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

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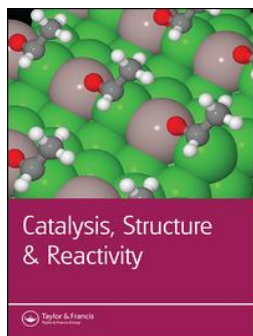
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## Understanding the role of promoters in catalysis: *operando* XAFS/DRIFTS study of $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$ during CO oxidation

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### ABSTRACT

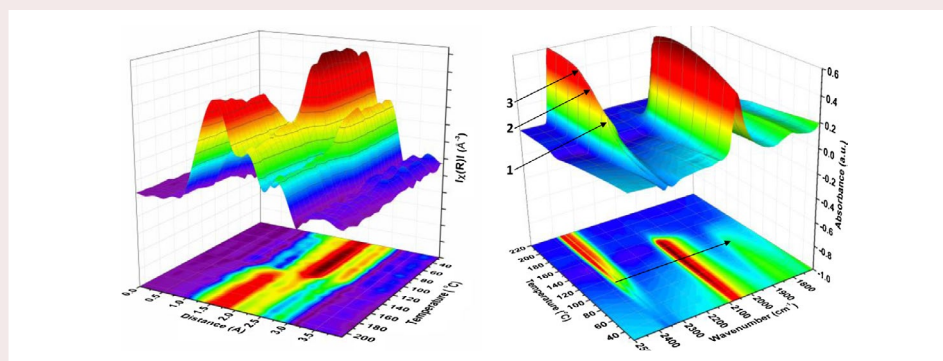
A combined *operando* XAFS/DRIFTS study on  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts has been performed during CO oxidation and provides insights into the changes in nanoparticle structure and adsorbed species during the reaction profile. The onset of  $\text{CO}_2$  formation is shown 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  $\text{CeO}_x$  is evidenced by the improved performance towards CO oxidation, compared to the non- $\text{CeO}_x$  modified  $\text{Pt}/\text{Al}_2\text{O}_3$ , and changes in the CO adsorption properties on Pt previously linked to Pt- $\text{CeO}_2$  interfaces.

### ARTICLE HISTORY

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*Operando*; XAFS; DRIFTS; CO oxidation;  $\text{Pt}/\text{Al}_2\text{O}_3$ ; catalysis; ceria



### 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  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalysts and their application for low temperature water gas shift (LTS) [4]. Here, a controlled amount of  $\text{CeO}_x$  was targeted at the Pt nanoparticles to maximise the relative interfacial area. The  $\text{CeO}_x$  is introduced onto preformed  $\text{Pt}/\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  support has a far reduced impact on the performance of these reactions compared to  $\text{CeO}_2$ . The study showed that small amounts of  $\text{CeO}_x$  (0.35 wt%) were able to dramatically change the reaction profile, with Ce exhibiting facile redox switching from  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  at room temperature under reducing and oxidising atmospheres, respectively. This method has also been used elsewhere to improve the properties of  $\text{Rh}/\text{Al}_2\text{O}_3$  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

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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  $\text{CeO}_x/\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  catalyst during CO oxidation using simultaneous XAFS/DRIFTS acquisition.

