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Understanding the role of promoters in catalysis: *operando* XAFS/DRIFTS study of CeO$_x$/Pt/Al$_2$O$_3$ during CO oxidation

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**ABSTRACT**

A combined *operando* XAFS/DRIFTS study on CeO$_x$/Pt/Al$_2$O$_3$ catalysts has been performed during CO oxidation and provides insights into the changes in nanoparticle structure and adsorbed species during the reaction profile. The onset of CO$_2$ formation is shown to be concurrent with a rapid re-oxidation of the Pt nanoparticles, evidenced by XAFS spectroscopy, and the loss of bridge bonded CO adsorbed on Pt, as shown by simultaneous DRIFTS acquisition. The continued appearance of linear bound CO on the catalyst surface is shown to remain long after catalytic light off. The interaction of Pt and CeO$_x$ is evidenced by the improved performance towards CO oxidation, compared to the non-CeO$_x$ modified Pt/Al$_2$O$_3$, and changes in the CO adsorption properties on Pt previously linked to Pt-CeO$_2$ interfaces.

**Introduction**

The special interplay between metal nanoparticles and metal oxide supports is well-reported [1]. The role of the support is not only through the benign advantage of providing highly dispersed nanoparticles, instead it governs the structural morphology of the nanoparticles [2], alongside contributing additional active chemical species (e.g. redox centres [3]). One of the challenges of studying this relationship is the low number of atoms present at the interface between the nanoparticle and the metal oxide relative to that in the bulk of the particles. Wells et al. recently published work on the preparation of CeO$_x$/Pt/Al$_2$O$_3$ catalysts and their application for low temperature water gas shift (LTS) [4]. Here, a controlled amount of CeO$_x$ was targeted at the Pt nanoparticles to maximise the relative interfacial area. The CeO$_x$ is introduced onto preformed Pt/Al$_2$O$_3$ by the controlled surface reaction [5] between the reduced Pt with an organometallic precursor of Ce. LTS, along with reactions such as CO oxidation, are good model processes as the Al$_2$O$_3$ support has a far reduced impact on the performance of these reactions compared to CeO$_2$. The study showed that small amounts of CeO$_x$ (0.35 wt%) were able to dramatically change the reaction profile, with Ce exhibiting facile redox switching from Ce$^{3+}$ to Ce$^{4+}$ at room temperature under reducing and oxidising atmospheres, respectively. This method has also been used elsewhere to improve the properties of Rh/Al$_2$O$_3$ catalysts for CO oxidation [6,7]. To understand these complex structure function relationships between metal nanoparticles and interfacial metal oxide clusters it is crucial to characterise the catalyst whilst it is operating under normal process conditions, this is to say, *operando*. X-ray absorption fine structure (XAFS) is an...
ideal technique for probing metal nanoparticles using *operando* spectroscopy; the high intensity X-rays provided by a synchrotron (often of high energy depending on the absorption edge) are able to penetrate a range of sample environments [8,9], with XAFS not reliant on long range order to provide structural information. One limitation is the per atom average of the XAFS technique, which often fails to reflect the chemistry occurring at the surface of a catalyst, which is of course, where the catalysis happens. The combination of XAFS with surface sensitive techniques, such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), is able to provide a description of both the nanoparticle structure and the chemistry of the catalyst surface [10,11]. This study takes both approaches of controlled addition of promoters and combined spectroscopic techniques to assess the evolution of a CeOₓ/Pt/Al₂O₃ catalyst during CO oxidation using simultaneous XAFS/DRIFTS acquisition.

**Experimental**

**Catalyst preparation**

Preparation of the CeOₓ/Pt/Al₂O₃ catalyst has been reported elsewhere alongside its physicochemical characteristics [4]. In brief, 4 wt% Pt/γ-Al₂O₃ supplied by Johnson Matthey was modified with CeOₓ in a manner similar to that employed previously [5,12]. The Pt/γ-Al₂O₃ was first reduced in flowing H₂(g) at 350 °C for 3 h and subsequently cooled to room temperature under flowing N₂(g). Ce(acac)₃·H₂O was dissolved in toluene, purged with N₂(g) and added to the reactor. H₂(g) was then bubbled through the solution whilst stirring and heating at 90 °C for 8 h. Finally, the reactor was cooled and flushed with N₂(g) before the solid was collected and air dried. The initial reduction step was then repeated. The catalyst in this study was prepared with a Ce:Pt surface atomic ratio of 4:1.

