Combined in situ XAFS/DRIFTS Studies of the Evolution of Nanoparticle Structures from Molecular Precursors.

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ABSTRACT: The rational design of catalyst materials is of great industrial significance, yet there is a fundamental lack of knowledge in some of the most well-established processes e.g. formation of supported nanoparticle structures through impregnation. Here, the choice of precursor has a significant influence on the resulting catalytic properties of the end material, yet the chemistry that governs the transformation from defined molecular systems to dispersed nanoparticles is often over-looked. A spectroscopic method for advanced in situ characterization is employed to capture the formation of PdO nanoparticles supported on γ-Al₂O₃ from two alternative molecular precursors; Pd(NO₃)₂ and Pd(NH₃)₄(OH)₂. Time resolved DRIFTS is able to identify the temperature assisted pathway for ligand decomposition, showing that NH₃ ligands are oxidised to N₂O and NO- species, whereas, NO₃- ligands assist in joining Pd centres via bidentate bridging coordination. Combining with simultaneous XAFS, the resulting nucleation and growth mechanism of the precious metal oxide nanoparticles are resolved. The bridging ability of palladium nitrate aids formation and growth of larger PdO nanoparticles at lower onset temperature (<250 °C). Conversely, impregnation from [Pd(NH₃)₄]²⁺ results in well isolated Pd centres, anchored to the support, which require higher temperature (>360°C) for migration to form observable Pd-Pd distances of PdO nanoparticles. These smaller nanoparticles have improved dispersion and an increased number of step and edge sites compared to those formed from the conventional Pd(NO₃)₂ salt, favouring a lower light off temperature for complete methane oxidation.

INTRODUCTION

Supported metal nanoparticles are a cornerstone of heterogeneous catalysis, and by extension, the chemical industry. Optimising the preparation method for smaller nanoparticle size and improved dispersion is a common theme in heterogeneous catalyst design; to improve specific surface area, lower precious metal content and increase metal-support interfacial regions, whilst maintaining thermostability towards sintering. There are various methods for the preparation of supported metal catalysts such as controlled colloidal routes, deposition precipitation, grafting techniques and atomic deposition; all of which result in nanoparticle materials with differing properties. Despite these efforts, the conventional route of incipient wetness impregnation is regarded as a reliable route, taking advantage of accessible precursor materials (inorganic metal salt), in a one-step batch process that can be scaled up for industrial production. Adjustments to the impregnation method by using alternative metal precursors result in differing properties of the final nanoparticle catalyst, together with any changes to temperature and atmospheric conditions of the proceeding drying and calcination steps. The amphoteric nature of common metal oxide supports
means that the pH of the impregnating solution is an important factor. Charged surface sites (eg. Al-O or Al-OH) can be created when the pH is above or below the iso-electric point of the support, which allow the impregnation of metal salts to occur via ion exchange or ligand substitution mechanisms.\(^8\) Nanoparticles prepared from chloride containing precursors are found to suffer from residual Cl\(^-\) blocking surface catalytic sites.\(^9\)\(^10\) Whereas organic precursors such as acetate or acetylacetone, as well as ammonia containing salts and nitrate precursors, have been reported to yield greater dispersion over the support.\(^6\)\(^9\)\(^11\) Despite investigations into the influence of preparation methods on the final metal dispersion and catalytic activity,\(^7\)\(^10\)\(^12\) there is often lack of evidence and reasoning for the chemical processes that govern the nanoparticle formation.