## Experimental

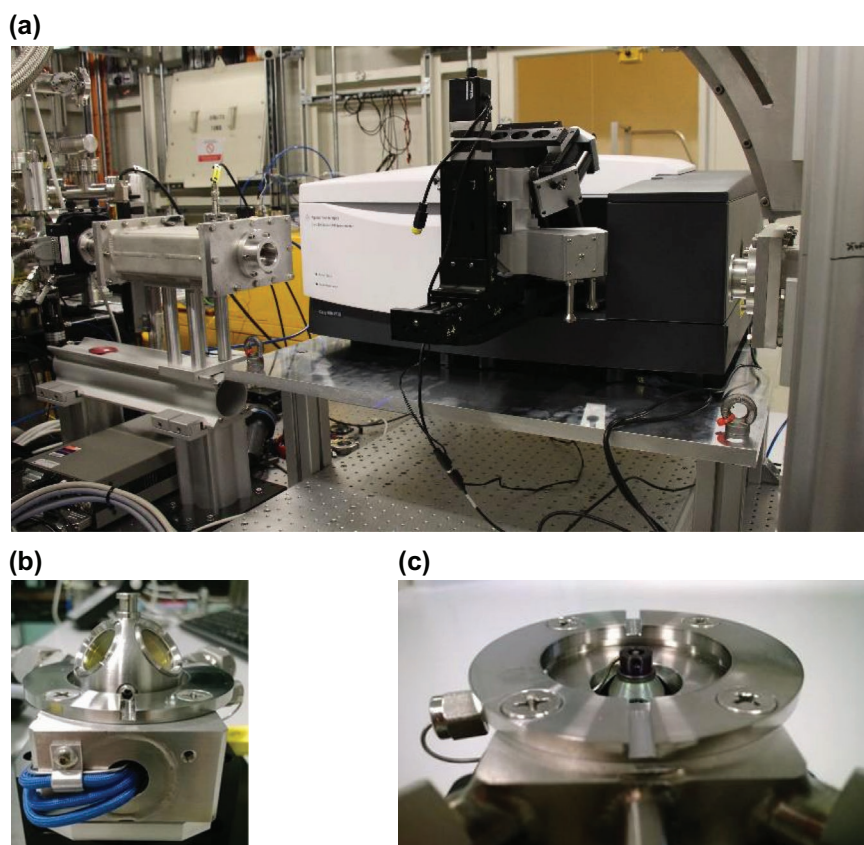
### Catalyst preparation

Preparation of the  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalyst has been reported elsewhere alongside its physicochemical characteristics [4]. In brief, 4 wt% Pt/ $\gamma\text{-Al}_2\text{O}_3$  supplied by Johnson Matthey was modified with  $\text{CeO}_x$  in a manner similar to that employed previously [5,12]. The Pt/

$\gamma\text{-Al}_2\text{O}_3$  was first reduced in flowing  $\text{H}_2(\text{g})$  at 350 °C for 3 h and subsequently cooled to room temperature under flowing  $\text{N}_2(\text{g})$ .  $\text{Ce}(\text{acac})_3 \cdot \text{H}_2\text{O}$  was dissolved in toluene, purged with  $\text{N}_2(\text{g})$  and added to the reactor.  $\text{H}_2(\text{g})$  was then bubbled through the solution whilst stirring and heating at 90 °C for 8 h. Finally, the reactor was cooled and flushed with  $\text{N}_2(\text{g})$  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  $L_3$  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 ( $k_{\text{max}} = 14$ ), with a Pt foil placed between  $I_t$  and  $I_{\text{ref}}$ . Combined XAFS/DRIFTS studies were performed using a set-up based on that previous 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.** (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.

spectrometer, to allow X-rays to pass through the reaction chamber, whilst maintaining a purged ( $N_2$ ) environment. The DaVinci arm was fitted with stepper motors to facilitate precise alignment with the X-ray beam, which provided movement in vertical and horizontal directions of 48 mm. The reaction chamber (Figure 1(b)), which has been described in detail elsewhere [13], is based on a conventional dome based Harrick high temperature and pressure reaction chamber fitted with ZnSe windows for the collection of DRIFTS data and glassy carbon windows for entry and exit of the X-ray beam. The sample cup (Figure 1(c)) has a diameter of 3 mm and is fitted with holes for the X-ray beam to pass through. The top of these holes are 0.37 mm from the surface of the catalyst bed. At this distance assuming an IR penetration depth in of  $\sim 1\text{--}2$  mm [14], the X-rays and IR beams should be sampling the same region of the catalyst bed [15]. The cell has a total dead volume of 14 ml, making it non ideal for kinetic measurements, therefore, no direct comparison of activity results are made between the XAFS/DRIFTS study and those of the fixed bed reactor. DRIFTS spectra were acquired with an Agilent Carey 680 FTIR spectrometer (64 scans, resolution  $4\text{ cm}^{-1}$ ) using a liquid nitrogen cooled MCT detector. CO oxidation experiments were carried out using 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, the space velocity in the reactor was  $11628\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$ . 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  $3\text{ }^\circ\text{C min}^{-1}$ , until a maximum temperature of  $220\text{ }^\circ\text{C}$  was achieved. Outlet gases were sample 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

