Supplementary online material

Physical mixing of metal acetates: a simple, scalable method to produce active chloride free bimetallic catalysts

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Catalyst characterisation

Powder X-ray diffraction

Characterisation was performed using powder X-ray diffraction (XRD) on a (θ-θ) PANalytical X'pert Pro powder diffractometer using a Cu K_α radiation source operating at 40 KeV and 40 mA. Standard analysis was performed using a 40 min scan with a back filled sample. Diffraction patterns of phases were identified using the ICDD data base. Diffraction patterns were analyzed using full pattern refinement, with background functions, zero shift and pseudo-Voigt profile functions. Reference crystal structure profiles were selected from the inorganic crystal structure database.

Scanning transmission electron microscopy

Samples for examination by scanning transmission electron microscopy (STEM) were prepared by dry dispersing the catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. Samples were then subjected to high angle annular field (HAADF) imaging and energy dispersive X-ray spectroscopy (XEDS) in order to determine particle size distributions and compositions. The instrument used for this analysis was an aberration corrected JEOL 2200 FS microscope operating at 200kV.

X-ray photoelectron spectroscopy

XPS measurements were made on a Kratos Axis Ultra DLD spectrometer using monochromatic Al K_α radiation (120 W source power). An analyser pass energy of 160 eV was used for survey scans, while 40 eV was employed for detailed regional scans. Samples were mounted using double-sided adhesive tape, and binding energies were referenced as discussed in the text.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Setaram TGA/DTA. All experiments were performed under nitrogen with 3-8 mg of metal acetate in each experiment.

Catalyst testing

Testing of catalysts for benzyl alcohol oxidation

Catalyst testing was performed using an stainless steel autoclave (Autoclave Engineers In-line MagneDrive III) with a nominal volume of 100 ml and a maximum working pressure of 2000 psi. The vessel was charged with benzyl alcohol (40 ml) and catalyst (25 mg). The autoclave was then purged three times with oxygen leaving the vessel at 10 bar. The pressure was maintained constant throughout the experiment; as the oxygen was consumed in the reaction, it was replenished. The stirrer speed was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature of 140 °C. Samples from the reactor were taken periodically *via* a sampling pipe, ensuring that the volume purged before sampling was higher than the tube volume, and analysed by GC (Varian 3800) using a CP-wax column.

Stability of catalysts for benzyl alcohol oxidation

To ascertain the stability of the materials, the catalysts were tested for re-use. To obtain sufficient catalyst for stability testing the autoclave was charged with benzyl alcohol (40 ml) and catalyst (200-500 mg). The autoclave was then purged three times with oxygen leaving the vessel at the desired pressure. This pressure was maintained constant throughout the experiment; as the oxygen was consumed in the reaction it was replenished. The stirrer speed was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature of 140 °C. After the reaction, the reaction mixture was filtered and washed with acetone. Following drying, 25mg of the catalyst was re-tested as described previously.

Testing of catalysts for H_2O_2 hydrogenation

Hydrogen peroxide hydrogenation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 mL and a maximum working pressure of 2000 psi. To test each catalyst for H_2O_2 hydrogenation, the autoclave was charged with catalyst (0.01 g) and a solution containing 4 wt% H_2O_2 (5.6 g CH_3OH, 2.22 H_2O and 0.68 g H_2O_2 50% w/w). The charged autoclave was then purged three times with 5% H_2/CO_2 (0.7 MPa) before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa at 20ºC. The temperature was then allowed to decrease to 2ºC followed by stirring (at 1200 rpm) the reaction mixture for 30 min. The amount of hydrogenated H_2O_2 was determined by titrating aliquots with acidified $Ce(SO_4)_2$ (0.0288M) in the presence of a ferroin indicator.

Testing of catalysts for direct H_2O_2 synthesis

Synthesis of H_2O_2 from H_2 and O_2 was performed using similar conditions to those described above, but in the presence of O_2 (5% H_2/CO_2 and 25% O_2/CO_2, 1:2 H_2/O_2 at 4.0 MPa; CH_3OH (5.6 g), H_2O (2.9 g), catalyst (0.01 g), 2ºC and 1200 rpm) without any added H_2O_2.