In this study, genesis of PdO nanoparticles from two different impregnated Pd precursors, Pd(NO\(_3\))\(_2\) and Pd(NH\(_2\))\(_2\)(OH)\(_2\) are investigated. The development of PdO nanoparticles on high surface area γ-Al\(_2\)O\(_3\) has been studied extensively for a number of catalytic applications; CO oxidation,\(^14\) H\(_2\)O\(_2\) synthesis,\(^15\) upgrading bio-oils\(^16\) and automotive three way catalysts.\(^7\) Of recent industrial interest is the use of Pd/γ-Al\(_2\)O\(_3\) in catalysing low temperature methane oxidation for the clean and efficient operation of compressed natural gas engines (CNGs).\(^18\)\(^21\) Mechanistic studies propose the oxidation of CH\(_4\) to occur on reducible PdO nanoparticle surface, close to the Al\(_2\)O\(_3\) interface where oxygen migration from the support can assist in re-oxidation of the Pd nanoparticle surface via a Mars-Van Krevelen mechanism.\(^21\) Therefore the preparation of Pd/γ-Al\(_2\)O\(_3\) with greatest dispersion of PdO for increased interfacial contact with the support is most desirable.

The advantage of synchrotron based techniques applied to investigate industrial catalyst preparation is highlighted in work by L. Espinosa-Alonso et al. for the formation of supported Ni materials.\(^22\) In this study, by combining two non-invasive, time-resolved spectroscopic techniques, the surface and bulk properties of the precursor materials are probed, in situ, under a controlled calcination environment. While diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) is used to follow the vibrational modes of adsorbed and coordinated inorganic molecular species at the surface, X-ray absorption fine structure (XAFS) is used to follow the local coordination environment and oxidation state of Pd throughout the bulk of the sample. Using both techniques at the same time, with on-line mass spectrometry of the effluent gas, gives the advantage of confidently assigning features that change with response to sample environment and allow interpretation of the mechanisms involved in ligand decomposition and metal nanoparticle formation.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Two 3wt% Pd/γ-Al\(_2\)O\(_3\) catalysts were prepared by incipient wetness impregnation of an aqueous solution of Pd salt onto a γ-Al\(_2\)O\(_3\) support (SASOL), followed by calcination (500°C, 2 hours). The first sample was prepared from an acidified aqueous solution of palladium nitrate (15.11 wt% Pd, Johnson Matthey) and a defined quantity of HNO\(_3\) corresponding to a molecular ratio NO\(_3\)/Pd = 3.8. The second sample was prepared from an aqueous solution of tetraamminepalladium(II) hydroxide (5.96 wt% Pd, Johnson Matthey), prepared by dissolution of tetraamminepalladium hydrogen carbonate (Johnson Matthey, 99.99%) in aqueous NH\(_3\)OH solution (28 wt%). Incipient wetness impregnations were realised at room temperature with calculated quantities of respective aqueous Pd solutions in order to obtain 3 wt% Pd catalysts. The impregnated precursors catalyst samples Pd(NO\(_3\))\(_2\)/γ-Al\(_2\)O\(_3\) and Pd(NH\(_2\))\(_2\)(OH)\(_2\)/γ-Al\(_2\)O\(_3\) were subsequently dried at 100°C overnight.

**In situ XAFS/DRIFTS Measurements.** In situ XAFS and DRIFTS measurements were conducted at BII, Diamond Light Source, Didcot, UK, of the impregnated, dried precursor samples during the calcination procedure using the modified Harrick DRIFTS cell. A DaVinci arm fitted with praying mantis optics was used to refocus the IR beam outside the FTIR spectrometer for positioning of the Harrick DRIFTS cell in the X-ray beam. The Harrick XAFS/DRIFTS cell which has been used and reported previously,\(^23\) has an X-ray path length of 3.17 mm positioned 1.04 mm below the surface of the catalyst bed. The sample was heated to 500°C (10°C min\(^{-1}\) under a constant controlled flow of air (30 ml min\(^{-1}\)), maintained at 500°C for a 2-hour dwell period, before being cooled back to room temperature. XAFS and DRIFTS spectra were recorded continuously throughout this period and the effluent gas was monitored on-line by a Hiden QGA mass spectrometer. XAFS measurements were performed at the Pd K-edge in transmission mode using QEEXAFS setup with a fast scanning Si(311) double crystal monochromator. All XAFS spectra were acquired with a Pd foil placed between I\(_t\) and I\(_{ref}\) and the time resolution was 21 sec spectrum\(^{-1}\) (k\(_{min} = 15.9\)). DRIFTS spectra were collected with an Agilent Carey 680 FTIR spectrometer taking 64 scans with a resolution of 4 cm\(^{-1}\) using the liquid nitrogen cooled MCT detector. The time resolution of DRIFTS were 30 sec spectrum\(^{-1}\).

