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In situ XAS with high-energy resolution: The changing structure of platinum during the oxidation of carbon monoxide

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ABSTRACT

The catalytically active species during the oxidation of carbon monoxide over a real alumina-supported platinum catalyst under atmospheric pressure are determined by combining in situ high-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD XAS) at the Pt L_3 edge and kinetic measurements. Catalysts were prepared by incipient wetness impregnation. The oxidation of carbon monoxide occurred in two distinctive regimes, a high-activity regime and a low-activity regime, which have high and low rates of reaction respectively. In the low-activity region, the catalyst is poisoned by carbon monoxide, limiting the dissociative adsorption of oxygen. In the high-activity regime, all CO is desorbed from the surface, increasing the rate of reaction. The low carbon monoxide concentration enables oxygen to react to the surface in this reaction regime generating a more reactive surface. HERFD showed that different phases are active depending on the reaction conditions in nano-sized catalyst particles.

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1. Introduction

Knowledge of the structure of the catalytically active sites in solid catalysts is essential to understand the functioning of solid catalysts and chemical processes. It enables the design of new and better catalysts. Despite decades of research, the structure of the adsorption sites of hydrocarbon molecules more complex than ethane, remain essentially unknown [1]. The structure of adsorbates and intermediates are generally determined using vibrational spectroscopy, but this provides only indirect information about the structure of the catalyst.

Adsorption of reactants and intermediates on the surface of transition metals involves the interaction of the atomic or molecular orbitals of the adsorbate with the bands on the metal. The interaction with the metal sp-band causes broadening of the orbital level, while that with the metal d band forms bonding and anti-bonding states. If the anti-bonding state is pushed completely, or partially above the Fermi-level, there is a driving force for the adsorbate to bond to the metal surface. An example is the bonding of hydrogen to platinum surfaces, which creates empty anti-bonding states; in contrast, the anti-bonding state between hydrogen and the (1 1 1) surface of gold is below the Fermi-level, so hydrogen does not bond to bulk gold [2]. The energy of the d band is the essential parameter that determines the bonding: the smaller is the gap between the d band and the Fermi-level, the stronger the metal–adsorbate bonds [3].

X-ray absorption spectroscopy provides the local structure by an EXAFS analysis and density of states by analysis of the near-edge structure. The K edge probes the transition of a 1s electron to np and the $L_{2,3}$ edges, those of a 2p to $(n-1)$d. As a result, the L_3 edge is sensitive to the d density of states and probes the oxidation state of transition metals. The first intense feature, also called the whiteline, in L_3 edge spectra is sensitive to the anti-bonding state after adsorption of reactants or intermediates. The shape and intensity depends on the structure of the adsorption site and adsorption sites of hydrogen atoms [4,5], carbon monoxide [4,6], and ethylene [7] have been observed. Because all atoms contribute to the XAS signal, an averaged signal is determined, which hampers a quantitative evaluation of all types of atoms. Moreover, the excitation of a core electron in an XAS experiment and its finite lifetime causes lifetime broadening, which results in a broad spectra, which further hampers evaluation and interpretation of the spectra. Using methods that subtract known contributions to the spectra aids in solving the first point. High-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) is a technique where XAS spectra are recorded with an instrumental broadening that is below the core

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hole lifetime broadenings. This effectively results in spectra with higher energy-resolution [6,8–11]. The sharpening effect is achieved by the selective detection of a fluorescence decay channel, which leaves a core hole with a longer lifetime and thus smaller broadening. The $L_{\alpha 1}$ lines of platinum and gold in supported metal catalysts were detected in such manner, which resulted in significant enhancement in spectral resolution [6,8–11]. Because both the absorption edge and the energy of the $L_{\alpha 1}$ line are in the regime of hard X-rays, such experiments do not require vacuum conditions and can be performed under in situ conditions [11].