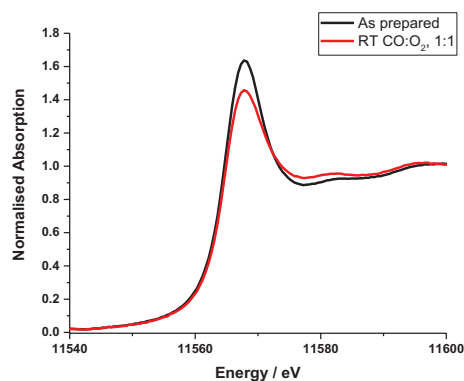
CO oxidation testing was carried out using a fixed bed reactor; 0.2 g of pelletised catalyst was loaded into the reactor tube on a bed of glass wool, ensuring the thermocouple was in the catalyst bed layer. The inlet gases were a mixture of  $N_2$ , 1% CO in  $N_2$ , and air with a total flow of  $300\text{ cm}^3\text{ min}^{-1}$ , the space velocity in the reactor was  $90000\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$ . 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

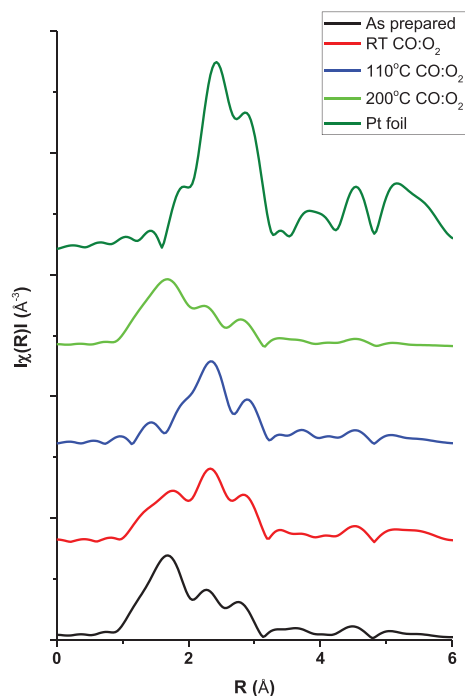
The physicochemical properties of the  $CeO_x/Pt/Al_2O_3$  catalyst have been reported elsewhere [4]. In brief, the catalyst was found to have Ce and Pt content of 2.3 and 3.8 wt%, respectively by ICP-OES analysis. Transmission electron microscopy identified Pt nanoparticles  $<2$  nm, however, dense agglomeration prevented an accurate assessment of the particle size distribution. Ce  $L_3$  XANES studies showed mixed valence Ce ( $Ce^{3+}$  and  $Ce^{4+}$ ) 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  $1.6\text{ \AA}$ ). 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.

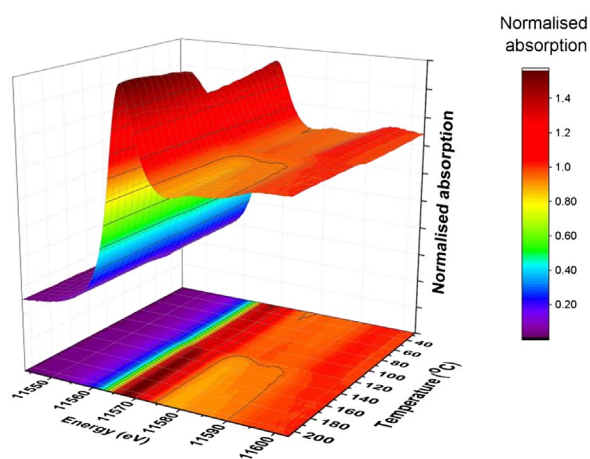
The Pt reduction under  $CO:O_2$  at room temperature was allowed to stabilise, before the temperature ramp was applied. The time resolved *operando* XANES and EXAFS ( $k^2$  Fourier transform) data during CO oxidation are shown in Figures 4 and 5, respectively.



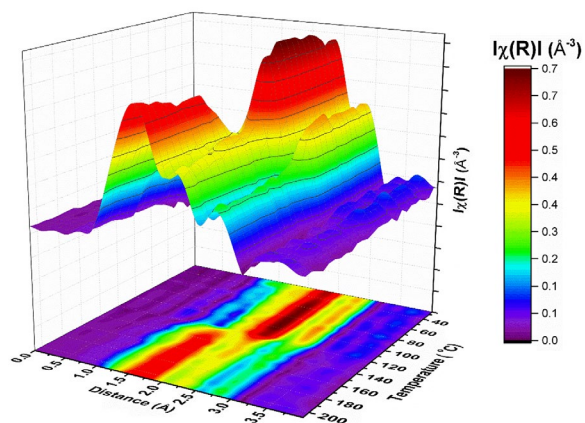
**Figure 2.** Normalised XANES spectra of  $CeO_x/Pt/Al_2O_3$  in air and a 1:1 mixture of 10% CO/He and 10%  $O_2$ /He.