**EXAFS Analysis.** Processing Extended X-ray Absorption Fine Structure (EXAFS) data was performed using IFEFFIT with the Horae package (Athena and Artemis). Athena was used to calibrate, align and normalise the spectra with respect to the Pd foil, for which E\(_0\) was set at 24358 eV. EXAFS data processing of k\(^2\) data used an appropriate k range for the data (3.2 to 13.4 Å\(^{-1}\)). Analysis of the Fourier transformed data was limited to fitting with the first two coordination shells (denoted Pd(0), PdO(O), PdN(N), PdO(O), Pd(Pd) and PdO(Pd)) using cif files of Pd(NO\(_3\))\(_2\) and PdO. The amplitude reduction factor, S\(^2\), was derived from fitting the Pd foil using a coordination number of 12, to give a value of 0.8. The value of σ\(^2\), the mean square relative displacement of absorber and backscatter atoms, is known to increase with temperature.\(^24\) Consequently, the linear dependence
of σ° with temperature was fitted using non-phase corrected Fourier transformed Pd K-edge data collected of the calcined PdO/γ-Al₂O₃ between 500°C to 20°C, where all other parameters (dehr and Sₖ) are assumed to be fixed. This variance in σ° with temperature, reported in Figure S1 of the Supporting Information, was used to fix σ° for the fitting of the EXAFS data collected during the calcination temperature ramp period.

**Ex situ Characterisation.** Thermogravimetric analysis has been carried out in a TA thermogravimetric analyser (instrument Q500/DSC Auto Q20), with a sample mass of 10 mg placed in a platinum crucible under continuous flow of 40% N₂ and 60% air, and ramped at 10°C min⁻¹. TEM images of the samples were obtained using a JEM JEM 2100 transmission electron microscope. Samples were prepared for TEM analysis by dispersing in high-purity ethanol using ultrasonication. 10 μL of the sonicated suspension were pipetted onto a holey carbon supporting Cu grid and the solvent evaporated. Ex situ Pd K-edge XAFS spectra of the calcined catalyst samples after reducing in H₂ (at 100°C) were taken in transmission mode on B8 at Diamond Light Source. CO chemisorption of the calcined catalyst samples were performed with FTIR analysis in transmission mode. Samples (20 mg) were pressed into self-supporting wafers (1.35 cm²), mounted in the transmission FTIR cell and dried at 100°C under constant flow of He. Several pulses of CO were introduced into the cell until saturation. The CO adsorption FTIR spectra were recorded (40 – 4500 cm⁻¹, 4 cm⁻¹ resolution) after purging the cell with He (15 minutes). Raman spectra were recorded using a Bruker Senterra microscope at B22, Diamond Light Source, using 532 nm laser at 5 mW. XRD diffraction patterns were collected using a Rigaku Miniflex diffractometer (ISIS Materials Characterisation Lab) with a 600 mW Cu tube source operated at 45 kV and 15 mA and using a 1D Si strip detector. Sherrer calculations of the average crystallite sizes used the full width half maximum of these peaks indicates the relative crystallite size of the observed PdO particles as per the Sherrer equation. Smaller intensity and increased broadening of PdO diffraction peaks for Pd/γ-Al₂O₃-Al(NO₃)₃ suggests this sample has smaller PdO crystallite size of 6 nm compared to 11 nm for Pd/γ-Al₂O₃-Al(NO₃). Further evidence for PdO structure is indicated by the presence of larger agglomerated particles (>15nm) observed only for Pd/γ-Al₂O₃-Al(NO₃), as shown clearly in the corresponding histogram of particle size distribution. Although only 5% of the 100 measured particles have a diameter greater than 15 nm, this is significant when considering the mass fraction of Pd located at the core of larger particles rather than contributing to catalysis at the surface.