In this study, we determined the structure of the catalytically active phases of alumina-supported platinum nanoparticles in the oxidation of carbon monoxide. The oxidation of carbon monoxide is probably the most-studied reaction and different reaction regimes have been identified [12–15]. The activity and structure of the surface and adsorbates on single crystals have been determined. Platinum surfaces showed different reconstructions into carbon monoxide-rich and oxygen-rich domains that differ in reaction rate under low-pressure conditions [12–14]. Also under high-pressure conditions, reaction regimes that have high respectively low activity were identified. In the low-activity regime, carbon monoxide poisoned the surface and its desorption was the rate-limiting step [15]. Recently, in situ surface X-ray diffraction showed the formation of αPtO_2 phase over a platinum (1 1 1) surface was paralleled by an increase in the rate of oxidation [16]. Also, in situ STM showed a roughening of the Pt(1 1 1) surface at high activity. However, platinum oxide has also shown to display low activity in the oxidation of carbon monoxide [20]. In supported metal catalysts, at low temperature, there is a general agreement that the catalyst surface is covered by carbon monoxide, which poisons the catalyst [17–20]. The catalyst structure of the high-activity state of a supported metal catalyst is not well known and various structures have been proposed [16,18,20–23]. We determined the structure of the active component in a supported platinum catalyst while it performed the oxidation of carbon monoxide using in situ high-energy resolution X-ray absorption spectroscopy.

2. Experimental

2.1. Catalyst preparation

Incipient wetness impregnation was applied to synthesize 2 wt% Pt/Al_2O_3. 0.197 g of tetra amine platinum nitrate was dissolved in de-ionized water corresponding to the pore volume of the required weight of alumina. The solution was well mixed with alumina, which was dried overnight at 393 K. The powder so obtained was dried at room temperature and calcined in a flow of air in two steps. Firstly, it was heated at 5 K/min from room temperature to 473 K where it was held for 4 h and later it was again ramped at 5 K/min to 673 K and held for another 4 h. The cooling was done in the same air flow. After calcination reduction was done in a flow of pure hydrogen at 723 K for 2 h.

2.2. Electron microscopy

The size of supported platinum particles was obtained using scanning transmission electron microscopy (STEM). The measurements were performed using a copper grid support and a carbon foil upon which the sample was placed after the evaporation of the ethanol. A Tecnai F30 microscope operating with a field-emission cathode at 300 kV using a high-angle annular dark-field (HAADF) detector was used to obtain the images. The bright spots in the images were identified as platinum particles by energy-dispersive X-ray spectroscopy.

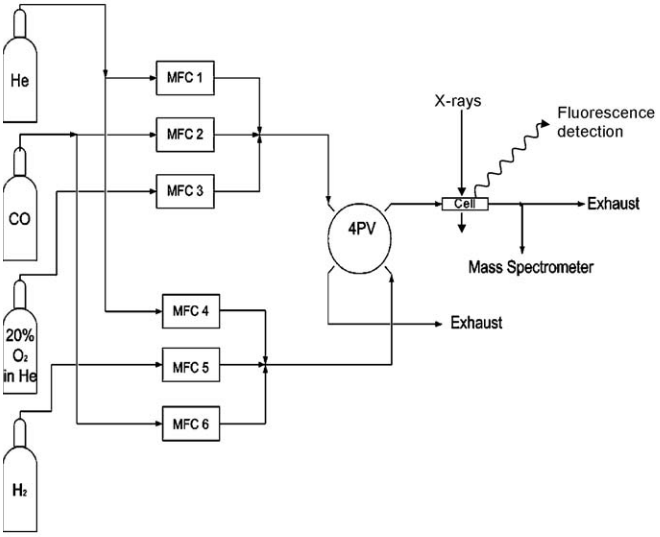

Fig. 1. Flow scheme of setup used for the oxidation of carbon monoxide over 2 wt% Pt/Al_2O_3 (MFC: mass-flow controller, 4 PV: four port valve).

2.3. Kinetic measurements

Fig. 1 shows the setup for the combined spectroscopic and kinetic measurements. Six mass-flow controllers, which were operated by computer, were used to direct the gases in the required proportion to the reactor cell via a four-port valve (4 PV). The purpose of using a 4-PV was to make sure that at no point during the experiment, oxygen and hydrogen were mixed. The reactor cell, details of which are available somewhere else [24], operating as a plug-flow reactor with a diameter of 1.6 mm, was used as a transmission/fluorescence cell with aluminum windows. The exhaust of the reactor was connected to a QIC-20 mass spectrometer (Hiden Analytical) to monitor the outlet gases to calculate carbon monoxide conversion and corresponding rate of reaction. The catalyst, with a mesh size of 255–325 μm, amounts approximately 18 mg for each experiment. The catalyst was always treated in 2% hydrogen in helium at 473 K before each experiment. The total volumetric flow gases through the reactor was kept constant at 25 ml/min corresponding to a space velocity of about 54,000 h^{-1}.

