Supporting Information

Gas-Phase Deposition of Au Nanoclusters To Produce Heterogeneous Glycerol Oxidation Catalysts.

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Experimental Details

Cluster Deposition - The Au clusters were generated in a magnetron sputtering, gas condensation cluster beam source as described in an earlier report.[1] The magnetron source (target purity: 99.99%) producing the Au atoms was located ~20 cm away from the exit nozzle of the chamber (the condensation length). The applied DC magnetron power was 10 W. Au atoms sputtered out of the target were cooled down in a mixed Ar/He gas (150 sccm for Ar and 20 sccm for He) to form Au clusters. The positively charged portion was extracted by a skimmer and then guided by ion optical lens system. An "octosphere" deflector was used to control the ultimate flight direction of the cluster beam, either to a lateral time-of-flight mass filter[2] to monitor the clusters' mass distribution or (by deflecting the beam electrostatically through 90°) into the deposition chamber.[2] In the deposition chamber the carbon powder supports (0.4 g) were continuously agitated in a stainless-steel cup during deposition, to maximize the exposure of the powder particle surfaces to the cluster beam. A negative potential of -900 V was applied to the vibration cup to accelerate the clusters before landing and thus improve their immobilization on the support.

Sol Immobilization Gold on carbon catalysts (1wt%Au/C) were prepared immobilization of a Au sol using PVP as a stabilizing polymer ligand according to a procedure previously reported.[3] Typically, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.8 mL, 12.5 mg Au/mL Sigma Aldrich, ≥49.0%) in 400 mL of de-ionised water was stirred vigorously, followed by polymer addition (polymer/Au wt/wt = 0.65, 1wt% PVP solution, Sigma Aldrich, average molecular weight MW = 10 000 g mol^{-1}). Following this a freshly prepared 0.1 M $NaBH_4$ solution (≥99.99%, Sigma Aldrich, mol $NaBH_4$/ mol Au = 5) was added to form a red sol and stirred for 30 min. The colloid was immobilized onto 0.99 g of carbon (Vulcan XC72R) by addition of 8 drops of concentrated H_2SO_4. After 1 h of continuous stirring, the catalyst was filtered, washed thoroughly with deionised water and dried (110 °C for 16 h).

Catalyst Characterization

X-Ray Photoelectron Spectra (XPS) were recorded with a Kratos Axis Ultra DLD XPS spectrometer, using a 300W Al Kα X-ray source. Binding energies were referenced against a C 1s reference (284.7 eV).

Inductively coupled plasma mass spectrometry (ICP-MS) Au metal content was determined using an Agilent 7900 ICP-MS. A known mass of catalyst was digested overnight in aqua regia in order to dissolve the metal followed by dilution using deioninsed water to a suitable concentration within the calibration range. Results of duplicate analysis were within 0.05wt%

Scanning transmission electron microscope (STEM) The cluster distribution was determined using a Thermo Fisher Titan STEM with a Cs probe corrector (CEOS) and ChemiSTEM Super-X EDX detector. The incident electron beam convergence angle was 21 mrad and a high-angle annual dark-field (HAADF) detector operating with inner angle of 55 mrad at 200 kV. STEM samples were prepared by dispersing the catalyst in deionized water, followed by sonication for several minutes and drop-casting onto a copper grid with an amorphous carbon film.

Glycerol Oxidation Glycerol oxidation under basic conditions was carried out using a glass reactor (Colaver®) in an oil bath (60 °C) and at elevated O_2 pressure (3 bar) with continuous stirring (1200 rpm). Glycerol (5 mL, 0.6 M, Sigma Aldrich, anhydrous, >99.5 %) and NaOH (5 mL, 1.2 M, Sigma Aldrich BioXtra >98%, pellets, anhydrous) were mixed to give 10 ml total reaction volume. The glycerol/metal(s) mole ratio was 5800:1 assuming a 1wt% Au catalyst and catalyst loading of 10 mg. The reaction was carried out for 4 h. The post-reaction solution was quenched and diluted x10 with deionised water prior to HPLC analysis using an Agilent 1260 Infinity HPLC with a Metacarb 67H column with a 0.1% wt solution of phosphoric acid as mobile phase. Based on duplicate experiments conversion and selectivity values were typically within 5% of each other on repeat reactions.

1) Cai, R.; Ellis, P. R.; Yin, J.; Liu, J.; Brown, C. M.; Griffin, R.; Chang, G.; Yang, D.; Ren, J.; Cooke, K.; Bishop, P. T.; Theis, W.; Palmer, R. E. Performance of Preformed Au/Cu Nanoclusters Deposited on MgO Powders in the Catalytic Reduction of 4-Nitrophenol in Solution. *Small* **2018,** 14 (13), 1703734.

2) von Issendorff, B.; Palmer, R. E. A new high transmission infinite range mass selector for cluster and nanoparticle beams *Review of Scientific Instruments* **1999,** 70 (12), 4497-4501.

3) Abis, L.; Dimitritatos, N.; Sankar, M.; Freakley, S. J.; Hutchings, G. J. The Effect of Polymer Addition on Base Catalysed Glycerol Oxidation Using Gold and Gold–Palladium Bimetallic Catalysts *Topics in Catalysis* **2019,** doi.org/10.1007/s11244-019-01212-y.