

Supporting information

Catalyst Synthesis

Materials

Palladium (II) nitrate solution (15% Pd, Johnson Matthey), sodium hydroxide (Alfa Aesar), titania powder (Evonik P25) and alpha alumina powder (Saint Gobain Norpro) were all used as received.

Incipient wetness impregnation

Incipient wetness impregnation is the synthesis of a catalyst by pore-filling a porous support material with a solution of a metal salt, followed by drying and thermal treatment to convert the metal salt to the desired form, in this case reduction with hydrogen to palladium metal.

In a typical synthesis, the desired amount of palladium nitrate solution was dissolved in the amount of water needed to fill the pores of the alpha-alumina support completely, but with no excess solution left over. A typical impregnation volume was 0.3ml water per gram of support. The impregnated solid was dried at 100°C and then reduced in flowing 5% H₂/N₂ mixture for two hours at 250°C.

Deposition-precipitation

Deposition-precipitation synthesis centres on the hydrolysis of acidic metal precursors by strong alkali metal bases in the presence of a suitable support. The metal hydroxide formed deposits onto the support. Again thermal treatments with hydrogen can be used to reduce the metal hydroxide to metal.

In a typical synthesis, palladium nitrate solution dissolved in water (0.05M solution) and sodium hydroxide solution (0.05M solution) were added to a slurry of alpha-alumina in water at 60°C. The pH of the solution was maintained at 9 by addition of appropriate amounts of the two solutions. Once the addition was complete, the slurry was heated to boiling, then cooled to room temperature. The slurry was filtered and the solid washed with hot water. The product was dried at 100°C and then reduced in 5% H₂/N₂ at 250°C for two hours.

Ion exchange

To investigate the effect of ion exchange sites on the catalyst, materials were prepared by ion exchange of palladium onto alpha alumina and titania. Here the support powder is stirred in a slurry with palladium nitrate. The solid is washed thoroughly to remove all but the strongly bound palladium. Drying and nitrate decomposition processes are the same as for the catalysts above.

In a typical synthesis, a 100ml solution containing enough palladium nitrate to make a 1% loaded catalyst was stirred with the support (10g) for two hours, after which time the support was separated

by filtration and washed well with water. The washed catalyst was dried at 100°C overnight and then reduced in flowing 5% H₂/N₂ gas mixture at 250°C for two hours.

Gas-Phase Cluster Deposition

Fig. S1 shows an overview of the GCD system. Atoms are sputtered out of a metal target into a vacuum chamber (< 2x10⁻⁶ mbar), cooled and condensed using liquid nitrogen, driving the formation of clusters. These clusters are charged and can be manipulated using applied voltages. The size distribution of the produced clusters can be measured in real time using a mass spectrometer.

The focussed beam of charged particles is targeted at an agitated cup containing the support powder. It is important to agitate the powder to ensure deposition across the entire powder. Without agitation, the clusters will deposit in a small region.

In these experiments we have used the whole size range of clusters produced. In a typical experiment, the cluster flux was around 10nA. It is possible to configure the instrument to select a fraction of the size distribution for deposition. Whilst this decreases the particle size range of the supported clusters, it severely diminishes the cluster flux onto the support.