2.4. In situ time-resolved high-energy resolution fluorescence detection X-ray absorption spectroscopy

X-ray absorption experiments were carried out at beamline ID 26 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The electron energy was 6.0 GeV, and the ring current varied from 50 to 90 mA. Two u35 undulators were used to perform the measurements. The X-ray beam measured 0.3 mm horizontal and 1 mm vertical; the total flux was 5×10^{12} photons/s. The energy was calibrated with a platinum foil. The incident energy was selected by means of a pair of Si(1 1 1) crystals with an energy bandwidth of 1.5 eV at the Pt L_3 edge. Higher harmonics were suppressed by using two mirrors, one coated with palladium and the other with chromium, working at 3 mrad in total reflection. High-energy resolution fluorescence detected (HERFD) absorption scans were recorded by measuring the intensity of the Pt $L\alpha_1$ line as a function of the incident (absorption) energy. An X-ray emission spectrometer based on perfect crystal Bragg optics was employed [10] for this purpose with an avalanche photodiode (APD) as photon counting detector. The instrumental bandwidth was 1.5 eV, which is smaller than the core hole lifetime broadenings. For comparison,

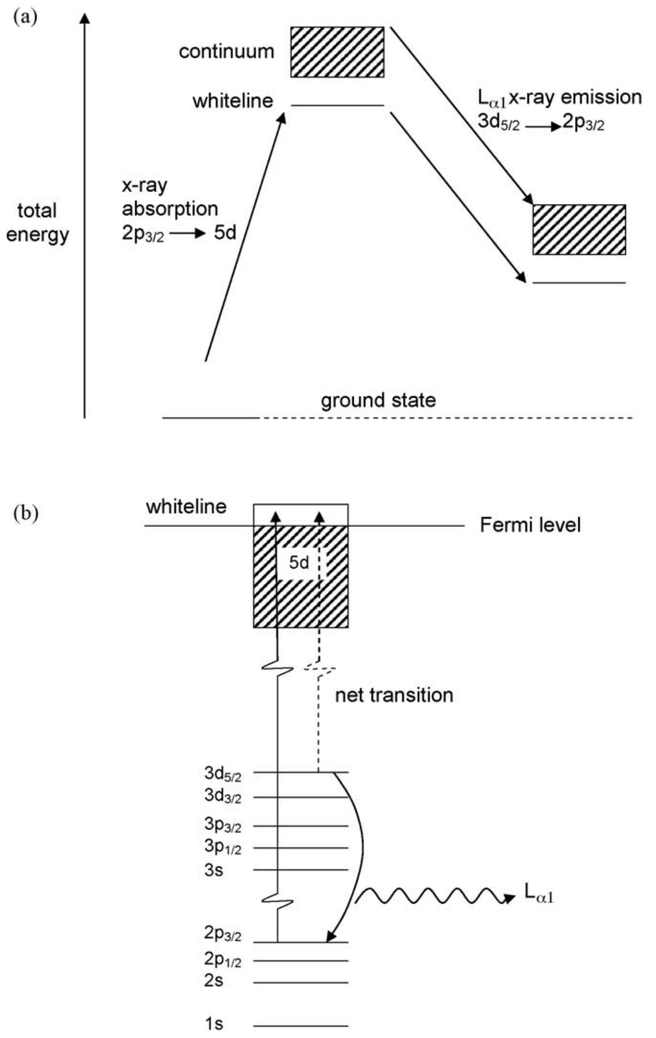

Fig. 2. Total energy scheme (a) of the electronic transitions (b).

a solid-state detector such as germanium would have an energy bandwidth of ~400 eV at this energy. The line-sharpening effect arises from the fact that the lifetime broadening in the final state is smaller than in the intermediate states of the absorption spectrum (Fig. 2). The lifetime broadening of L_3 and M_5 levels tabulated in FEFF8.2 code is equal to 5.2 and 2.4 eV respectively. According to the equation given in Ref. [25], the broadening of HERFD spectra will be equal to 2.2 eV. The HERFD broadening (Lorentzian) is convoluted with the experimental broadening (Gaussian) and the width of platinum whiteline in the HERFD experiment is calculated to 2.9 eV, which is similar to the value observed in the experiment. A Canberra silicon photodiode was mounted to measure the total fluorescence simultaneously with the HERFD XAS. The catalyst was heated at 5 K/min from room temperature to the temperature of maximum conversion, and cooled back to room temperature, with simultaneous collection of spectra with a time resolution of 1 min.

