In situ XAS probes partially oxidized platinum generating high activity for CO oxidation

E M C Alayon¹,², J Singh¹, M Nachtegaal², M Harfouche², and J A van Bokhoven¹,³

¹ Institute for Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland
² Paul Scherrer Institute, General Energy Research Department, Laboratory for Energy and Material Cycles, 5232 Villigen PSI, Switzerland

E-mail: jeroen.vanbokhoven@chem.ethz.ch

Abstract. In situ x-ray absorption spectroscopy identified partially oxidized platinum as the active phase for generating high activity during carbon monoxide oxidation over Pt/Al₂O₃. CO covers and poisons metallic platinum, which results in a low catalytic activity. The conversion in CO abruptly increased during ignition, switching from low activity to high activity, accompanied by oxidation as observed in the increased intensity of the XANES. EXAFS analysis indicated breaking of Pt-Pt bonds and the appearance of a Pt-O scatterer. The partially oxidized catalyst had a lower oxygen coordination number and shorter Pt–O bond length than bulk PtO₂, suggesting that a strongly defected platinum oxide was formed with a coordination possibly lower than octahedral. From infrared data, ignition was accompanied by the abrupt disappearance of CO adsorbed on metallic particles. The reverse changes happen with the sudden decrease in CO conversion during extinction: partially oxidized catalyst becomes reduced and covered with CO.

1. Introduction
The catalytic capability of platinum has long been known and studied. However, the fundamental mechanisms that occur during the catalytic reaction, which is strongly linked to the structure of platinum, remain elusive. For oxidation of CO, studies on single crystals report a surface reconstruction [1] when a critical CO concentration is reached. A roughening of the single crystal platinum surface was recently observed [2] that was attributed to a switch from metallic to oxidic surface coinciding with a sudden increase in catalytic activity. On supported platinum catalysts, the reaction becomes sustainable above an ignition temperature and a new surface carbon monoxide species, that is active for oxidation, was identified [3]. However, the enhancement of conversion at higher temperature and the lesser affinity of the oxidic species for CO adsorption merited the metallic phase as the active surface [4,5]. Oxidation was associated with catalyst deactivation when the supported platinum surface periodically oxidized and reduced [6]. Recent results show an autocatalytic ignition of the reaction with depletion of surface carbon monoxide, which was closely tied to surface oxidation [7].

³ Author to whom correspondence should be addressed
We have exploited in situ X-ray absorption spectroscopy at the Pt L₃ edge to resolve local structural information of platinum under catalytically relevant reaction conditions [8,9]. The Pt L₃ whiteline intensity is a signature of the empty d-density of states and so is sensitive to the oxidation state. The XANES gives information on local geometry and the presence of adsorbates [10]. The EXAFS provides the local structure of platinum with its nearest neighbors, expressed in coordination number, inter-atomic distance and Debye-Waller factor. We measured nano-sized supported particles of Pt/Al₂O₃. Infrared measurements were also performed for information on adsorbed species during the reaction. In situ XAS measurement results for bigger particles of Pt/Al₂O₃ and platinum on TiO₂ and SiO₂ are described elsewhere [11].

2. Experimental Methods
Two weight percent Pt/Al₂O₃ was prepared by incipient wetness impregnation, which is described elsewhere [11]. The platinum particle size distribution was deduced from TEM measurements. 18.4 mg of the catalyst was loaded on a plug flow reactor for transmission and fluorescence XAS measurements [12]. High purity gases (Messer, >99.995 vol%) were fed to the reactor at 30 mL/min total flow. The catalysts were reduced in 10% hydrogen in helium at 200°C before a reaction. The feed gas for the reaction consisted of 1 mL/min oxygen, 1 mL/min CO, and the balance helium. Online gas product analysis during heating and cooling at 0.5 °C/min was registered by an Omnistar quadrupole mass spectrometer by Pfeiffer Vacuum.

In situ XAS experiments were performed at SuperXAS of the Swiss Light Source at PSI using a Si-111 double crystal monochromator, with a beam size approximately 100 µm horizontal by 115 µm vertical. Spectra were collected either in transmission or fluorescence geometry. In transmission, a platinum foil spectrum is simultaneously collected for internal energy calibration. A 13-channel Ge detector collected the fluorescence signal. A XANES spectrum was measured from 11.545 to 11.600 keV. Multiple EXAFS spectra were taken to improve the signal to noise ratio. Processing of EXAFS spectra followed standard procedures [13] with XDAP [14] and is described in more detail elsewhere [11].