**RESULTS AND DISCUSSION**

**Ex situ characterisation.** Two 3wt% PdO catalysts supported on γ-Al₂O₃ were prepared by the impregnation and calcination from Pd(NO₃)₂ and Pd(NH₃)₄(OH)₂ to give catalysts Pd/γ-Al₂O₃-Al(NO₃)₃ and Pd/γ-Al₂O₃-Al(NO₃). TEM images of the calcined catalysts (Figure 1) show dark Pd nanoparticles dispersed upon the contrasting lighter coloured γ-Al₂O₃ support. Particle size analysis conducted over 100 measured particles revealed smaller average particle diameter (3.1 nm) for catalyst Pd/γ-Al₂O₃-Al(NO₃) compared to Pd/γ-Al₂O₃-Al(NO₃) (4.4 nm). This is consistent with the presence of larger agglomerated particles (>15nm) observed only for Pd/γ-Al₂O₃-Al(NO₃), as shown clearly in the corresponding histogram of particle size distribution. Although only 5% of the 100 measured particles have a diameter greater than 15 nm, this is significant when considering the mass fraction of Pd located at the core of larger particles rather than contributing to catalysis at the surface.

![Figure 1. Particle size histogram and representative image of (A) Pd/γ-Al₂O₃-Al(NO₃) and (B) Pd/γ-Al₂O₃-Al(NO₃).](image)

X-ray diffraction patterns of both calcined catalyst samples show diffraction peaks assigned to cubic γ-Al₂O₃ (JCPDS card no. 06-004-1290) similar to that of the fresh support, labelled with arrows in Figure 2, proving that structural integrity of the support is maintained after impregnation. Additional diffraction peaks located at 2θ angles of 42.6, 55.6 and 72.7°, labelled with asterisks in Figure 2, can be attributed to crystalline domains of tetragonal PdO (JCPDS card no. 06-004-1432). The full width half maximum of these peaks indicates the relative crystallite size of the observed PdO particles as per the Sherrer equation. Smaller intensity and increased broadening of PdO diffraction peaks for Pd/γ-Al₂O₃-Al(NO₃) suggests this sample has smaller PdO crystallite size of 6 nm compared to 11 nm for Pd/γ-Al₂O₃-Al(NO₃). Further evidence for PdO structure is indicated by the Raman spectra of Pd/γ-Al₂O₃-Al(NO₃) and Pd/γ-Al₂O₃-Al(NO₃), (Supporting Information, Figure S2), which show well resolved bands positioned at 439 and 640 cm⁻¹ associated with Raman active E₀ and B₄g vibrational modes of PdO, respectively, in a PdO lattice. Difference in the respective peak area of the B₄g band (averaged from 6 spectra taken at different positions over each sample) measures for a greater number of Pd-O vibrations from Pd/γ-Al₂O₃-Al(NO₃) compared to Pd/γ-Al₂O₃-Al(NO₃), again indicating larger PdO crystallite size for Pd/γ-Al₂O₃-Al(NO₃).
Table 1. Calcined Pd/γ-Al₂O₃ catalyst characterisation; TEM average particle size, EXAFS average particle size, XRD PdO crystallite size, linear/bridged ratio (CO adsorption FTIR), and temperature required to achieve 50% CH₄ conversion during lean CH₄ oxidation catalytic test (Tₜ₀).