3. Results and discussion

The oxidation of carbon monoxide on supported platinum catalysts proceeds in two regimes, a high-activity and a low-activity one. In this work, the oxidation of carbon monoxide over a 2-wt% Pt/Al_2O_3 catalyst was carried out for oxygen to carbon monoxide ration of one, two, and five. Fig. 3a shows a STEM micrograph of the catalyst. The platinum nanoparticles were identified as bright tiny spots and well dispersed on alumina support. Fig. 3b shows the particle size distribution showing a mean particle size of about 1 nm. Table 1 summarizes the kinetic results of the oxidation of carbon monoxide in various ratios. The data were reproduced from the previous work [31]. At all ratios, the conversion of carbon monoxide increased exponentially with temperature until at a specific temperature, a large jump in the conversion occurred. We call this jump "ignition" of the reaction. At this point, the rate of reaction increased significantly compared to the rate at temperature less than the ignition temperature. Afterwards, the rate became constant with increase in temperature signifying the complete conversion of carbon monoxide. This phenomenon of two different reaction regimes has been observed on single crystals and supported platinum catalysts [14,15,19,20,26–30] but so far has not been unambiguously correlated with changes in the platinum catalyst. Most of the data on catalyst structure were derived from vibrational spectroscopy, which provide information about the adsorbing reactant molecule. The adsorbate is probed and only indirect information about the catalyst is obtained. The HERFD XAS technique, as applied in our experiment, provides complementary information to that obtained from the vibrational techniques; i.e. gives the geometric and electronic structure of the catalytic metal site during reaction. It is also complementary to

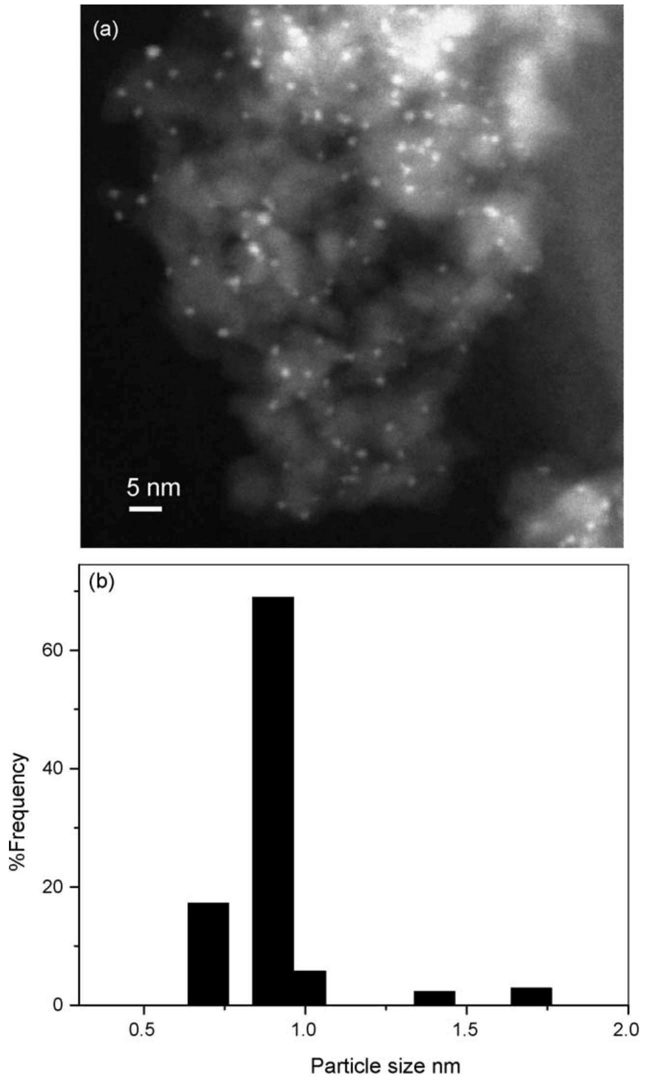

Fig. 3. (a) STEM micrograph of 2 wt% Pt/Al_2O_3 prepared by incipient wetness impregnation and (b) particle size distribution of platinum particles.

Table 1
Results of the kinetic measurements for the oxidation of carbon monoxide over a 2 wt% Pt/Al_2O_3 catalyst.

O_2/CO ratio	Below ignition		Temperature of ignition (K)
	Rate of reaction (cm^3/(min gcat))	Temperature (K)	
1	0.0056	428	472
2	0.0120	428	445
5	0.0195	428	433

surface X-ray diffraction experiments that prove the surface structure of single crystals [16].