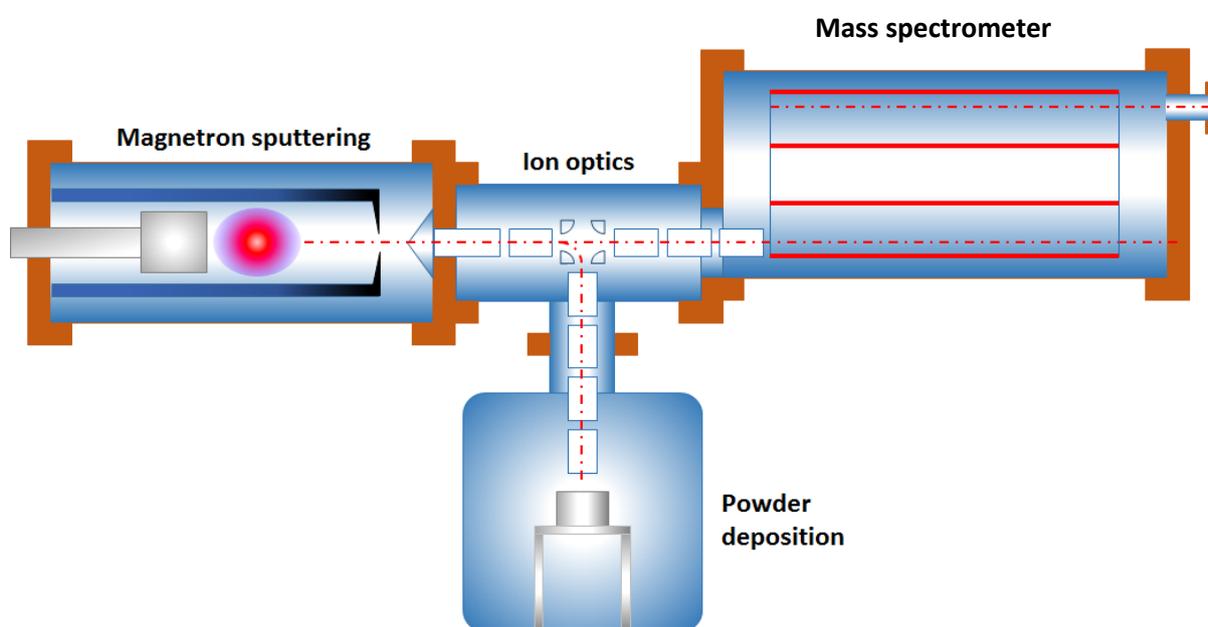


Fig. S1. Gas-phase Cluster Deposition Apparatus.

A typical synthesis used a palladium metal target (Johnson Matthey) and the same alpha alumina or titania powders as above. The system pressure was reduced and liquid nitrogen flow used to cool the magnetron sputtering chamber.

Gas flow (100 sccm, 4:1 Ar:He) is admitted to the magnetron sputtering chamber. This flow drives the movement of clusters from the sputtering chamber (0.3 mbar) into the vacuum system (0.001 mbar). Power is applied to the magnetron (5-10W) and a plasma is ignited, this sputters atoms and the gas-phase synthesis process begins.

A typical deposition used 1g of support powder, had a cluster flux of 10nA and lasted ten hours. At the end of the synthesis the catalyst was removed from the vacuum system into the air.

Characterisation Methods

Analysis of metal content was performed using ICP-ES (ion-coupled plasma-atomic emission spectroscopy) using a Perkin Elmer Optima instrument. A total digestion was performed on the sample to ensure the entire metal content was analysed.

Bright-field and dark-field Scanning Transmission Electron Microscope images were obtained using a JEOL 2800 TEM with voltage 200kV and objective aperture either 30 μ m or 50 μ m. Samples were set in resin and microtomed to give 50nm thick slices. These were ground between two glass slides before being dusted onto a holey carbon containing copper TEM grid before being presented to the microscope.

Non-Aberration Corrected dark-field images were obtained using a Hitachi HD-2000 Scanning Transmission Electron Microscope using a voltage of 200kV and objective aperture of 30 μ m. Sample preparation was as above.

Bright-field non-aberration corrected images were obtained using a Tecnai F20 Transmission Electron Microscope using a 200kV voltage, and apertures of either 30 μ m or 50 μ m.