Stability of catalysts for hydrogen peroxide production

The autoclave was charged with the catalyst (0.05 g), solvent (5.6 g CH_3OH and 2.9 g H_2O), purged three times with 5% H_2/CO_2 (0.7 MPa) and then filled with 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa) to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 4.0 MPa. Stirring (1200 rpm) was commenced on reaching the desired temperature (2ºC), and experiments were carried out for 30 min. After filtration, the catalyst was then dried in the oven at 110 ºC for 2 hours. 0.01 g of catalyst was re-used as described in the H_2O synthesis procedure.

Table 1: Catalyst re-use data for (i) benzyl alcohol oxidation and (ii) hydrogen peroxide formation for a 2.5%Au + 2.5%Pd/C catalyst prepared by the physical grinding method.

Catalyst Use	**Benzyl Alcohol Conversion (%)**		**Benzaldehyde Selectivity (%)**		**Hydrogen Peroxide Productivity (mol Kg^{-1}h^{-1})**
	0.5h	**1h**	**0.5h**	**1h**	
1st	50.8	74.3	82.4	79.0	100
2nd	46.3	77.6	80.2	76.33	100

Table 2: Energy dispersive X-ray analysis of 2.5%Au + 2.5%Pd/TiO_2 catalyst prepared by the physical grinding method.

Compound	**Weight (%) average of 3 spectra**
Au	2.4
Pd	2.5
TiO_2	95.1

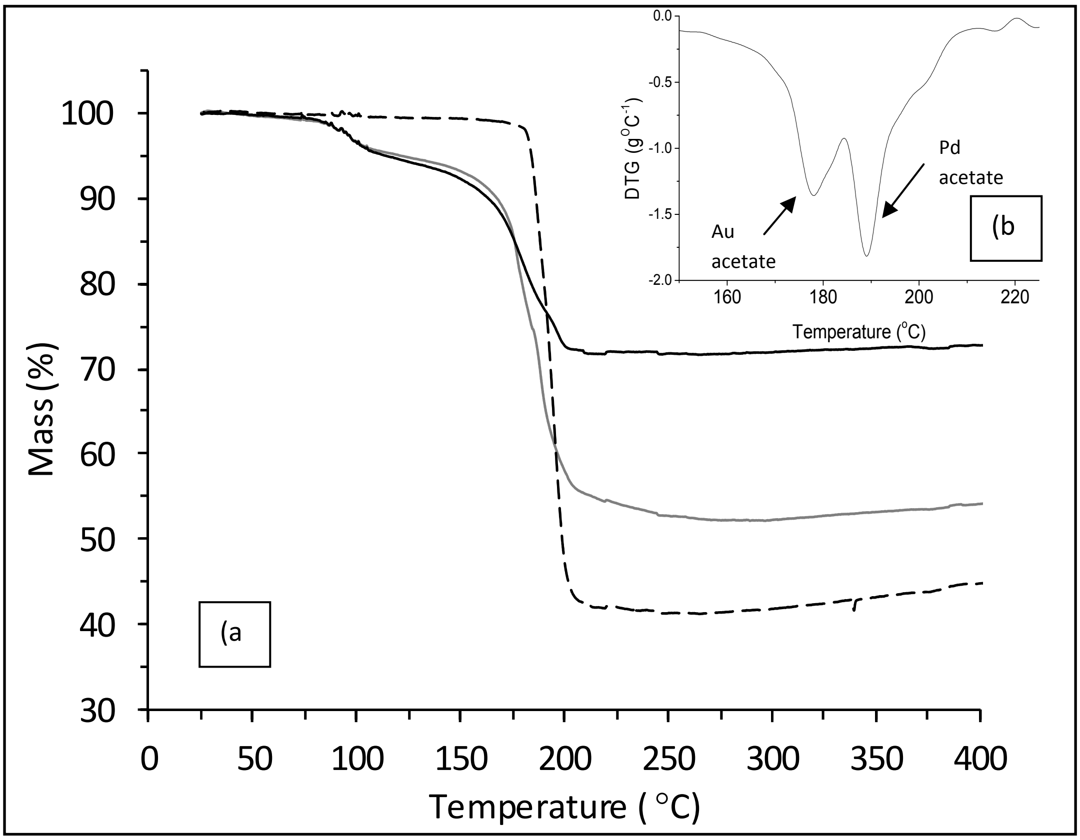

Figure S1: (a TGA of metal acetate salts under flowing nitrogen with 5 °C min^{-1} ramp rate Black line: palladium (II) acetate, grey line: gold (III) acetate, dashed line 1:1 mixture b) Derivative of Au:Pd mixture to demonstrate presence of discrete mass losses