As the concentration of oxygen increased in the reactant gases, with increasing oxygen to carbon monoxide ratio, the temperature of ignition decreased (Table 1). Also at any particular temperature, the rate of reaction was higher for the higher oxygen to carbon monoxide ratios. During cooling, a similar phenomenon occurred. Upon cooling, the conversion of carbon monoxide decreased strongly in a very narrow temperature interval. We call this extinction of the reaction. Further decreasing the temperature showed a normal exponential decrease in conversion. The temperature of extinction, similar to the ignition temperature, was lower under higher oxygen concentration.

Fig. 4 reproduces the conventional L_3 edge XAS and HERFD XAS of a supported platinum catalyst after treatment in three atmospheres: helium, 1% carbon monoxide in helium, and a mixture of oxygen and helium [6]. The shape and intensity of the whiteline varied in each atmosphere, and small shifts in the edge position were observed. The changes in the spectra showed much better resolution in the HERFD XAS data. The intensity of the whiteline in the spectrum of already reduced catalyst under helium was lower than that of the catalyst under oxygen, reflecting the oxidation of platinum. This increase is visible both in the conventionally detected fluorescence and in the spectrum of HERFD spectroscopy. In the case of the catalyst with adsorbed carbon monoxide, the HERFD spectrum revealed a double feature, which was broader on the high-energy side of the whiteline compared to that in bare platinum. This doublet has been assigned to atop adsorption of carbon monoxide [6]. The spectral feature was attributed to the anti-bonding state above the Fermi-level that forms when the platinum d orbitals and the $2\pi^*$ orbitals of carbon and oxygen overlap. Although the conventionally measured XAS spectra show spectral edges, the high-resolution data are much more sensitive in detecting any spectral changes. We used the spectra in Fig. 4 as reference spectra when comparing the changes in the spectra of the platinum catalysts that were measured during the oxidation of carbon monoxide under various conditions.

Fig. 5a shows the Pt L_3 edge HERFD XAS spectra of Pt/Al_2O_3 below and above the ignition temperature in an atmosphere of oxygen and carbon monoxide in ratios of one, two, and five. These spectra were recorded while heating the sample. The spectrum below ignition showed the doublet characteristic of adsorbed carbon monoxide. Its intensity was low compared to the spectra that were measured at lower temperature (spectra not shown) [31]. In the low-activity regime, oxygen has a positive effect on the reaction rate and the reaction has a positive order in oxygen [15,32,33]. Adsorbed carbon monoxide on reduced platinum was observed (Fig. 5), in general agreement with infra-red data on supported metal catalysts and single crystals [15,17–20,27,28]. This adsorbed carbon monoxide prevents the catalyst surface from oxidizing even in an overdose of oxygen at sufficiently low temperature. Before oxygen can be activated to react to carbon monoxide, a carbon monoxide molecule has to desorb. The amount of carbon monoxide adsorbed on the metal surface decreases with temperature; at a certain ignition temperature, the conversion of carbon monoxide and the rate of the reaction increases suddenly and significantly. At a temperature above the ignition temperature, the spectra in all the three ratios showed a strong increase in the intensity of the whiteline while the edge shifted slightly to lower energy. These changes are characteristic of oxidized platinum [6]. The sudden increase in the whiteline intensity was in accordance with the increased rate of reaction at this point. This high activity is found only at elevated temperature [18]. We observed that the