TEM Images

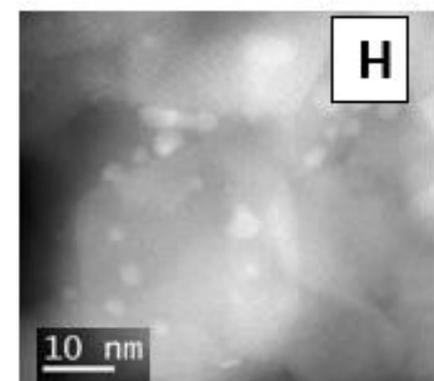
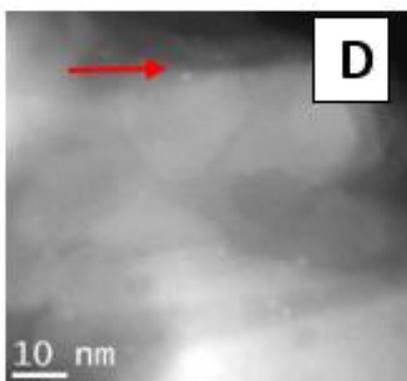
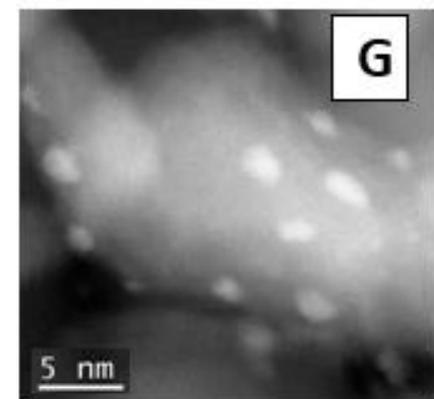
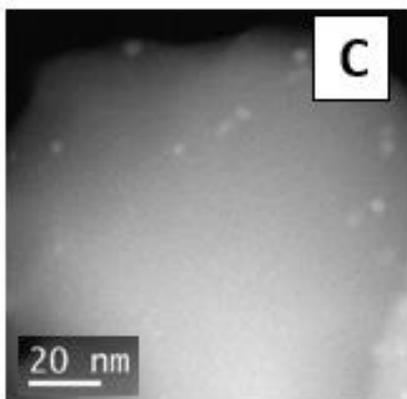
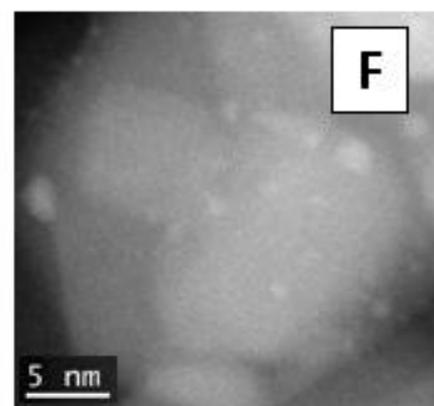
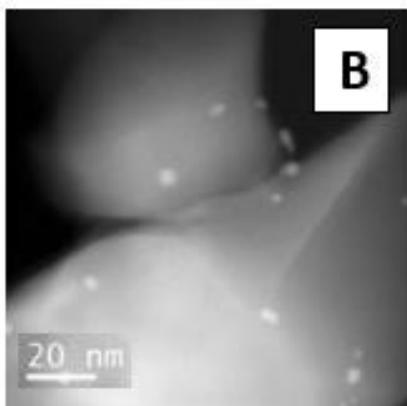
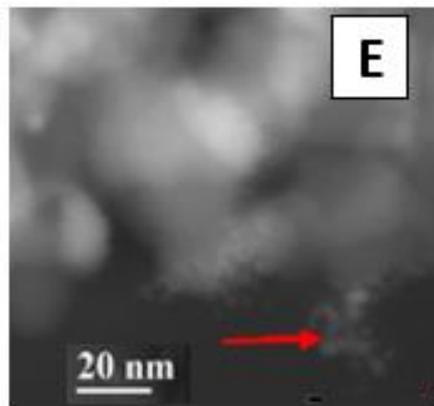
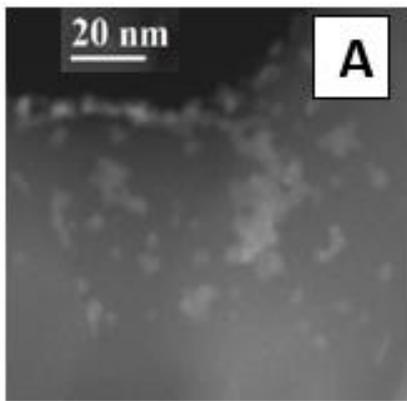


Fig. S2. Representative dark field aberration-corrected STEM images of the catalysts: Pd/ α -Al₂O₃ prepared by (A) Gas-phase cluster deposition; (B) Impregnation; (C) Deposition-precipitation (D) Ion exchange; Pd/TiO₂ prepared by (E) Gas-phase cluster deposition, (F) Impregnation, (G) Deposition-precipitation; (H) Ion exchange. In images (D) and (E), Pd particles are highlighted with arrows for clarity.

