Supplementary Materials for

Control of Metal Nanocrystal Size Reveals Metal-Support Interface Role for Ceria Catalysts

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Materials and Methods

Synthesis of Ni, Pd and Pt nanocrystals

All syntheses were performed using standard Schlenk techniques. Ni(acac)₂ (95%, Sigma-Aldrich), Pd(acac)₂ (35% Pd, Acros Organics) and Pt(acac)₂ (98%, Acros Organics) were used as metal precursors. Benzyl ether (BE, 98%), oleylamine (OLAM, 70%), trioctylphosphine (TOP, 97%) and oleic acid (OLAC, 90%) were purchased from Sigma-Aldrich and used as received. The general methodology is as follows: 150 mg of the metal salt were mixed in benzyl ether (15 mL) together with oleylamine (OLAM) and in certain cases oleic acid (OLAC) in a three-necked flask (See Table S1 for further details). The mixture was evacuated at RT for 15 minutes, the flask flushed with nitrogen and TOP was first added, then evacuated again and the mixture heated to 100 °C. The solution was left under vacuum for 30 minutes to remove all water and other impurities. At this point, green, orange or pale yellow transparent solutions (for Ni, Pd and Pt, respectively) were obtained. The reaction flask was then flushed again with nitrogen and heated very quickly (~ 40 °C min⁻¹) to the desired temperature. By adjusting the concentrations of the surfactants and the reaction temperature, monodisperse nanocrystals with a range of sizes were isolated. A change in color to black was observed at different temperatures depending on the metal, indicating the formation of metal clusters. After 15 minutes of reaction at the appropriate temperature and magnetic stirring, the solution was allowed to cool to RT. The particles were isolated by addition of isopropanol and centrifugation (8000 rpm, 3 minutes). No size selective procedures were employed. The particles were soluble in low-polar solvents (hexanes, toluene, chloroform, THF) and were finally dissolved in toluene or hexanes for further analysis. It was found that a small volume of OLAM (50 µL) was generally needed to ensure the complete redissolution of the particles. An additional benefit of this procedure is that the yields for all steps are quantitative (100 % metal yield) based on the amount of acetylacetonate precursor, unlike cases where synthesis methods give low yields due to selective fractionation steps or incomplete conversion of the precursors.

Preparation of the catalysts

An appropriate amount of metal nanocrystals (to give a final loading of 0.5 wt. % and verified by ICP-OES) dissolved in toluene was added to a dispersion of ceria (obtained by calcination of Ce(NO₃)₃ in air at 450 °C for 20 h) or alumina (Sasol TH100/150, calcined at 900 °C for 24 h) in 10 mL of toluene. Complete adsorption occurred immediately, but the mixture was left stirring overnight. The solid was recovered by centrifugation and washed twice with acetone (30 mL), with sonication and centrifugation (8000 rpm). Final powders were dried at 100 °C overnight and calcined at 300 °C for 5 h using a heating ramp of 3 °C min⁻¹.

Catalytic tests

All the experiments were conducted at atmospheric pressure. Kinetic measurements were performed in a U-shaped quartz microreactor with an internal diameter of 4 mm. The catalyst (16-32 mg) was sieved below 150 µm of grain size, mixed with alumina (Puralox TH100/150 from Sasol, received with grain size below 150 µm) and loaded into the reactor to give a bed length of about 0.5 cm, between two layers of granular quartz,
used both for preventing displacement of the catalyst powder and pre-heating the reagents. The reactor was heated by a Micromeritics Eurotherm 847 oven and the temperature of the catalyst was measured with a K-type thermocouple inserted inside the reactor and touching the catalytic bed. No appreciable conversions were found when only quartz or the bare supports (ceria and alumina) were placed in the reactor, in the range of temperatures used for this study (under our conditions, bare ceria starts to give >1 % CO conversion only above 150 °C).

The reactant mixture composition was controlled by varying the flow rates of CO, O₂ and Ar while the total flow rate was kept constant at 80 mL min⁻¹. The conditions corresponded to Gas Hourly Space Velocities (GHSV) in the range 45000-150000 mL g⁻¹ h⁻¹. Three conditions were used:

<table>
<thead>
<tr>
<th>Condition</th>
<th>CO concentration (vol. %)¹</th>
<th>O₂ concentration (vol. %)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Stoichiometric</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Rich</td>
<td>4.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

¹ Balanced with Ar.