**Figure 3.** Non phase-corrected  $k^2$  weighted Fourier transform EXAFS data of  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  in air and a 1:1 mixture of 10% CO/He and 10%  $\text{O}_2$ /He at room temperature, 110, 200 °C. A Pt foil is included for comparison.



**Figure 4.** Operando XANES data of  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  during CO oxidation conditions.



**Figure 5.** Operando EXAFS data of  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  during CO oxidation conditions.

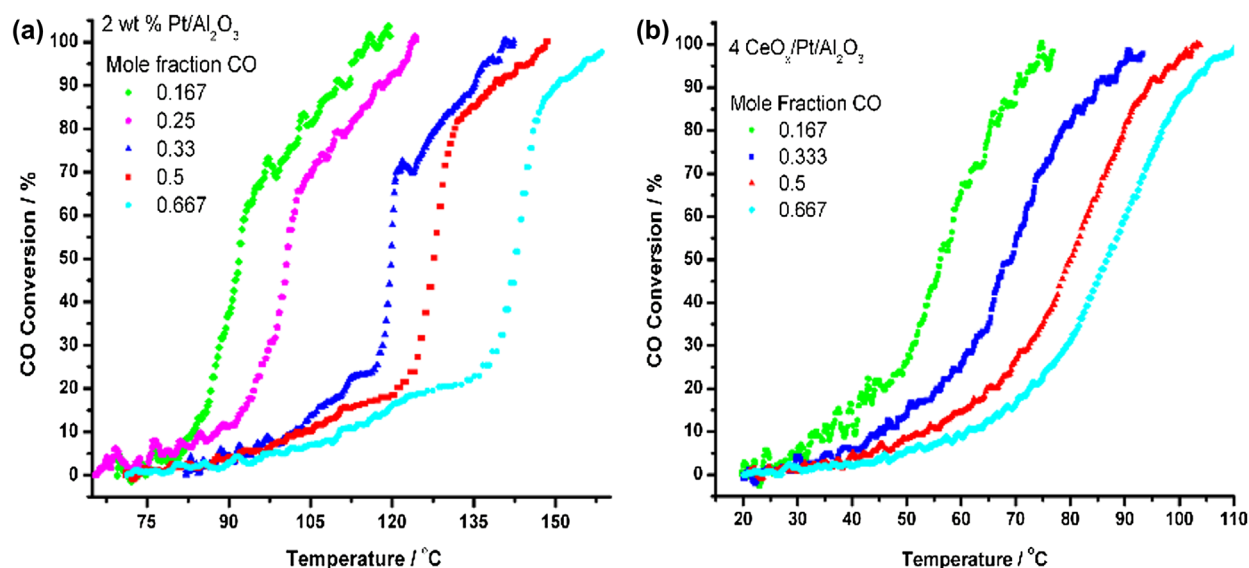
The XANES data show that the onset of the increased temperature was accompanied by a further gradual reduction of Pt, before a sharp re-oxidation between 120 and 130 °C. This can be rationalised as the temperature at which catalytic ‘light off’ occurs. After this point the CO has been completely oxidised to  $\text{CO}_2$ , 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  $\sim 1.6$  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 ( $\pm 1$ ), 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  $\text{Pt}/\text{Al}_2\text{O}_3$  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  $\text{CO}_2$ . Another difference with this study is the temperature of light off, which occurs  $\sim 60$  °C higher than we report here. Indeed, to assess the effect of  $\text{CeO}_x$  the modified  $\text{Pt}/\text{Al}_2\text{O}_3$  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

**Table 1.** EXAFS fitting parameters of  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$ .

Condition	Abs. Sc.	$N$	$R/\text{Å}$	$2\sigma^2/\text{Å}^2$	$E_0/\text{eV}$	$R_{\text{factor}}$
As pre-prepared	Pt–O	2.4 (4)	2.01 (2)	0.005 (2)	10 (2)	0.01
	Pt–Pt	4(2)	2.74 (1)	0.007 (3)		
110 °C $\text{CO}:\text{O}_2$	Pt–Pt	10 (1)	2.76 (1)	0.011 (1)	7(1)	0.02
200 °C $\text{CO}:\text{O}_2$	Pt–O	1.8 (3)	2.00 (1)	0.005 (2)	7(2)	0.007
	Pt–Pt	6 (2)	2.73 (2)	0.011 (2)		

Note: Fitting parameters:  $S_0^2 = 0.85$ ; Fit range  $3.1 < k < 11$ ,  $1.1 < R < 3$ ; # of independent points = 9.



