 mm upstream of the quartz substrate. Evidence for Au deposition is only observed after heating to 400 °C. Final reaction temperatures of 200 and 300 °C do not lead to detectable Au deposition, presumably because the activation barrier for the formation of the volatile species cannot be overcome. At 500 °C, very little Au is deposited, suggesting that the lifetime of the volatile species is too short at this temperature. From the mass flow and the distance between the Au supply and the quartz substrate we estimate that a gas phase species with a minimum lifetime of a few 100 ms is required.

That the transport of Au requires the presence of CO suggests that a carbonyl is formed during the reduction of Au<sub>2</sub>O<sub>3</sub>. While carbonyl-based transport is well known for many transition metals,<sup>8</sup> a sufficiently long-lived, volatile carbonyl of Au has previously not been reported. Because the volatile species is derived from a Au(III) compound it is likely to contain oxidised Au rather than a neutral or anionic species. A cationic carbonyl of Au might be formed directly from Au(III) or through a partially reduced intermediate, possibly a Au(I) compound. Alternatively, CO might react with nuclei of surface oxide formed by highly reactive Au atoms at defect sites on freshly reduced, metallic Au particles. Such a surface oxidation mechanism is known to occur at defects on planar Au electrodes.<sup>9</sup> Possible candidates for the gas phase species are the cationic carbonyl complexes Au(CO)<sup>+</sup>,<sup>10</sup> Au(CO)<sub>2</sub><sup>+</sup><sup>10–12</sup> and Au(CO)<sub>3</sub><sup>+</sup>,<sup>13</sup> some of which are known to be stable at room temperature in the presence of strong acids.<sup>10–12</sup> Mass spectrometric analysis of gas phase reactions and calculations have indicated that the Au–C bond in Au(CO)<sup>+</sup> is quite stable, with a dissociation energy of approximately 210 kJ mol<sup>-1</sup>.<sup>14</sup> Plausible counter ions in neutral gas phase species would be OH<sup>-</sup> (the Au<sub>2</sub>O<sub>3</sub> samples are XRD-amorphous and contain hydrate, which cannot be removed by heating below the decomposition temperature of Au<sub>2</sub>O<sub>3</sub><sup>1</sup> or oxygen ions, such as O<sub>2</sub><sup>-</sup>). Indeed, evidence for the existence of the labile complex Au(CO)O<sub>2</sub> has been reported for matrix experiments at 40 K.<sup>15</sup> Note that no evidence for a stable carbonate species of Au has ever been reported. The formation of intermediate carbonate species during the CO-oxidation by Au was also excluded in a recent study, which identified the anionic complexes Au<sub>2</sub>(CO)O<sub>2</sub><sup>-</sup>, Au<sub>3</sub>(CO)O<sub>2</sub><sup>-</sup> and Au<sub>3</sub>(CO)(O<sub>2</sub>)<sub>2</sub><sup>-</sup> as intermediates in the catalytic oxidation of CO by negatively charged Au clusters.<sup>16</sup>

For temperatures below 300 °C deposition of Au was not achieved, despite the fact that the MS analysis of the reactor effluent indicated the vigorous reduction of Au<sub>2</sub>O<sub>3</sub> by CO already at room temperature. In line with this, the XRD analysis of all Au<sub>2</sub>O<sub>3</sub> samples exposed to CO revealed the presence of metallic Au only (Fig. 3). However, the colour of the reduced Au<sub>2</sub>O<sub>3</sub> powders varied from black after reaction below 100 °C via dark brown and light brown to pink at *T* > 400 °C. This suggests that a considerable fraction of highly disordered gold and/or residual oxide component persists after the initial treatment of Au<sub>2</sub>O<sub>3</sub> with CO at room temperature. This would support a view that either defect-rich metallic Au, residual oxide and/or adsorbed oxygen species are involved in the formation of the volatile Au species at 400 °C. It should also be noted that the catalytic oxidation of CO to CO<sub>2</sub> occurred when the temperature of the reactor was raised to 400 °C, in line with previous investigations of CO-oxidation over metallic Au.<sup>17</sup> It appears that activated complexes between metallic Au, O<sub>2</sub> (or atomic O) and CO can be formed in the temperature range where the Au transport reaction occurs; this might explain why the addition of O<sub>2</sub> to the gas stream is beneficial for the transport reaction.