<table>
<thead>
<tr>
<th></th>
<th>Average Particle Size / nm</th>
<th>PdO Crystallite Size (XRD) / nm</th>
<th>L/B ratio (CO FTIR)</th>
<th>Tₜ₀ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEM</td>
<td>EXAFS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/ γ-Al₂O₃-ex(NO₃)</td>
<td>4.4</td>
<td>2.7(6)</td>
<td>11</td>
<td>394</td>
</tr>
<tr>
<td>Pd/ γ-Al₂O₃-ex(NH₃)₂(OH)₂</td>
<td>3.1</td>
<td>1.1(1)</td>
<td>6</td>
<td>385</td>
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CO used as a probe molecule in FTIR adsorption experiments can be used to investigate surface adsorption properties of the catalyst materials. Linear and bridge bonding of CO adsorbed on both Pd/γ-Al₂O₃ samples have been identified by the sharp band at 2071 cm⁻¹ and the broad band between 1869 and 1830 cm⁻¹, respectively (Figure 3b). The significant difference in intensity of CO adsorption bands from the two catalyst samples is consistent with Pd/γ-Al₂O₃-ex(NH₃) having larger surface area due to smaller particle size. Additionally, the type of surface sites that can be clarified from the relative linear to bridge bonding adsorption band intensity ratio, reported in Table 1. The greater ratio of linear to bridge bonded CO on Pd/γ-Al₂O₃-ex(NH₃) is indicative of a rough Pd surface with greater number of step and edge sites. The discrepancy between average particle size calculated by the different methods, reported in Table 1, is not surprising. The TEM is limited to the resolution and field of view of the microscope, XRD is limited to assess particles with sufficiently large crystalline domains, while EXAFS probes all Pd species in the sample. Despite these differences, there is consistent evidence for Pd/γ-Al₂O₃-ex(NH₃) providing smaller average PdO crystallite size and greater dispersion over the support compared to Pd/γ-Al₂O₃-ex(NO₃). Light off curves for CH₄ conversion, (Supporting Information, Figure S4), confirm that the catalyst with improved dispersion and smaller particle size, Pd/γ-Al₂O₃-ex(NH₃) is able to catalyse the complete oxidation of methane at lower temperature than the catalyst that possessing some larger agglomerated particles, Pd/γ-Al₂O₃-ex(NO₃).
In situ XAFS/DRIFTS of the Preparation Route. Pd K-edge EXAFS analysis of the impregnated precursor samples, Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$ and Pd(NH$_3$)$_2$(OH)$_2$/γ-Al$_2$O$_3$ gave structural information of the initial Pd coordination environment after impregnation onto the γ-Al$_2$O$_3$ at room temperature. The $k^2$ weighted χ($k$) EXAFS spectrum of the impregnate Pd(NH$_3$)$_2$(OH)$_2$/γ-Al$_2$O$_3$ compares closely to that of the unsupported aqueous Pd(NH$_3$)$_2$(OH)$_2$(aq) solution (Figure 4a). Conversely, the $k^2$ weighted χ($k$) EXAFS spectra of the impregnated precursor Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$ shows greater long range structure from EXAFS oscillations extending to greater $k$ range (~10.4 Å$^{-1}$), with additional scattering feature at 9 Å$^{-1}$ (annotated with an asterisk in Figure 4b), that is absent from the χ($k$) EXAFS spectrum of the unsupported Pd(NO$_3$)$_2$(H$_2$O)$_3$/γ-Al$_2$O$_3$ reference. A simple fitting model was constructed from one calculated scattering path representative of four light atomic neighbouring atoms (145 atomic number, Z = 6), located at 2.049 Å from the absorbing Pd atom. This model was sufficient to fit the Fourier transformed EXAFS data of unsupported Pd(NH$_3$)$_2$(OH)$_2$(aq) and impregnated Pd(NH$_3$)$_2$(OH)$_2$/γ-Al$_2$O$_3$ (Figure 4c), showing that the Pd coordination centre in each case is coordinated to four oxygen or nitrogen atoms of ammonia, hydroxyl or water ligands with little or no longer range structure, consistent with a [Pd(NH$_3$)$_2$]$_2$ complex. This model was, however, inadequate to fit that of the impregnated Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$. In this case, additional structure observed in the EXAFS data requires an additional scattering path to refine the EXAFS fitting model to this sample. A refined fit to Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$ displayed as the red dashed line of Figure 4d, includes an additional scattering contribution from neighbouring Pd atoms located 3.43 Å from absorbing Pd. This is the distance to a Pd atom in a second coordination shell from the absorbing Pd, which corresponds to neighbouring Pd centres adjoined by bridging ligand coordination. It is noted that such a Pd distance (3.43 Å) is close to that of the second coordination shell Pd atom in the crystal structure of tetrahedral PdO.