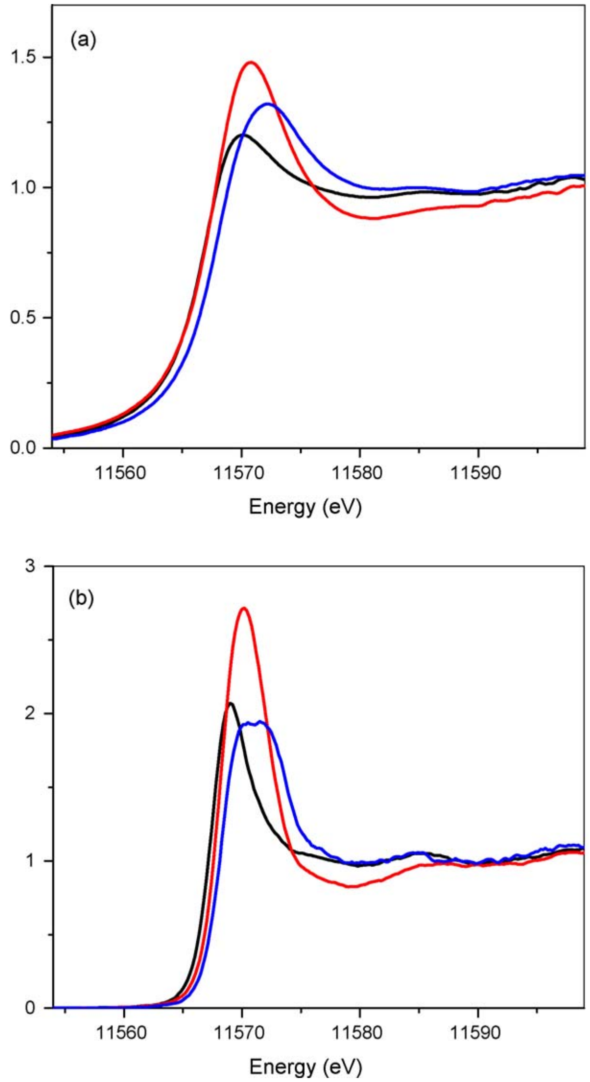

Fig. 4. Pt L_3 edge XANES of 5 wt% Pt/Al_2O_3 after reduction in different atmospheres: helium (black), helium (oxygen) (red), and 1% carbon monoxide in helium (blue) measured (a) using traditional fluorescence detection and (b) using HERFD XAS spectroscopy. Reprinted with the permission from J. Phys. Chem. B. (Letter) 110 (2006) 16162. Copyright (2006) American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