**Combined XAFS/DRIFTS**

Pt L₃ edge XAFS studies were performed at the Diamond Light Source, UK, on beamline B18. Measurements were performed in transmission mode using ion chamber detectors with a fast scanning (QEXAFS) Si (1 1 1) double crystal monochromator. Each spectrum took 90 s to acquire (k_max = 14), with a Pt foil placed between I and I_ref. Combined XAFS/DRIFTS studies were performed using a set-up based on that previously reported [13]. The experimental configuration involves a fast scanning FTIR spectrometer, equipped with a Harrick DaVinci arm, Praying Mantis optics, and a bespoke XAFS/DRIFTS reaction chamber, which was mounted on the experimental table (Figure 1(a)). The role of the DaVinci arm fitted with Praying Mantis optics was to refocus the beam onto the top of the sample external to the FTIR

![Figure 1](image-url) (a) Combined XAFS/DRIFTS system mounted on the beamline, B18 at Diamond Light Source, (b) external view on reaction chamber, and (c) internal view of reaction chamber.
was 90000 cm$^3$ g$^{-1}$ h$^{-1}$. The flow of air was kept constant at a 1:1 ratio of 10% CO/He and 10% O$_2$/He over approximately 129 mg of catalyst, the total flow was 25 mL/min, giving a space velocity in the reactor was 11628 cm$^3$ g$^{-1}$ h$^{-1}$. DRIFTS spectra were acquired with an Agilent Cary 680 FTIR spectrometer (64 scans, resolution 4 cm$^{-1}$) using a liquid nitrogen cooled MCT detector. XAFS/DRIFTS data was first collected under He at room temperature before the introduction of reactant gases. The temperature was increased at a steady ramp rate of 3 °C min$^{-1}$, until a maximum temperature of 220 °C was achieved. Outlet gases were sampled continuously with an online MKS mass spectrometer. During reaction XAFS and DRIFTS spectra were sampled continuously with a time resolution of 90 s and 30 s, respectively.

**CO oxidation testing**

CO oxidation testing was carried out using a fixed bed reactor; 0.2 g of pelletised catalyst was loaded into the reactor tube on a bed of glass wool, ensuring the thermocouple was in the catalyst bed layer. The inlet gases were a mixture of N$_2$, 1% CO in N$_2$, and air with a total flow of 300 cm$^3$ min$^{-1}$, the space velocity in the reactor was 90000 cm$^3$ g$^{-1}$ h$^{-1}$. The flow of air was kept constant and the flows of N$_2$ and CO were adjusted to control the mole fraction of CO. The temperature was ramped manually, the procedure involved simultaneously heating the furnace and cooling with liquid nitrogen to facilitate a very slow heating rate and combat the exothermic reaction conditions. The gas analysis was performed using a Maihak s710 analyzer comprising of a H$_2$ detector and IR CO and CO$_2$ sensors. Three thermocouples are placed inside the reactor chamber to monitor the temperature of the gas inlet, gas outlet and the catalyst bed.

**Results**

The physicochemical properties of the CeO$_x$/Pt/Al$_2$O$_3$ catalyst have been reported elsewhere [4]. In brief, the catalyst was found to have Ce and Pt content of 2.3 and 3.8 wt%, respectively by ICP-OES analysis. Transmission electron microscopy identified Pt nanoparticles <2 nm, however, dense agglomeration prevented an accurate assessment of the particle size distribution. Ce L$_3$ XANES studies showed mixed valence Ce (Ce$^{4+}$ and Ce$^{3+}$) at room temperature under an atmosphere of air, progressing to complete reduction to Ce$^{3+}$ under atmospheres of H$_2$ and CO. This facile reduction properties of Ce at room temperature served as evidence of the co-locality of Ce and Pt.