DRIFTS spectra of both precursor samples before calcination are reported in Figure 5a. The broad band centred at 3500 cm$^{-1}$ can be assigned to symmetric and antisymmetric O-H stretching vibrations of lattice water, and a sharp band at 1420 cm$^{-1}$ is assigned to carbonate ions on the oxide support. Loss of these absorption bands indicate removal of H$_2$O and CO$_3^{2-}$ upon heating to 200°C. The intensity of the FTIR absorption bands in the spectral range 1250 – 1800 cm$^{-1}$ during the calcination temperature ramp are shown as a colour map in Figure 5b. The nitrate species of sample Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$ can be identified by two molecular vibrational bands of N=O stretching between 1650 and 1500 cm$^{-1}$, and O-N-O asymmetrical stretching between 1350 and 1200 cm$^{-1}$. Consistent with the calculated N=O stretching frequency of bridging nitrates on an Al$_2$O$_3$ surface. Comparison with the DRIFTS spectra of the unsupported Pd(NO$_3$)$_2$(H$_2$O)$_3$/γ-Al$_2$O$_3$ precursor and an acid treated γ-Al$_2$O$_3$/HNO$_3$ (Supporting Information, Figure S5) shows the O-N-O asymmetrical stretching of nitrate coordinated to Pd$^{2+}$ and γ-Al$_2$O$_3$ as absorption bands at 1320 cm$^{-1}$ and 1300 cm$^{-1}$, respectively. This indicates that the broad character of the O-N-O stretching band of Pd(NO$_3$)$_2$/γ-Al$_2$O$_3$ results from nitrate coordinated to both the Pd$^{2+}$ cation and Lewis acid Al$^{3+}$ sites of the γ-Al$_2$O$_3$. Beyond 100°C the broad band initially centred at 1300 cm$^{-1}$ begins to narrow and shift to lower frequency until it is centred at 1270 cm$^{-1}$ by 200°C. The nitrate band previously centred at 1510 cm$^{-1}$ also broadens and shifts over the same temperature range but towards higher wavenumbers, until it is centred at 1570 cm$^{-1}$ by 200°C (annotated by arrows, Figure 5b). The shift in nitrate bands to greater...
separation is consistent with increased bidentate nitrate coordination to a metal centre.\textsuperscript{38} The early pre-association of Pd species of Pd(NO$_3$)$_2/\gamma$-Al$_2$O$_3$, as indicated from EXAFS, can therefore also be supported by the DRIFTS spectra which provide evidence for neighbouring Pd centres to be linked by bridging nitrate coordination.