**Figure 6.** CO oxidation testing of (a) Pt/Al<sub>2</sub>O<sub>3</sub>, and (b) CeO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub>.

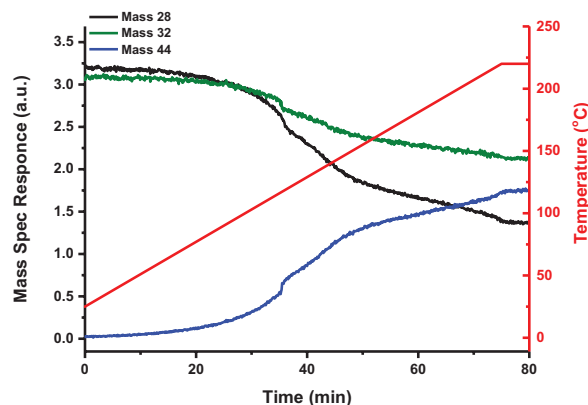
therefore report different values for CO oxidation performance, as we wished to assess the reaction rate order with respect to CO.

Figure 6(a) shows the CO conversion plot for Pt/Al<sub>2</sub>O<sub>3</sub>. 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 CeO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the light-off temperature is defined here as the temperature at which 50% CO conversion ( $T_{50}$ ) was obtained. CeO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub> (Figure 6(b)) is the more active catalyst and has a  $T_{50}$  value (Table 2) of 69 °C for  $X_{CO} = 0.33$ . This compares to the value of 120 °C for Pt/Al<sub>2</sub>O<sub>3</sub>. Moreover, the CO conversion plot for the CeO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub> has different features to that of Pt/Al<sub>2</sub>O<sub>3</sub>; there is a more gradual increase in CO conversion with increasing temperature than the intense light off feature associated with Pt/Al<sub>2</sub>O<sub>3</sub>.

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> production rate are consistent with the XAFS

results which showed a fast re-oxidation of Pt between 120–130 °C.

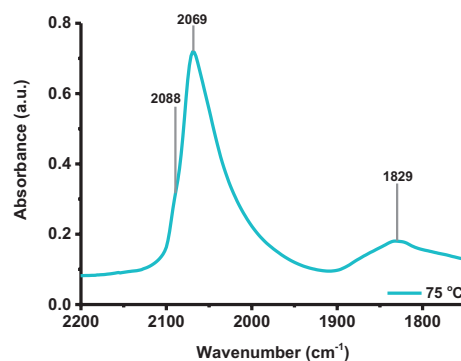
The simultaneous DRIFTS study allows us to follow changes in Pt speciation by assessing changes in CO



**Figure 7.** Mass spectrometer response during temperature ramp, (3 °C min<sup>-1</sup>) showing traces of masses 18, 28, 32 and 44 representing H<sub>2</sub>O, CO (and CO<sub>2</sub>), O<sub>2</sub> and CO<sub>2</sub> respectively. The temperature profile is shown in red.

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

Catalyst	$T_{50}$ at different values of $X_{CO}$ /°C			
	$X_{CO} = 0.167$ %CO = 0.8 CO:O <sub>2</sub> = 1:5.3	$X_{CO} = 0.33$ %CO = 0.17 CO:O <sub>2</sub> = 1:2.5	$X_{CO} = 0.5$ %CO = 0.25 CO:O <sub>2</sub> = 1:1.7	$X_{CO} = 0.667$ %CO = 0.33 CO:O <sub>2</sub> = 1:1.3
Pt/Al <sub>2</sub> O <sub>3</sub>	92	120	128	143
CeO <sub>x</sub> /Pt/ Al <sub>2</sub> O <sub>3</sub>	56	69	80	87