1-Pentyne Hydrogenation Catalysis

Pentyne selective hydrogenation testing was performed using a fixed bed reactor. The catalyst was held in a tube by two plugs of quartz wool. The amount of catalyst used was selected to keep the amount of palladium constant at 7.5 μ g. The catalyst was diluted with the support (either titania or alpha alumina) to make the total mass 10mg in order to maintain a constant bed size.

The gas feed consisted of 40% H₂/He at 400ml min⁻¹ and 1M pentyne solution in n-hexane with 1M iso-hexane as internal standard at 0.12ml min⁻¹. Once flushing was complete, the catalyst was heated to 240°C at 2°C min⁻¹. Analysis was performed using an online GC calibrated using standard solutions of known compounds.

To assess the gas-phase cluster deposition materials at iso-conversion with the other catalysts, they were re-tested at increased catalyst loading until the T₈₀ values were in the region of interest. The catalysts prepared by conventional routes were not re-tested. The test data for the gas-phase cluster deposition materials is shown in Fig. S3 below.

In the modified testing procedure, the mass of palladium tested and the flows of hydrogen, helium and 1-pentyne were kept constant. The gas feed was increased to 500ml min⁻¹ of 40% H₂/He and 0.12ml min⁻¹ of 1M 1-pentyne in n-hexane with 1M iso-hexane as internal standard. In these experiments the catalyst was heated to 240°C at 2°C/min, holding at 240°C for three hours to assess changes in selectivity and deactivation. Analysis was in the same manner as the standard experiments above.

Blank experiments using alpha alumina or titania powders without palladium added were performed using the standard experimental method. No 1-pentyne conversion was found for either support.

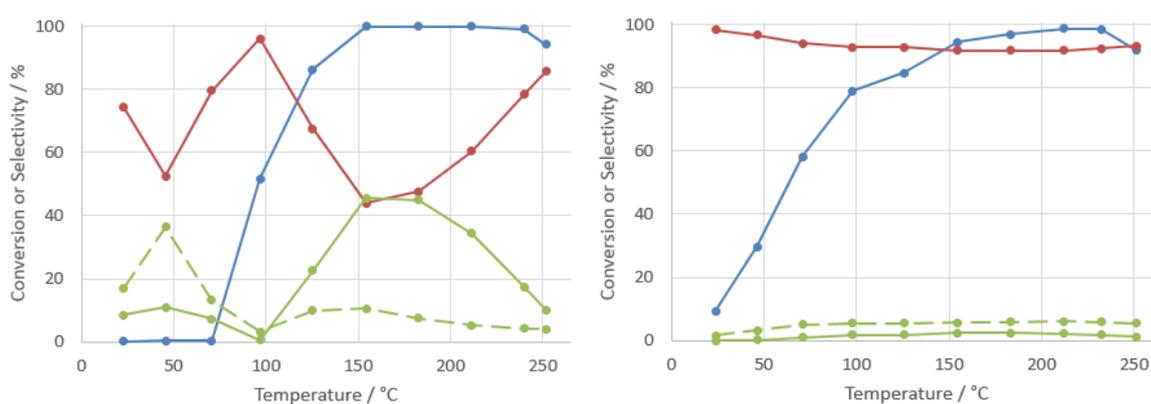


Fig. S3. Catalyst testing of Pd/alpha alumina (*left*) and Pd/titania (*right*) prepared by gas-phase cluster deposition. Charts show 1-pentyne conversion (blue), 1-pentene selectivity (red), pentane selectivity (green, dashed line) and 2-pentenes selectivity (green, solid line).