DRIFTS spectra of the precursor sample Pd(NH$_3$)$_4$(OH)$_2/\gamma$-Al$_2$O$_3$ at room temperature show H-N-H vibrational modes of surface NH$_3$ species as bands at 1490 cm$^{-1}$ and 1345 cm$^{-1}$. Upon increasing temperature, the position of the bands remain but also show steady decrease in intensity until complete removal by 225°C. The detection of N$_2$O in the effluent gas by mass spectrometry up to this temperature (Supporting Information, Figure S6b) shows that the NH$_3$ species are oxidised before leaving the chamber, consistent with previously reported catalytic activity for low temperature NH$_3$ oxidation at Pd surface. Following the removal of NH$_3$, weak intensity absorption bands for N=O stretching vibrations of surface nitrosyl (NO$_{\text{ads}}$) are revealed at 1510 cm$^{-1}$ and 1556 cm$^{-1}$, respectively, highlighted by the red circle in in Figure 5c. The formation of NO$_2$ can be attributed to oxidative decomposition of NH$_3$ ligands, which then form strong interaction with the $\gamma$-Al$_2$O$_3$ surface. The nitrosyl absorption bands are present in the DRIFTS spectra up to 400°C, which is consistent with previous temperature studies for stability of NO$_{\text{ads}}$ adsorbed onto $\gamma$-Al$_2$O$_3$ surface.\textsuperscript{40-42} The M/Z 30 signal detected by on-line mass spectrometry of the effluent gas from sample Pd(NH$_3$)$_4$(OH)$_2/\gamma$-Al$_2$O$_3$ between 390 - 450°C (Supporting Information, Figure S6b) indicates a release of NO$_{\text{ads}}$ as NO gas at this temperature. Note that in the case of the Pd(NO$_3$)$_2/\gamma$-Al$_2$O$_3$ sample, the formation of NO$_2$ species is unlikely as the nitrogen of the nitrate ligands is already in higher oxidation state, and thus is released in the oxidising environment directly as NO gas (or NO$_2$) which is detected as M/Z 30 between 100 and 400°C (Supporting Information, Figure S6a).

Figure 4. Pd K-edge $k^2$ weighted $\chi(k)$ EXAFS spectra and corresponding Fourier transformed EXAFS data of Pd(NH$_3$)$_4$(OH)$_2/\gamma$-Al$_2$O$_3$ (top) and Pd(NO$_3$)$_2/\gamma$-Al$_2$O$_3$ (bottom). Non-phase corrected Fourier transformed EXAFS data of precursor sample (black) plotted with corresponding unsupported reference Pd(NH$_3$)$_4$(OH)$_2$ (aq) and Pd(NO$_3$)$_2$ (blue) and the fitting model using first shell Pd(N) or Pd(O) and second shell Pd(Pd) scattering paths (red, dashed).
The nucleation and growth of PdO nanoparticles from each impregnated precursor can be followed from the amplitude of the scattering features of the Fourier transformed Pd K-edge EXAFS data collected during the calcination ramp period, shown in Figure 6. The scattering features at 2.5 and 3 Å correspond to scattering from nearest neighbour Pd atoms (located at real distances of 3.05 and 3.43 Å) in the tetrahedral PdO crystal structure. An increase in amplitude of these features at higher temperatures, despite increasing thermal motion and thus increased dampening from thermal disorder, indicates an increase in coordination to neighbouring Pd atoms and thus growth of the PdO structure. For Pd(NO$_3$)$_2$/$\gamma$-Al$_2$O$_3$, the scattering feature at 3 Å in the Fourier transformed EXAFS data is first observed at room temperature (Figure 4d) and starts to increase in amplitude when the sample is heated beyond 200°C (Figure 6a). This shows that the distances between neighbouring Pd atoms of the impregnated sample before calcination, thought to be associated via bridging nitrate coordination, do not change significantly upon adopting the Pd-O-Pd arrangement of tetrahedral PdO. For precursor sample Pd(NH$_3$)$_4$(OH)$_2$/$\gamma$-Al$_2$O$_3$, the amplitude of scattering features in this low temperature period (200 - 360°C) decrease with temperature, due to the dampening effect of increasing EXAFS Debye Waller factor ($\sigma^2$) with increasing thermal disorder. This is a clear indication that there is no increase in local coordination around the absorbing Pd atoms during this low temperature period. Introduction of the second shell Pd-Pd distance (3.43 Å) appears beyond 360°C. This is shown in Figure 6b by the formation and growth in amplitude of the scattering feature at 3 Å. The coordination number of neighbouring palladium atoms, located at 3.43 Å from the absorbing palladium, is plotted against temperature for both samples (Supporting Information, Figure S7). This shows that nucleation of PdO nanoparticles from the Pd(NH$_3$)$_4$(OH)$_2$ precursor occurs later in the calcination step than for Pd(NO$_3$)$_2$ precursor and growth occurs to a lesser extent. The PdO nanoparticle formation from ion...
CONCLUSIONS