Prior to applying the temperature ramp in the XAFS/DRIFTS reaction chamber under the CO and O$_2$ gas mixture, XAFS spectra were recorded at room temperature before and after the introduction of reactant gases. The comparison of these two states is highlighted by assessing the X-ray absorption near edge structure (XANES), as seen in Figure 2, and the extended X-ray absorption fine structure (EXAFS), as seen in Figure 3. Both sets of data provide evidence for an initial catalyst that is highly oxidised; the XANES shows an intense white line and the EXAFS is dominated by a primary scattering path associated with Pt-O (non phase-corrected position of 1.6 Å). The Pt–Pt features in the EXAFS data are consistent with Pt$^0$, and confirm that initially Pt is present as small metal nanoparticles with an oxidic skin. There is no evidence of longer oxygen bridged Pt–Pt distances, characteristic of PtO. On addition of the reactant gas mixture the intensity of the white line is reduced, as is the feature in the Fourier transform indicative of Pt–O. This shows that despite the excess of O$_2$, CO acts as an able reductant and the surface oxide is removed.

The Pt reduction under CO:O$_2$ at room temperature was allowed to stabilise, before the temperature ramp was applied. The time resolved *operando* XANES and EXAFS ($k^2$ Fourier transform) data during CO oxidation are shown in Figures 4 and 5, respectively.
The XANES data show that the onset of the increased temperature was accompanied by a further gradual reduction of Pt, before a sharp re-oxidation between 120 and 130 °C. This can be rationalised as the temperature at which catalytic ‘light off’ occurs. After this point the CO has been completely oxidised to CO₂, which will be assessed by the online mass spectrometry and DRIFTS spectra in the following section, and the gas environment returns to net oxidising conditions. The initial reduction of white line intensity on increasing the temperature, observed in the XANES, correlates with a reduction in the region of the Fourier transform (non phase-corrected distance ~1.6 Å) associated with Pt–O scattering paths, however, the effect is less pronounced. Immediately prior to light off the EXAFS is consistent with entirely metallic Pt with no Pt–O interactions, this is highlighted by a comparison of this state with a Pt foil reference spectrum (Figure 3). Fitting the EXAFS data (Table 1) of this reduced state of Pt, provides a primary Pt–Pt coordination number of 10 (±1), which when applying the method of Beale et al. [16], can be used to deduce an average particle size of 2.4 nm. In this instance only the 1st shell contributions have been included in the fitting analysis as this adequate for determining the extent of oxidation, and in the case of the purely metallic system the particle size determination.

An investigation by van Bokhoven and co-workers looked at a Pt/Al₂O₃ catalyst under similar CO oxidation conditions using XAFS [17]. Their study showed similar trends and highlighted that the Pt–Pt bond distance, contracted after light off as a consequence of surface relaxation by adsorbed CO. We also observe this change in distance (Table 1) between the reduced form of Pt and that post light off. However, the Pt–Pt distance post light off, is the same as the initial catalyst (within error), prior to CO exposure. Indeed, we find the Pt–Pt distance similar to that of other surface oxidised Pt nanoparticles reported elsewhere in the literature [18]. This observation is consistent with the fact that post light off the surface coverage is significantly oxygen rich as CO is continually being converted to CO₂. Another difference with this study is the temperature of light off, which occurs ~60 °C higher than we report here. Indeed, to assess the effect of CeOₓ the modified Pt/Al₂O₃ and reference samples were tested using a fixed bed reactor set-up (Figure 6). The conditions were different to that used in the combined XAFS/DRIFTS study, and

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Table 1. EXAFS fitting parameters of CeOₓ/Pt/Al₂O₃.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Abs. Sc.</th>
<th>N</th>
<th>R/Å</th>
<th>2πR/Å</th>
<th>E_eV</th>
<th>R_factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>Pt–O</td>
<td>2.4 (4)</td>
<td>2.01 (2)</td>
<td>0.005 (2)</td>
<td>10 (2)</td>
<td>0.01</td>
</tr>
<tr>
<td>110 °C CO₂</td>
<td>Pt–Pt</td>
<td>4(2)</td>
<td>2.74 (1)</td>
<td>0.007 (3)</td>
<td>7(1)</td>
<td>0.02</td>
</tr>
<tr>
<td>200 °C CO₂</td>
<td>Pt–Pt</td>
<td>6 (2)</td>
<td>2.73 (2)</td>
<td>0.011 (2)</td>
<td>7(2)</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Note: Fitting parameters: \(\chi^2 = 0.85\); Fit range 3.1 < k < 11.1 < R < 3; # of independent points = 9.
results which showed a fast re-oxidation of Pt between 120–130 °C.