CO Oxidation Catalysis

10mg of catalyst was suspended in a quartz reactor between plugs of quartz wool. A gas of composition 1% CO/21% O₂/He was flowed over the catalyst at 65 ml/min. Once the system was purged the temperature was increased from ambient to 250°C at 5°C/min. Analysis of the products was by online NDIR analyser. Activity in CO oxidation is often compared by measuring T₅₀ values. These are presented in the Table below.

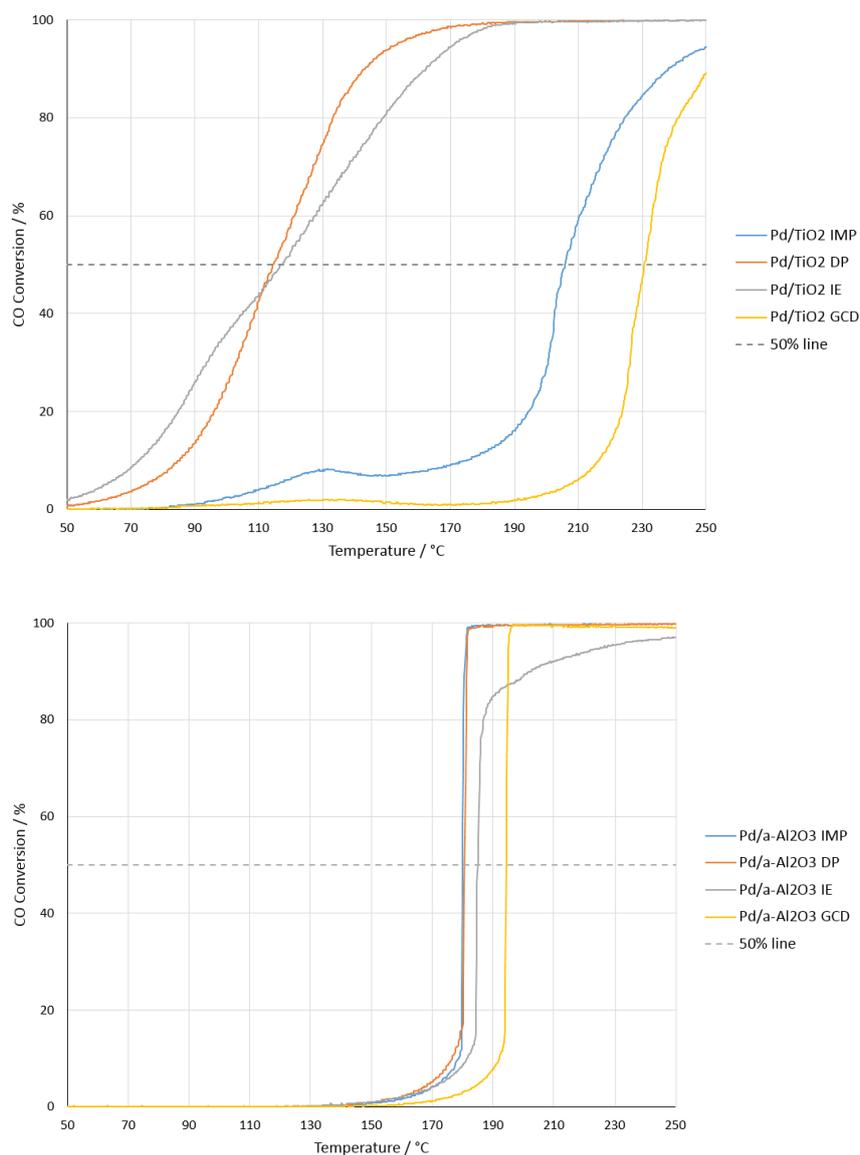


Fig. S4. CO Oxidation results for Pd/TiO₂ (*top*) and Pd/ α -Al₂O₃ (*bottom*) catalysts.

Sample		T ₅₀ /°C
Pd/TiO ₂	GCD	231
	IMP	206
	DP	117
	IE	114
Pd/ α -Al ₂ O ₃	GCD	194
	IMP	180
	DP	181
	IE	185

Table S1. CO Oxidation results for Pd catalysts. T₅₀ is the temperature at which 50% of the CO is converted.