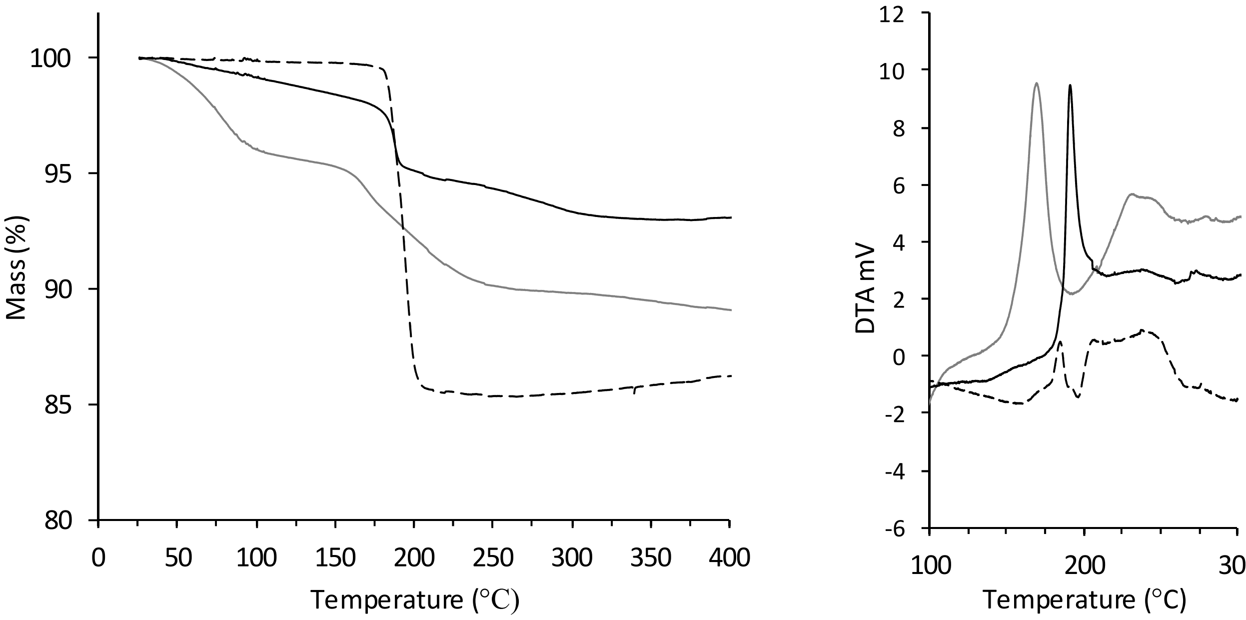

Figure S2: TGA and DTA of palladium acetate decomposition, with G60 and P25 TiO_2 supports, under flowing nitrogen with 5 °C min^{-1} ramp rate. Black line : palladium (II) acetate with TiO_2,grey line: palladium (II) acetate with G60 carbon, dashed line: palladium (II) acetate only (mass loss divided by 4 so all TGA profiles comparable). Support masses chosen to give 5% pd loading.