Typical conversions of the limiting reagent were always kept well below 5 %, and most of the times below 2 %, to guarantee differential working conditions. The operating pressure was 1 atm, and the pressure drop (<0.02 atm) was neglected.

The composition of the effluent gases was monitored on-line using either a quadrupole Mass Spectrometer (MS) (Hiden Analytical HPR20) equipped with a Secondary Electron Multiplier (SEM) detector or a Gas Chromatograph (GC) (Buck Scientific 910). In the case of MS analysis, this detector was used to follow the parent molecular ions for CO (28 amu), O₂ (32 amu) and CO₂ (44 amu). The CO signal was corrected for the contribution from the cracking pattern of CO₂. In the case of GC analysis, a Thermal Conductivity Detector (TCD) was employed using He as the carrier gas.

Prior to measuring rates, each catalyst was cleaned under a flow of O₂ (5%) in Ar at 40 mL min⁻¹ for 15 minutes at 250 °C, after heating from room temperature at 10 °C min⁻¹. Then, the sample was cooled to 150 °C and reduced under a flowing mixture of H₂ (5%) in Ar at 40 mL min⁻¹ for 15 minutes. After cooling the sample to room temperature, the reactant mixture was then introduced, and when a stable CO₂ production was observed the reactor was heated up to the desired temperature at 3 °C min⁻¹. Reaction rates were calculated on the basis of the accessible metal surface area calculated from CO chemisorption measurements (see below).

Characterization techniques

Bright-field TEM characterization was performed using a JEOL JEM-1400 microscope operating at 120 kV. Samples were either drop-cast onto TEM grids from concentrated toluene solutions, or subjected to a self-assembly at the liquid-air interface as previously reported (13) using diethylene glycol as the subphase.

Aberration-corrected HR-TEM images were recorded on a FEI Titan equipped with an objective-lens aberration corrector and aberration-corrected HAADF STEM images
and EELS maps were recorded using a probe-corrected Hitachi HD2700C dedicated STEM, both at the Center for Functional Nanomaterials, Brookhaven National Laboratory. Pd(0.5 wt%)/CeO₂ catalyst samples were dissolved in 2-propanol and drop casted onto 400-mesh copper grids coated with lacey Formvar, purchased from Ted Pella. To reduce high-intensity beam effects, the images were recorded at 80 kV in the TEM. At this voltage, no remarkable changes in particle size and shape were noticed during the investigations. The STEM images were obtained at 200kV, and the inherently lower dose of the STEM acquisition again leads to no remarkable changes in particle size and shape during imaging.

¹H-, ¹³C- and ³¹P-NMR spectra were obtained at 25 °C as CDCl₃ solutions on a Bruker DMX 300 operating at 300 MHz for proton.

XRD patterns were obtained on a Rigaku Smartlab diffractometer. Powder XRD patterns were measured in the 2θ range of 20-80 ° (Cu Kα radiation, λ = 1.5418 Å), and samples were prepared by depositing a thick film of the particles from hexanes solution on a glass substrate. Transmission Small Angle X-ray Scattering (SAXS) experiments were performed on toluene solutions of the nanocrystals loaded into a 1.0 mm glass capillary and the patterns were fitted using NANO-Solver (Rigaku software).

Quantitative elemental analysis was performed on an ICP-OES Spectro Genesis system, for each sample the supported metals were dissolved in aqua regia and diluted prior to measurement.

CO chemisorption experiments were carried out on a Micromeritics ASAP 2020C. The samples were placed in a U-shaped quartz reactor, heated in flowing O₂ (5%) in Ar at 250 °C for 1 h and reduced in flowing H₂ (5%) in Ar at 300 °C for 1 h, and then evacuated at 300 °C for 4 h. CO chemisorption experiments were performed at 35 °C either in the low pressure range (2-20 torr) for CeO₂-based systems or in the high-pressure range (100-400 torr) for Al₂O₃-based systems, using a double isotherm to remove the contribution from physisorption. Adsorption values were obtained by linear extrapolation to zero pressure.

Before each temperature programmed reduction (TPR) experiment, the samples were pre-treated in flowing O₂ (5%) in Ar mixtures at 250 °C. The measurements were performed in a conventional system equipped with a thermal conductivity detector (TCD), under H₂ (5%) in Ar mixtures, using a gas flow rate of 25 mL min⁻¹ and a heating rate 10 °C min⁻¹. CO-TPR experiments were performed using a MS (Hiden HPR20) as the detector.