The simultaneous DRIFTS study allows us to follow changes in Pt speciation by assessing changes in CO performance, as we wished to assess the reaction rate order with respect to CO.

Figures 6(a) shows the CO conversion plot for Pt/Al₂O₃. It can be seen that the plot shows a characteristic light off feature, where there is a sharp increase in the conversion of CO. As a steep light-off curve is not observed for the CeOₓ/Pt/Al₂O₃ catalyst, the light-off temperature is defined here as the temperature at which 50% CO conversion (∝_{50}) was obtained. CeOₓ/Pt/Al₂O₃ (Figure 6(b)) is the more active catalyst and has a ∝_{50} value (Table 2) of 69 °C for X_{CO} = 0.33. This compares to the value of 120 °C for Pt/Al₂O₃. Moreover, the CO conversion plot for the CeOₓ/Pt/Al₂O₃ has different features to that of Pt/Al₂O₃; there is a more gradual increase in CO conversion with increasing temperature than the intense light off feature associated with Pt/Al₂O₃.

The CO oxidation reaction was also assessed during the combined XAFS/DRIFTS study with the mass spectrometry results shown in Figure 7. Three rates of CO₂ production are observed during the temperature ramp, a gradual increase from 100° with a step at 117 °C, followed by a more gradual increase up to ~143 °C, after which the rate of CO₂ production slows until 220 °C (75 min), at which point the temperature was maintained at 220 °C. The first sharp increase and the second faster CO₂ production rate are consistent with the XAFS results which showed a fast re-oxidation of Pt between 120–130 °C.

The simultaneous DRIFTS study allows us to follow changes in Pt speciation by assessing changes in CO.

Table 2. Temperature at which 50% CO conversion was attained (∝_{50}) for the CO oxidation testing at different mole fractions of CO for different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>∝_{50} at different values of X CO/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al₂O₃</td>
<td>X_{CO} = 0.167 X_{CO} = 0.25 X_{CO} = 0.33 X_{CO} = 0.5 X_{CO} = 0.667</td>
</tr>
<tr>
<td>%CO</td>
<td>0.8 0.25 0.17 0.25 0.33</td>
</tr>
<tr>
<td>CO₂/O₂</td>
<td>1.53 1.25 1.25 1.17 1.13</td>
</tr>
<tr>
<td>CeOₓ/Pt/Al₂O₃</td>
<td>56 69 80 87</td>
</tr>
</tbody>
</table>

Figure 6. CO oxidation testing of (a) Pt/Al₂O₃, and (b) CeOₓ/Pt/Al₂O₃.

Figure 7. Mass spectrometer response during temperature ramp, (3 °C min⁻¹) showing traces of masses 18, 28, 32 and 44 representing H₂O, CO (and CO₂), O₂ and CO₂ respectively. The temperature profile is shown in red.

Figure 8. DRIFTS spectra collected during CO oxidation XAFS/DRIFTS experiment at 75 °C.
binding modes on the Pt surface. One example of this is the intense linear bound CO adsorption bands centred ~2070 cm⁻¹, shown in Figure 8. This band has a shoulder at 2087 cm⁻¹ and a broad tail towards lower wavenumbers, ~2020 cm⁻¹. These linearly bound CO adsorption bands are very similar to those observed in the literature for CO adsorbed on Pt-CeO₂/Al₂O₃ catalysts, with the intense band at 2070 cm⁻¹ assigned to CO adsorbed on steps or corners of Pt particles, and the shoulder at 2088 cm⁻¹ being attributed to CO linearly adsorbed on Pt with a neighbouring Pt atom containing adsorbed O [19,20]. Both of these bands shift to lower wavenumber during reaction, at 25 °C they appear at 2091 and 2070 cm⁻¹ shifting to 2088 and 2062 cm⁻¹ respectively, by 150 °C. Which is consistent with a loss in vibrational coupling between the CO molecules which occurs at high coverage [21,22]. The broad tail at ~2020 cm⁻¹ may provide evidence of the close proximity of the Pt and CeO₂, as this band has been previously assigned to CO adsorbed on Pt interacting with CeO₂ and similarly for Rh/CeO₂ samples where it was assigned to CO adsorbed on Rh atoms at the metal-support interface [20,23,24].