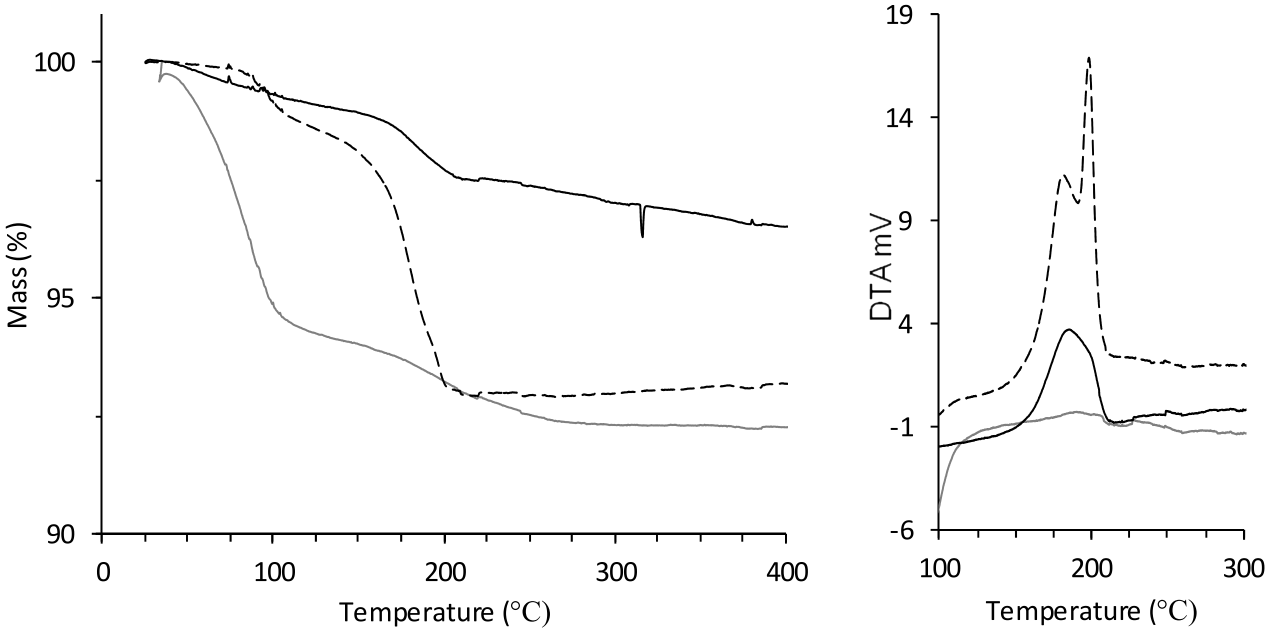

Figure S3: TGA and DTA of gold acetate decomposition, with G60 and P25 TiO_2 supports, under flowing nitrogen with 5 °C min^{-1} ramp rate. Black line: gold (III) acetate with TiO_2,grey line: gold (III) acetate with G60 carbon, dashed line: gold (III) acetate only (mass loss divided by 4 so all TGA profiles comparable). Support masses chosen to give 5% Au loading.

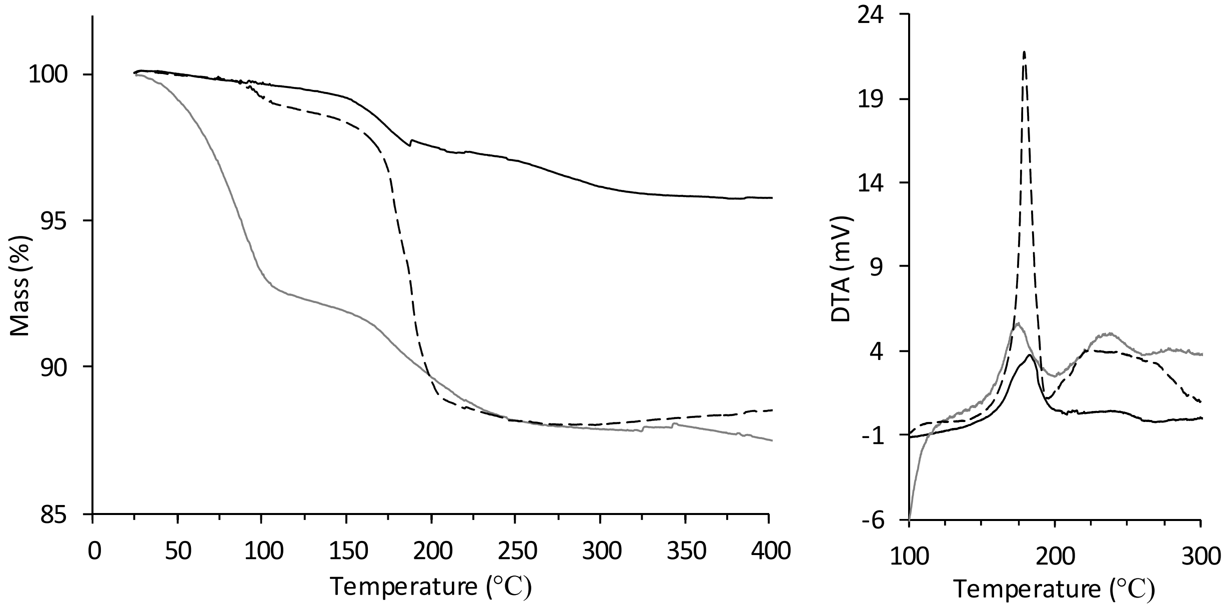

Figure S4: TGA and DTA of palladium/gold acetate mixture decomposition, with G60 and P25 TiO_2 supports, under flowing nitrogen with 5 °C min^{-1} ramp rate. Black line :) acetate mixture with TiO_2, grey line: acetate mixture with G60 carbon, dashed line: acetate mixture only (mass loss divided by 4 so all TGA profiles comparable). Support masses chosen to give 5% metal loading.