Physical model

The physical model we use is similar to what has been described elsewhere (17-18). The most representative morphology observed by microscopy after calcination and reaction was utilized for each metal. For Pd and Pt clusters, a cuboctahedral model was used, while for Ni it was a spherical model. Although the particles were initially deposited as spheres, the calcination treatment leads to the spread of the particles onto the support with a consequent increase of the average size of the particles (measured as the longest possible distance), but the size dispersity is maintained. In the case of Ni, the formation of hollow spheres increased the average particle size but the final particles were found to contain the same amount of metal as the starting particles. In this case, it was assumed that only the atoms in contact with the support were relevant for the
catalytic reaction and were counted in the model. The model particles were prepared with Accelrys Materials Studio 4.4, using the bulk metal lattice constants (0.352, 0.389 and 0.392 nm for Ni, Pd and Pt respectively). The model particles were built with the appropriate dimensions as obtained from the TEM analysis of the calcined samples. No appreciable differences in particle size and shape were found after the reaction. The fraction of corner, perimeter and surface sites were calculated from the models. The corner atoms are designated as those with coordination number equal to 4 and directly in contact with the support.
Scheme S1.

Schematic representation of the procedure followed in this work: preparation of monodisperse group VIII metal nanocrystals with different average particle sizes, deposition onto alumina and ceria, calcination to remove the organic surfactants and catalytic testing for CO oxidation.
Fig. S1.

Representative TEM images of Ni (A, B, C), Pd (D, E, F) and Pt (G, H, I) metal nanocrystals. Images A, D and G correspond to small particles, B, E and H to medium and C, F and I to large, respectively (see text for further details).
Transmission small-angle X-ray scattering (TSAXS, left) and wide-angle X-ray diffraction (XRD, right) patterns of Pd nanocrystals of different average dimensions. The TSAXS patterns were successfully fitted to a spherical model with a size distribution of ~6 %.
Fig. S3.

Representative HAADF STEM images of Ni/Al$_2$O$_3$ (A-C), Pd/Al$_2$O$_3$ (D-F), Pt/Al$_2$O$_3$ (G-I) and Pt/CeO$_2$ (L-N) samples after calcination to 300 °C for 5 hours. Column A-L represents Small particle size, column B-M Medium and columns C-N Large.
Representative example of how the Pd signal is extracted during EELS mapping in the STEM mode for the sample Pd/CeO$_2$-Large after calcination. A) HAADF-STEM image as acquired. B) Two Pd particles appear much brighter after taking the signal coming from the Pd region of the EELS spectrum (C). This technique was applied to Ni/CeO$_2$ and Pd/CeO$_2$ samples to determine average particle size and size distribution after calcination of the samples.
Fig. S5.

Average particle size as determined by TEM on Ni, Pd or Pt samples after deposition and calcination on Al₂O₃ (A) or CeO₂ (B). Inset: histograms of particle size distribution for Pt samples (S, M, L: Small, Medium and Large samples, respectively).
Fig. S6.

ETEM images of Pd/CeO$_2$ samples (A, B: Small; C, D: Medium; E, F: Large) after in-situ heating under air at 300 °C for 2 h.
Additional representative HR-STEM images of calcined Pd/CeO$_2$-Large (A, B and C) and Pd/Al$_2$O$_3$-Large (D, E and F).
Effect of pre-treatments on the activity of Pd(0.5%)/CeO$_2$-Small catalyst. Red squares: catalyst calcined at 300 °C for 5 h and pre-reduced under H$_2$(5%)/Ar at 150 °C for 15 minutes; blue triangles: catalyst calcined but not pre-reduced; orange circles: catalyst not calcined but pre-reduced. Reduction of all the ceria catalysts in hydrogen mixtures before reaction was found to be necessary for obtaining the best results, indicating that metallic phases are needed to coordinate and activate CO and that at low temperatures. The uncalcined catalysts, even if pre-reduced, were found to be inactive for the reaction because organic ligands hampered the surface of the metals from adsorbing CO. Alumina catalysts, furthermore, were found to be unaffected by a pre-reduction treatment.
Rates for CO oxidation for Pt/CeO₂-Small catalyst measured as pure powder or diluted with inert alumina at 1/3 and 1/10 w/w ratios (stoichiometric conditions, GHSV = 150,000 mL g⁻¹ h⁻¹). The CO oxidation was not affected by dilution even to higher ratios, demonstrating that the kinetic measurements were not affected by thermal or mass diffusion limitations.
Reaction orders for CO and O₂ for Pt-Small systems; top, ceria; bottom; alumina.
GHSV = 150,000 mL g⁻¹ h⁻¹.
Fig. S11.