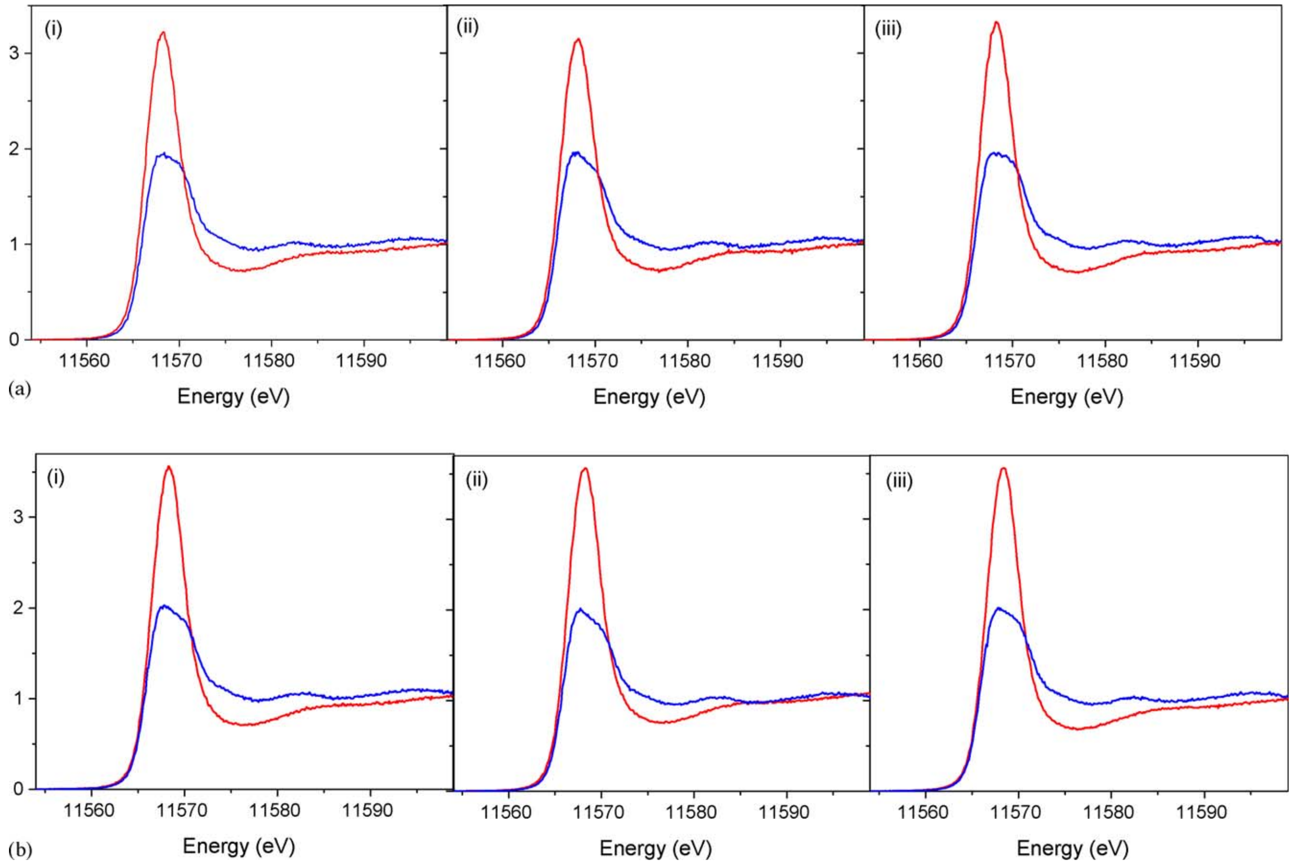

Fig. 5. Pt L_3 edge HERFD XANES of 2 wt% Pt/Al_2O_3 during the oxidation of carbon monoxide (a) above (red) and below (blue) ignition during heating, and (b) above (blue) and below (red) extinction during cooling for ratios of oxygen to carbon monoxide of (i) one, (ii) two, and (iii) five. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

structure of the supported platinum particles is very different in this regime. A large fraction of the platinum is oxidized. Fig. 5b shows the Pt L_3 edge HERFD XAS spectra of Pt/Al_2O_3 above and below the extinction temperature in atmospheres of oxygen and carbon monoxide in ratios of one, two, and five measured while cooling. Below the extinction temperature, the whiteline intensity had dropped and the doublet feature appeared in the spectra. This doublet feature got more intense with further cooling down (spectra not shown). This sudden decrease in the intensity of the whiteline and the re-emergence of the doublet corresponding to adsorbed carbon monoxide was observed in all the three cases. The re-emergence of the doublet feature corresponded to 453, 445, and 433 K for oxygen to carbon monoxide ratios of one, two, and five respectively and was accompanied by the extinction of the reaction (Table 1). Based on our in situ HERFD XAS data, the occurrence of sudden changes in the reaction rate can be assigned to two different platinum phases in the two regimes. HERFD XAS shows that at low activity (below ignition temperature), platinum is covered with carbon monoxide, which inhibits the reaction from proceeding at higher rates and, thus, poisons the surface [15]. Therefore, in this region, the rate-limiting step is desorption of carbon monoxide, which is necessary for the activation of oxygen [17,19,21,33]. At high activity, above ignition, the platinum species are partially oxidized (Fig. 5). The rate of oxidation increased and the reaction proceeds via a different rate-limiting step. As the surface is no longer poisoned by carbon monoxide, a higher rate is obtained. Because of the low concentration of carbon monoxide, oxygen can react to the surface, forming the platinum oxide phase. Although PtO_2 has been shown to be less active [20], partially oxidized platinum catalyst showed high activity. This correlates to the high activity observed for partially oxidized ruthenium surfaces [34]. Fig. 6 compares the Pt L_3 edge HERFD XAS spectra of Pt/Al_2O_3 in 5% oxygen in helium oxygen and in an atmosphere of oxygen and carbon monoxide at a ratio of one, two, and five at a temperature above the ignition temperature, thus at high rate of reaction. In case of oxygen to carbon monoxide ratio of two, the spectrum above the ignition temperature is compared with the spectrum recorded under 5% oxygen in helium at 458 K. For the other two ratios, the spectra were compared to spectra recorded at 398 K under 5% oxygen in helium. In all cases, spectra above ignition and under 5% oxygen in helium showed almost the same intensity of the whiteline, indicating a high degree of oxidation of the platinum catalyst above ignition of the reaction. This suggests that the extent of oxidation is similar under both sets of conditions. Oxidized nano-sized platinum particles have been shown to be more reactive than reduced platinum with adsorbed carbon monoxide on its surface [26]. Our data suggests that the amount of oxide that is formed above ignition is similar to that under pure oxygen. The concentration of carbon monoxide at the surface is very low, causing the extent of oxidation to be very similar. The diffusion of carbon monoxide to the surface may become rate limiting over the highly active surface of the catalyst. These platinum oxide species are formed at temperatures above the ignition temperatures of 472, 445, and 433 K, at oxygen to carbon monoxide ratios of one, two, and five respectively. These oxidic species form only when the oxygen concentration is considerably higher than that of carbon monoxide and at temperatures at which carbon monoxide has partially desorbed from the surface and its concentration decreased because of conversion.