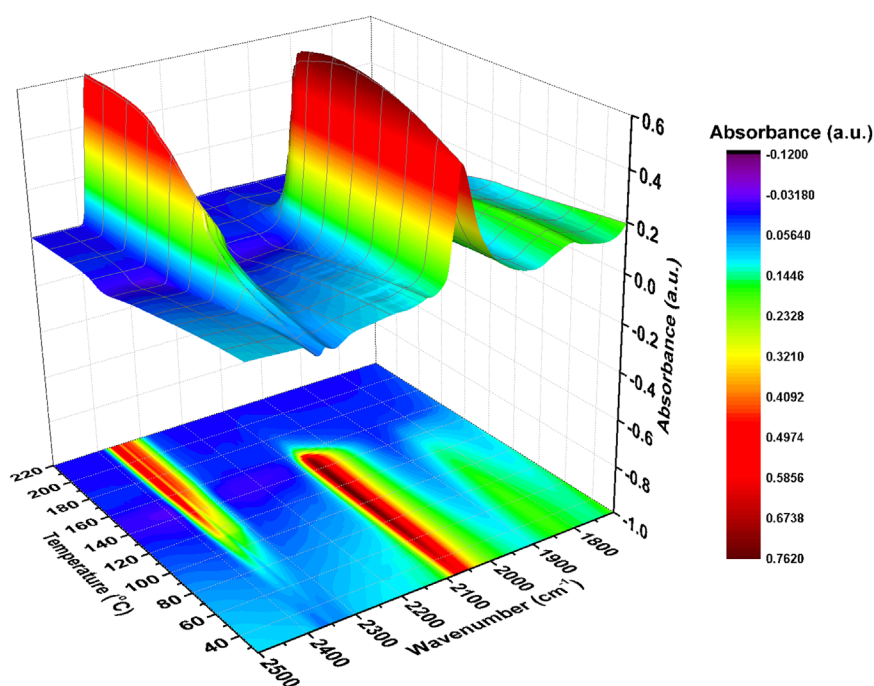


**Figure 8.** DRIFTS spectra collected during CO oxidation XAFS/DRIFTS experiment at 75 °C.

binding modes on the Pt surface. One example of this is the intense linear bound CO adsorption bands centred  $\sim 2070\text{ cm}^{-1}$ , shown in Figure 8. This band has a shoulder at  $2087\text{ cm}^{-1}$  and a broad tail towards lower wavenumbers,  $\sim 2020\text{ cm}^{-1}$ . These linearly bound CO adsorption bands are very similar to those observed in the literature for CO adsorbed on Pt-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, with the intense band at  $2070\text{ cm}^{-1}$  assigned to CO adsorbed on steps or corners of Pt particles, and the shoulder at  $2088\text{ cm}^{-1}$  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  $25\text{ }^{\circ}\text{C}$  they appear at  $2091$  and  $2070\text{ cm}^{-1}$  shifting to  $2088$  and  $2062\text{ cm}^{-1}$  respectively, by  $150\text{ }^{\circ}\text{C}$ . Which is consistent with a loss in vibrational coupling between the CO molecules which occurs at high coverage [21,22]. The broad tail at  $\sim 2020\text{ cm}^{-1}$  may provide evidence of the close proximity of the Pt and CeO<sub>2</sub>, as this band has been previously assigned to CO adsorbed on Pt interacting with CeO<sub>2</sub> and similarly for Rh/CeO<sub>2</sub> samples where it was assigned to CO adsorbed on Rh atoms at the metal-support interface [20,23,24].