A 3D plot of the evolution of the gas phase CO₂ bands and CO adsorption bands with temperature during the CO oxidation ramp is shown in Figure 9. In agreement with the mass spectrometry data, three regions of CO₂ production are observed. The gas phase CO₂ bands, observed between 2395-2273 cm⁻¹, increase sharply at 110–120 °C, then more gradually up to 150 °C, with the third slower rate of production observed from 150 to 220 °C. The integration of the CO₂ region compared to the CO conversion is shown in Figure 10. Linearly adsorbed CO on metallic Pt, the band centred at 2071 cm⁻¹, reaches a maximum intensity at ~120 °C, notably this is after the reaction light-off. The linear adsorbed CO decreases gradually during the second CO₂ production region, from 120 to 155 °C before desorbing suddenly at 160 °C, and consistent with a decrease in CO coverage, this band shifts to lower wavenumber during reaction. The initial fast CO₂ production rate from 110 to 120 °C coincides with the disappearance of the broad band centred at 1829 cm⁻¹, which is consistent with CO bridge bonded to metallic Pt sites [20]. Correlating these changes in CO adsorption bands with the CO₂ production temperatures, we propose that the bridge bonded CO species are most likely involved in the fast CO₂ production at 110–120 °C and the linear bound CO species on corner sites, ~2069 cm⁻¹, are associated with the second and third slower regions of CO₂ production. The comparison of the steep decrease in bridged CO species coincident with the first sharp increase in CO conversion, can be more clearly observed from the integrated intensities of the IR bands compared with the CO conversion in Figure 10. Our observation of strongly bound linearly adsorbed CO species, resisting desorption or reaction above significant conversion, differs to literature reports of CO oxidation over Pt/Al₂O₃ and Pt/CeO₂-Al₂O₃ [25]. In this literature study the linearly adsorbed CO correlates directly with CO₂ production. However, our approach of applying multiple spectroscopic probes allows us to understand this process in greater detail.

Figure 9. 3D plot of the DRIFTS spectra collected during CO oxidation XAFS/DRIFTS experiment. The numbers, 1,2,3 refer to the CO₂ production regions, and the arrow on the bottom projection of band intensities highlights the correlation between the bridged bond CO band at 1829 cm⁻¹ and the initial increase in the CO₂ bands.
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Disclosure statement

No potential conflict of interest was reported by the authors.

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Conclusion

The combined operando XAFS/DRIFTS study of a CeOx/Pt/Al2O3 catalyst during CO oxidation reported here shows how catalytic properties can be dramatically altered by small addition of promoters, in this case CeOx. Our testing data shows that the addition of CeOx increases the performance towards CO oxidation by changing the reaction rate order with respect to CO. We also show that significant conversion of CO to CO2 is achieved through the loss of bridge bonded CO adsorbed on Pt. Indeed, there is relatively little change in CO conversion after the linearly adsorbed CO is removed ~40 °C later. Moreover, the loss of bridge-bonded CO is concurrent with the rapid re-oxidation of Pt NPs, as evidenced by the time resolved XAFS studies. There is slight increase in white line intensity around 160 °C, however it essentially negligible compared to the rapid change observed at 120 °C, shown in Figure 10. This confirms that the majority of Pt sites are involved in bridge bonding of CO and why the activity, with regards to CO2 production, is linked to the loss of these species in the DRIFTS spectra. Further evidence of the Pt–CeOx interaction is shown through changes in the shape of the linearly bound CO adsorption band, where a clear tailing is observed and has been previously been linked to Pt–CeOx interfaces. In fine, the study shows that by preparing model materials and performing combined operando spectroscopy we are able to correlate both changes in NP properties and adsorbed surface species with the reaction profile.

Figure 10. Integrated area of IR (a) CO band compared to the CO conversion and (b) comparison of the integrated band area of linear CO band (2064 cm−1), CO2 (2340–2360 cm−1) compared to the intensity of the white line from the XAFS data.
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