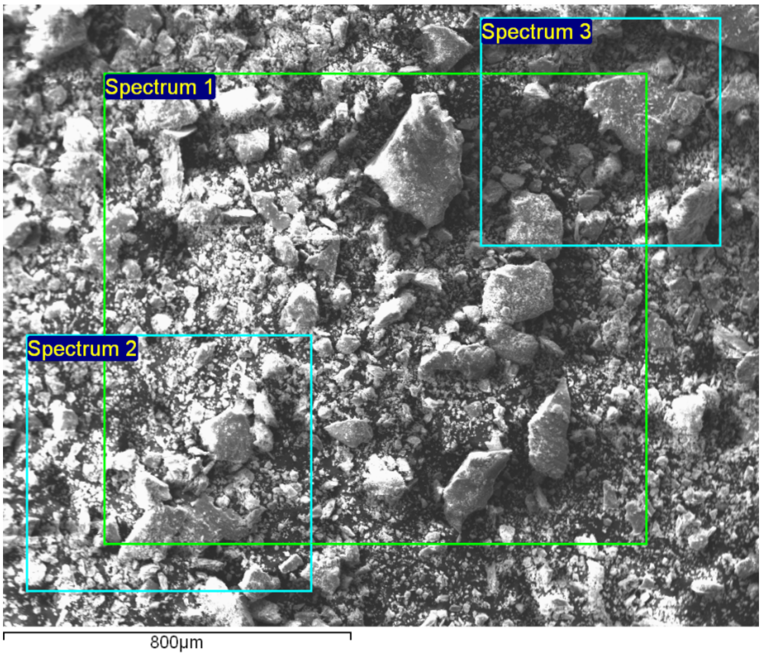

Figure S5: SEM micrograph of the areas analysed by EDX for a 2.5%Au + 2.5%Pd/TiO_2 catalyst prepared by the physical grinding method (see Table 2).

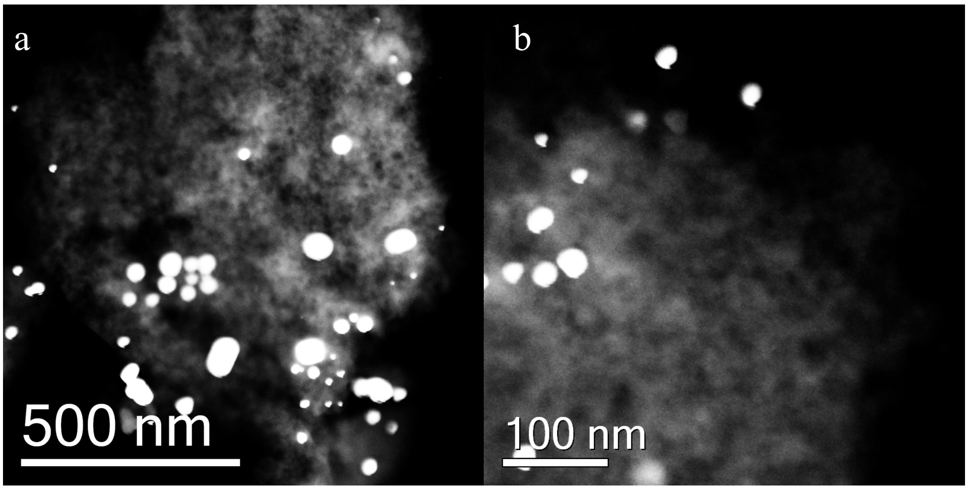

Figure S6: Representative STEM HAADF micrographs of the 5.0% monometallic Au /C catalyst prepared by the physical grinding method showing Au particles predominantly in the 20-40nm size range.