Finally, we should point out that there is considerable interest in developing new, clean processes for the growth of Au films



**Fig. 3** Powder X-ray diffraction diagrams of the Au<sub>2</sub>O<sub>3</sub> supply used for the treatment to the quartz samples treated in the reactor as a function of the final heating temperature. In all cases, only diffraction lines due to metallic Au are visible. The slightly curved background functions in some of the patterns are due to scattering from the Si sample holder.

by chemical vapour deposition (CVD).<sup>18</sup> A considerable advantage of a carbonyl-based Au CVD process would be the absence of impurities in the metal deposits due to decomposed or co-adsorbed organometallic ligands. However, before the possibility of an efficient CVD process can be assessed the gas phase species underlying the observed transport reaction should be identified to enable optimisation of the volatilisation rate.

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## Notes and references

† Balzers QMG-112, base pressure of 10<sup>-9</sup> mbar. The effluent from the gas-flow reactor was analysed at a pressure of 10<sup>-7</sup> mbar by means of a differentially pumped steel capillary and a leak valve.

‡ Helium (99.999%), O<sub>2</sub> (99.9%) and CO (99.9%) were supplied by Messer-Griesheim, Germany, and used for experiments without further purification.

§ Philips PW1710; Bragg-Brentano geometry; ~5 mg sample was slurried on a polished Si single crystal sample holder; we thank H. Hartl and I. Brüdgam (FU Berlin) for access to the diffractometer.

- C. Klanner, Diploma Thesis, Freie Universität Berlin, 2000.
- S. J. Ashcroft and E. Schwarzmann, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1360.
- Gmelin Handbook of Inorganic and Organometallic Chemistry. Au—Gold Supplement, Vol. B1*, Springer-Verlag, Berlin, 1992, 59–99.
- H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures*, Wiley, New York, 2nd edn., 1974.
- R. Dehlez, T. H. de Keijser, J. I. Langford, D. Louer, E. J. Mittemeijer and E. J. Sonneveld, *Int. Union Crystallogr. Monogr. Crystallogr.*, 1993, **5**, 30.
- S. Krumm, *Acta Univ. Carolinae Geol.*, 1994, **38**, 253.
- S. Krumm, *Mater. Sci. Forum*, 1996, **228–231**, 183.
- N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth Heinemann, Oxford, 1998.
- L. D. Burke and A. P. O'Mullane, *J. Solid State Electrochem.*, 2000, **4**, 285.
- H. Willner and F. Aubke, *Inorg. Chem.*, 1990, **29**, 2195.
- R. Küster and K. Seppelt, *Z. Anorg. Allg. Chem.*, 2000, **626**, 236.
- H. Willner, J. Schaebis, J. Hwang, F. Mistry, R. Jones, J. Trotter and F. Aubke, *J. Am. Chem. Soc.*, 1992, **114**, 8972.
- A. J. Lupinetti, V. Jonas, W. Thiel, S. H. Strauss and G. Frenking, *Chem. Europ. J.*, 1999, **5**, 2573.
- D. Schröder, J. Hrusak, R. H. Hertwig, W. Koch, P. Schwerdtfeger and H. Schwarz, *Organometallics*, 1995, **14**, 312.
- H. Huber, D. McIntosh and G. A. Ozin, *Inorg. Chem.*, 1977, **16**, 975.
- J. Hagen, L. D. Socaciu, M. Eljazyfer, U. Heiz, T. M. Bernhardt and L. Wöste, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1707.
- G. C. Bond and D. Thompson, *Catal. Rev.-Sci. Eng.*, 1999, **41**, 319.
- R. J. Puddephatt, *Polyhedron*, 1994, **13**, 1233.