

Electronic Supplementary Information (ESI) : detailed synthesis and experimental.

5 Gold of 99.9999 purity in sponge from Fluka, Na₂PdCl₄ 99.998%, NaAuCl₄·2H₂O 99.0% and K₂PtCl₆ 99.0% purity from Aldrich and activated carbon from Camel (X40S; SA=1100-1200 m²g⁻¹; pH 8-9) were employed. Before use the carbon was suspended in HCl 6M and left under stirring for 12h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6-6.5. At the

10 end the carbon was filtered off and dried for 5-6 h at 150°C in air. The final water content was evaluated to be <3%.

NaBH₄ 99.0% purity and polyvinylalcohol 87-89% hydrolysed (PVA) (average M_w 13,000-23,000) from Aldrich were used. NaOH was from Fluka of the highest purity available. Gaseous oxygen and hydrogen from

15 SIAD was 99.99% pure. Glycerol (88% wt solution), glyceric acid and all the intermediates were from Fluka. Milli-Q water was used in all the preparations.

Monometallic catalysts were prepared as reported elsewhere by using a

preformed metallic sol^[10]. Bimetallic catalysts were prepared by using

20 two different methodologies:

a) one step synthesis
Bimetallic sols were prepared as reported in^[10]. NaAuCl₄·2H₂O (0.095

25 mmol) was dissolved in 190 ml of H₂O and PVA (2% w/w) was added (2.8 ml PVA). After 3 min, 0.1 M NaBH₄ (2.9 ml) was added under vigorous magnetic stirring. The red Au(0) sol was immediately formed. After another 3 min, Na₂PdCl₄ solution (10%wt in Pd) (0.095 mmol) and NaBH₄ solution (2.0 ml) were added, obtaining a dark brown sol. Within a few minutes of sol generation, the colloid (acidified to pH 1, by sulphuric acid) was immobilised by adding activated carbon under vigorous

30 stirring. The amount of support was calculated as having a final total metal loading of 1% wt. After 2 h the slurry was filtered, the catalyst was washed thoroughly with distilled water (neutral mother liquors) and was dried at 120 °C for 4h. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

b) two step synthesis
NaAuCl₄·2H₂O (0.072 mmol) was dissolved in 140 ml of H₂O and PVA (2% w/w) was added (0.706 ml). The yellow solution was stirred for 3

35 minutes and 0.1 M NaBH₄ (2.15 ml) was added under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. An UV-visible spectrum of the gold sol was recorded to check the complete AuCl₄⁻ reduction and the formation of plasmon peak. Within a few minutes of sol generation, the gold sol (acidified to pH 2 by sulphuric acid) was immobilised by adding activated carbon under vigorous stirring. The amount of support was calculated as having a final metal loading of

40 0.73%wt. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors). ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon. The Au/C was then dispersed in 140 ml of water; Na₂PdCl₄ solution (10%wt in Pd) (0.0386 ml) and PVA (2% w/w) (0.225

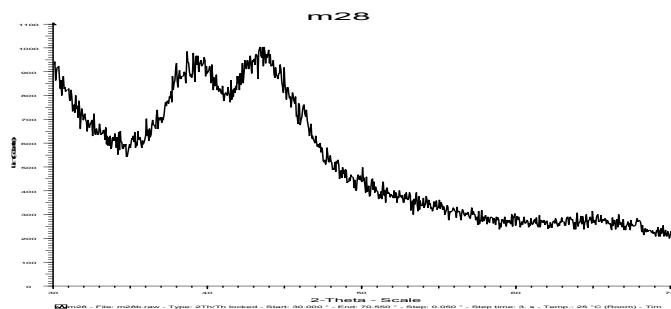
45 ml) were added. H₂ was then bubbled (50 ml/min) under atmospheric pressure and at room temperature for 2 h. After additional 18 h the slurry was filtered, the catalyst washed thoroughly with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

50 55 Characterisations
a) The gold and palladium content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24. The water content was determined by drying a sample at 150°C in air for 5 h.

60 b) UV-visible spectra of the filtrate were performed on HP8452 and HP8453 Hewlett-Packard spectrophotometers in Milli-Q water between 190 and 800 nm, in a quartz cuvette. The reactions were followed by observing the disappearance of the UV bands of the AuCl₄⁻ and PdCl₄²⁻ anions located at 204 and 210 nm, respectively.

65 c) For TEM investigations, the powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto a copper grids covered with holy carbon film. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan imaging

70 filter, GIF100, was used for TEM observation. EDX analysis was performed in the same microscope using a DX4 analyzer system (EDAX). e) X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu-Kα radiation, equipped with a graphite monochromator in the diffracted beam.



75 Oxidation experiments
The reactions were carried out in a thermostatted glass reactor (30 ml) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5,000 ml) containing oxygen at 300 kPa. The oxygen

80 uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. Glycerol (0.3 M), NaOH (NaOH/glycerol=4 mol/mol) and the catalyst (glycerol/metals = 3000 mol/mol) were mixed in distilled water. The reactor was pressurised at 300 kPa of O₂ and thermostatted at 50°C. After

85 an equilibration time of 10 min, the reaction was started up by stirring and samples were taken every 15 min and analysed by HPLC. Analysis of products
Analyses were performed on a Varian 9010 HPLC equipped with a Varian 9050 UV (210 nm) and a Waters R.I. detector in series. An Alltech

90 OA-10308 column (300 mm x 7.8 mm) was used with aqueous H₃PO₄ 0.1% wt/wt M (0.5 ml/min) as the eluent. Samples of the reaction mixture (0.5 ml) were diluted (5 ml) using the eluent. Products were recognized by comparison with authentic samples and quantified by calibration curves. Selectivities were calculated from the formula: Product Sel.%=

95 mol product/ (initial reagent mol – final reagent mol). Mass balance was calculated on C mol and in all the reactions was >98%