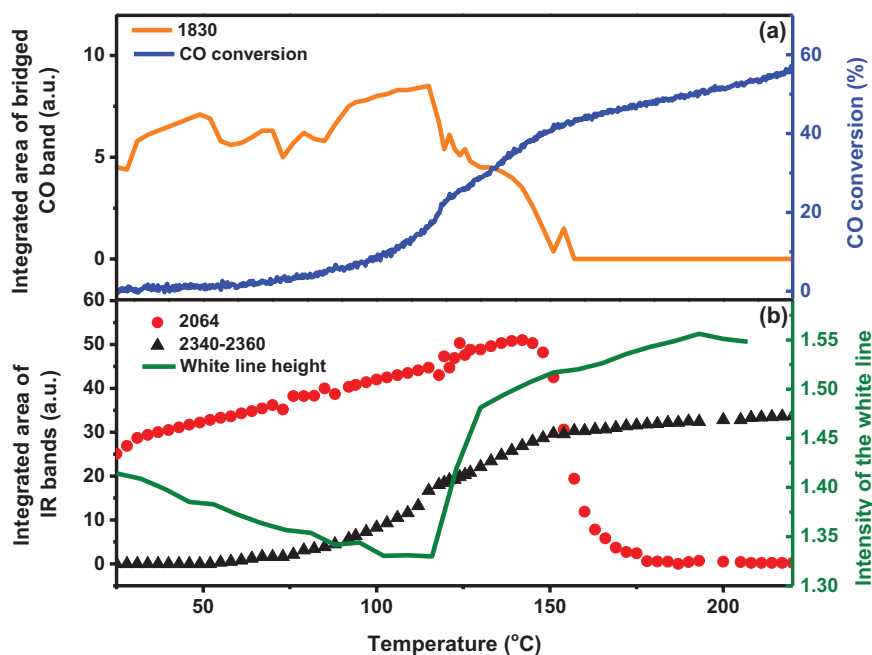
A 3D plot of the evolution of the gas phase CO<sub>2</sub> bands and CO adsorption bands with temperature during the CO oxidation ramp is shown in Figure 9. In agreement with the mass spectrometry data, three regions of CO<sub>2</sub> production are observed. The gas phase CO<sub>2</sub> bands, observed between  $2395\text{--}2273\text{ cm}^{-1}$ , increase sharply at  $110\text{--}120\text{ }^{\circ}\text{C}$ , then more gradually up to  $150\text{ }^{\circ}\text{C}$ , with the third slower rate of production observed from  $150$  to  $220\text{ }^{\circ}\text{C}$ . The integration of the CO<sub>2</sub> region compared

to the CO conversion is shown in Figure 10. Linearly adsorbed CO on metallic Pt, the band centred at  $2071\text{ cm}^{-1}$ , reaches a maximum intensity at  $\sim 120\text{ }^{\circ}\text{C}$ , notably this is after the reaction light-off. The linearly adsorbed CO decreases gradually during the second CO<sub>2</sub> production region, from  $120$  to  $155\text{ }^{\circ}\text{C}$  before desorbing suddenly at  $160\text{ }^{\circ}\text{C}$ , and consistent with a decrease in CO coverage, this band shifts to lower wavenumber during reaction. The initial fast CO<sub>2</sub> production rate from  $110$  to  $120\text{ }^{\circ}\text{C}$  coincides with the disappearance of the broad band centred at  $1829\text{ cm}^{-1}$ , which is consistent with CO bridge bonded to metallic Pt sites [20]. Correlating these changes in CO adsorption bands with the CO<sub>2</sub> production temperatures, we propose that the bridge bonded CO species are most likely involved in the fast CO<sub>2</sub> production at  $110\text{--}120\text{ }^{\circ}\text{C}$  and the linear bound CO species on corner sites,  $\sim 2069\text{ cm}^{-1}$ , are associated with the second and third slower regions of CO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [25]. In this literature study the linearly adsorbed CO correlates directly with CO<sub>2</sub> 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 CO<sub>2</sub> production regions, and the arrow on the bottom projection of band intensities highlights the correlation between the bridged bonded CO band at  $1829\text{ cm}^{-1}$  and the initial increase in the CO<sub>2</sub> bands.





**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 ( $2064\text{ cm}^{-1}$ ),  $\text{CO}_2$  ( $2340\text{--}2360\text{ cm}^{-1}$ ) compared to the intensity of the white line from the XAFS data.

## Conclusion

The combined *operando* XAFS/DRIFTS study of a  $\text{CeO}_x/\text{Pt}/\text{Al}_2\text{O}_3$  catalyst during CO oxidation reported here shows how catalytic properties can be dramatically altered by small addition of promoters, in this case  $\text{CeO}_x$ . Our testing data shows that the addition of  $\text{CeO}_x$  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  $\text{CO}_2$ , 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  $\sim 40^\circ\text{C}$  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  $160^\circ\text{C}$ , however it is essentially negligible compared to the rapid change observed at  $120^\circ\text{C}$ , 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  $\text{CO}_2$  production, is linked to the loss of these species in the DRIFTS spectra. Further evidence of the Pt– $\text{CeO}_x$  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– $\text{CeO}_2$  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.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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