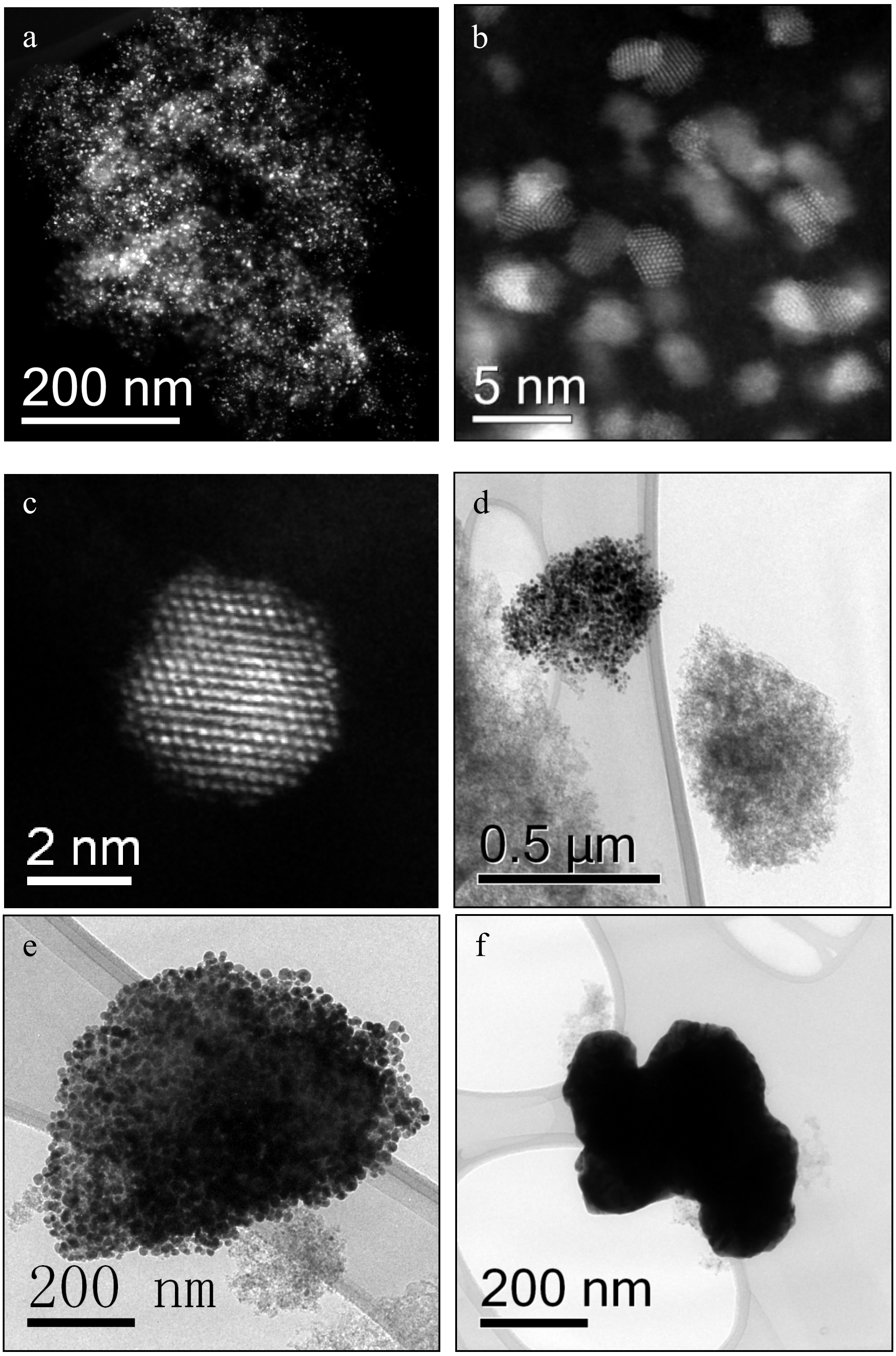

Figure S7: Representative STEM HAADF (a-c) and BF-TEM (d-f) micrographs of the 5.0% monometallic Pd/C catalyst prepared by the physical grinding method. Three distinct morphologies were observed. Firstly, there was a fine dispersion of 2-4nm metallic Pd particles homogeneously dispersed over the support (see a, b & c). Secondly, there were occasional micron-scale agglomerates of ~20nm Pd particles held together in a carbonaceous matrix (see d & e). Thirdly, there were also very occasional ~0.5µm dense Pd particles (see f).