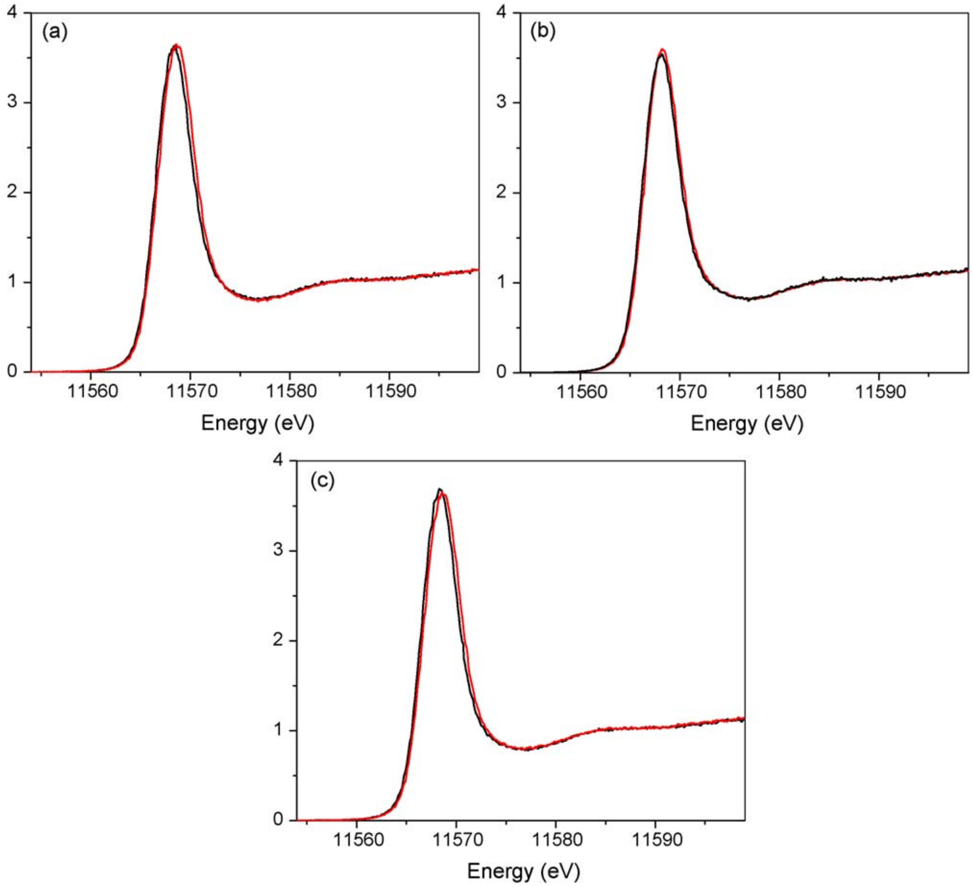

Fig. 6. Pt L_3 edge HERFD XANES of 2 wt% Pt/Al_2O_3 (a) in 5% oxygen in helium at 398 K (red), and during the oxidation of carbon monoxide for a ratio of oxygen to carbon monoxide of one at 491 K (black), (b) in 5% oxygen in helium at 458 K (red), and during the oxidation of carbon monoxide for a ratio of oxygen to carbon monoxide of two at 472 K (black), and (c) in 5% oxygen in helium at 398 K (red), and during the oxidation of carbon monoxide for a ratio of oxygen to carbon monoxide of five at 454 K (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

4. Conclusion

Platinum nanoparticles, supported on alumina and prepared by incipient wetness impregnation have different activities in the oxidation of carbon monoxide in different gas atmospheres. The catalyst shows different structure in a low- and high-activity regime: adsorbed carbon monoxide on platinum in the low-activity regime, that poisons the surface and oxidic platinum in the high-activity regime as observed with in situ HERFD XAS. The rate in the low-activity regime is determined by the desorption of carbon monoxide from the surface and subsequent dissociative adsorption of oxygen. In the high-activity regime, the catalyst is no longer poisoned by carbon monoxide, because of its low concentration at the catalyst surface. As a result the catalyst is partially oxidized. This surface shows a high rate of reaction. High temperature and a high oxygen concentration benefits the formation of the more active catalyst. High resolution XAS enables to determine the structure of supported nanoparticles of loadings as low as 2 wt%. Because only hard X-rays are involved in this experiment, it can be performed under in situ conditions providing structural information while the catalyst is under real working conditions.

Acknowledgements

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