Using a combined XAFS/DRIFTS approach to study the formation of supported nanoparticles, during calcination of impregnated metal oxides, a molecular insight into the role of different inorganic precursors was achieved. Pd/γ-Al₂O₃ prepared from incipient wetness impregnation of aqueous Pd(NH₃)₄(OH)₂ solution benefits from smaller Pd particle size and improved dispersion over the support which in turn favours a lower light off temperature for CH₄ oxidation, compared to the catalyst prepared from Pd(NO₃)₂.

The nucleation and growth of PdO nanoparticles during calcination was identified from the EXAFS data by an increase in the Pd-Pd scattering contribution, located at a distance (3.43 Å) consistent with a Pd-Pd distance of crystalline PdO. For Pd(NO₃)₂/γ-Al₂O₃, early association of Pd neighbours at this distance (3.43 Å) was observed in the EXAFS data of the sample before heat treatment; the bridging nature of nitrate ligands in this sample, evidenced by N=O and O newly appeared vibrations from this sample, evidenced by loss of N=O stretching bands in DRIFTS spectra and evolution of NO in effluent gas between 360 - 400°C, correlates with the temperature at which Pd-Pd scattering paths first identified from the EXAFS data. The stabilising effect of NO species has been previously postulated in multiple studies by Sietsma et al. whereby introducing NO gas into the calcination atmosphere was shown to suppress nanoparticle agglomeration over metal oxide support. It is possible that a combination of, both, high initial Pd dispersion and NO (ads) stabilisation contributed to the later formation and suppressed growth of PdO nanoparticles from the Pd(NH₃)₄(OH)₂ precursor.

Figure 6. Non-phase corrected Fourier transformed EXAFS plots of A) Pd(NO₃)₂/γ-Al₂O₃ and B) Pd(NH₃)₄(OH)₂/γ-Al₂O₃ at increasing temperatures during the calcination ramp, and reference PdO sample (dashed) at room temperature.
M/Z 30 in mass spectrometry of the effluent gas upon their removal. Strong ionic interaction of [Pd(NH₃)₂]²⁺ with the support, and the possible role of adsorbed NO⁻, result in stabilisation of isolated PdO species on γ-Al₂O₃ for the preparation of a highly dispersed Pd/γ-Al₂O₃ catalyst material.

ASSOCIATED CONTENT

Supporting Information. Figures not included in the main text are found in the Supporting information. EXAFS fitting parameters, Raman emission spectra, XANES spectra, EXAFS particles size calculations, catalytic light off curves, reference DRIFTS spectra, TGA curves and mass spectrometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Notes
Any additional relevant notes should be placed here.

ACKNOWLEDGMENT

The authors acknowledge Diamond Light Source, and beamline staff for provision of beamtime (Experiment No. sp10306). The RCaH are acknowledged for use of facilities and staff support. Gavin Stenning at ISIS Materials Characterisation Lab must be acknowledged for training and use of their instrumentation in this study. Mark Frogley at B22, Diamond Light Source is thanked for assistance with operating the Raman microscope. Johnson Matthey are acknowledged for their provision of precursor materials, and catalytic testing facility. The UK Catalysis Hub are kindly thanked for resources and support provided via our membership of the UK Catalysis Hub Consortium. UCL and EPSRC are thanked for the iCASE studentship of E.K.D.

ABBREVIATIONS

DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy
EXAFS, extended X-ray absorption fine structure
XANES, X-ray absorption near-edge structure
TEM, transmission electron microscopy
FTIR, Fourier transformed infrared
XAFS, X-ray absorption fine structure
XRD, X-ray diffraction

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