Apparent activation energies for M/CeO$_2$ and M/Al$_2$O$_3$ for CO oxidation.
Fig. S12.

Light-off curves for CO oxidation on Ni, Pd or Pt (0.5 wt. %) on Al₂O₃ (A) or CeO₂ (B).
Calculated number of sites with a particular geometry (surface and perimeter or corner atoms in contact with the support) as a function of diameter (left) and TOFs at 80 °C of the nine ceria-based samples under the three conditions investigated in the present work (right).
Kinetic data for CO oxidation on M(0.5 wt. %) on CeO$_2$ under lean (A), stoichiometric (B) and rich (C) conditions.
Fig. S15.

Apparent activation energies for M/CeO$_2$ catalysts for CO oxidation under the three conditions investigated in this work.
### Table S1. Reaction conditions used in this work for the synthesis of the different group VIII metal nanocrystals and average particle sizes and size distributions obtained by TEM analysis.

<table>
<thead>
<tr>
<th>Label</th>
<th>Precursor</th>
<th>TOP (eq.)(^a)</th>
<th>OLAM (eq.)(^a)</th>
<th>OLAC (eq.)(^a)</th>
<th>Temperature (°C)</th>
<th>Average size (nm)</th>
<th>Size dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Small</td>
<td>Ni(acac)(_2)</td>
<td>150</td>
<td>150</td>
<td>-</td>
<td>230</td>
<td>4.0</td>
<td>4</td>
</tr>
<tr>
<td>Ni-Medium</td>
<td>Ni(acac)(_2)</td>
<td>10</td>
<td>20</td>
<td>-</td>
<td>230</td>
<td>8.5</td>
<td>4</td>
</tr>
<tr>
<td>Ni-Large</td>
<td>Ni(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>-</td>
<td>230</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Pd-Small</td>
<td>Pd(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>-</td>
<td>250</td>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>Pd-Medium</td>
<td>Pd(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>-</td>
<td>270</td>
<td>3.9</td>
<td>6</td>
</tr>
<tr>
<td>Pd-Large</td>
<td>Pd(acac)(_2)</td>
<td>10</td>
<td>20</td>
<td>-</td>
<td>290</td>
<td>6.3</td>
<td>5</td>
</tr>
<tr>
<td>Pt-Small</td>
<td>Pt(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>-</td>
<td>290-300(^b)</td>
<td>1.6</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Medium</td>
<td>Pt(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>5</td>
<td>290-300(^b)</td>
<td>2.3</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Large</td>
<td>Pt(acac)(_2)</td>
<td>2.5</td>
<td>10</td>
<td>20</td>
<td>290-300(^b)</td>
<td>2.9</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\) Molar ratio surfactant / metal precursor.
\(^b\) Reflux of the solution occurred as the reaction proceeded.
Table S2. Apparent dispersion, exposed metallic surface area and average particle size measured by CO chemisorption at 35 °C on the different catalysts.

<table>
<thead>
<tr>
<th></th>
<th>CeO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D (%)</td>
<td>S (m² g⁻¹)</td>
</tr>
<tr>
<td>Ni Small</td>
<td>28</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni Medium</td>
<td>14</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni Large</td>
<td>8</td>
<td>0.13</td>
</tr>
<tr>
<td>Pd Small</td>
<td>44</td>
<td>0.92</td>
</tr>
<tr>
<td>Pd Medium</td>
<td>31</td>
<td>0.69</td>
</tr>
<tr>
<td>Pd Large</td>
<td>19</td>
<td>0.42</td>
</tr>
<tr>
<td>Pt Small</td>
<td>68</td>
<td>0.80</td>
</tr>
<tr>
<td>Pt Medium</td>
<td>53</td>
<td>0.62</td>
</tr>
<tr>
<td>Pt Large</td>
<td>39</td>
<td>0.46</td>
</tr>
</tbody>
</table>

*a Average apparent metal dispersions.
*b Exposed metallic surface area per gram of catalyst.
*c Average diameter calculated assuming a truncated cuboctahedral particle shape.