For the infrared experiments, 11 mg of the catalyst was pressed into a pellet of 7 mm diameter using 2 tons force for 10 seconds in a hydraulic press and placed inside a DRIFT cell in a Bio-Rad infrared set-up and was connected to the gas lines and temperature controller. The reaction mixture consisted of 1.2 mL/min oxygen and 4.8 mL/min of the 5% carbon monoxide in helium mixture (O₂/CO=5). A mass spectrometer simultaneously monitored the outgoing gases. The MCT detectors were cooled with liquid nitrogen. Before every run, the catalysts were reduced in 10% hydrogen in helium atmosphere at 200°C for 15 minutes, then the gas environment was switched to pure helium for one hour to remove hydrogen. The total flow of the gas was maintained at 6 mL/min. Background spectra of the catalyst in helium were taken every 10 °C interval for subtraction. Heating and cooling ramp was 2°C/min. Fifty spectra at a resolution of 2 cm⁻¹ were averaged to one scan to improve the signal to noise ratio.

3. Results and Discussion
TEM measurements indicate a Pt/Al₂O₃ particle size of 0.9 nm. Figure 1 shows the CO conversion curve for the heating and cooling cycles at 0.5 °C/min at O₂/CO=1. The conversion in CO increases slowly with temperature and reaches a point where it shoots up to near maximum. The temperature at which the conversion jumps is called ignition, the reverse during cooling is called extinction. Ignition and extinction occurred at 180 and 164 °C respectively. Figure 1 also shows the Pt L₃ XANES spectra recorded during the heating and cooling of Pt/Al₂O₃ near ignition and extinction, where one spectrum spans 2 °C. The spectra below ignition show a low whiteline intensity that is broadened towards higher energy. This is characteristic of reduced platinum particles with CO adsorbed on the surface [10]. The spectra above ignition show increased whiteline intensity and a dip after the absorption edge, characteristics of oxidic platinum [11]. The spectrum taken at 179 °C shows the very sudden switch from the metallic to the partially oxidic spectrum at 11.577 keV, which corresponds to the moment of
ignition. During cooling, the whiteline intensity of the spectra decreases with extinction, and reverts back to the broadened whiteline shape. The structural changes to platinum and jumps in the CO conversion curve are reversible with heating and cooling, albeit showing hysteresis. This leads to the identification of a high and low activity regime catalyzed by oxidic and metallic configurations of platinum particles, respectively.

Figure 1. Pt L3 XANES spectra recorded during a) heating and b) cooling at 0.5 °C/min of Pt/Al2O3 at the corresponding temperatures indicated in the conversion curves; ignition and extinction occurred at 180 and 163 °C, respectively.

Table 1 summarizes the results of the fitting of the corresponding EXAFS spectra. Small particles of platinum in helium, after reduction and removal of hydrogen, show a Pt-Pt coordination number of 5.5, which correlates to a particle size of around 1 nm [15], and a Pt-Pt distance of 2.72 Å, which is smaller than the 2.76 Å Pt-Pt distance of bulk platinum, indicating a contraction of the cluster with the small size [16]. The EXAFS fit of the spectrum taken in an O2/CO atmosphere below ignition shows a slight increase in the Pt-Pt distance to 2.77 Å, which indicates a bond length relaxation induced by adsorbed CO, similar to the phenomenon after adsorption of hydrogen [17]. Above ignition, the coordination number of the Pt-Pt contribution decreases to 2.0, which indicates breaking of Pt-Pt
bonds. This is accompanied by the appearance of an additional Pt-O contribution with a distance of 1.99 Å that is in good agreement with the Pt-O distances of platinum oxides [18]. This is likewise in agreement with the increasing intensity and switch to characteristic features of oxidic species of platinum in the XANES spectra accompanying ignition. The EXAFS fit of the spectrum at room temperature in O₂/CO at the end of cooling, after extinction (data not shown), had a coordination number of 5.6 for and 2.76 Å Pt-Pt distance, similar to the values at the start of heating in the same conditions. This indicates that the platinum particles have the same size before and after the heating and cooling cycle and rules away sintering of the platinum particles during the switch to high activity.

Table 1. EXAFS fit parameters.

| Catalyst Conditions | Ab-Sc pair | N     | DW (Å²)      | R (Å)  | E₀ (eV) |
|---------------------|------------|-------|--------------|--------|---------|
| Pt/Al₂O₃ 0.9 nm     | Pt-Pt      | 5.5±0.2 | 0.0040±0.0003 | 2.72±0.01 | 1.7±0.2 |
| In helium           | Pt-Pt      | 5.7±1.2 | 0.0047±0.0006 | 2.77±0.01 | 0.5±0.1 |
| Below ignition      | Pt-Pt      | 2.0±0.6 | 0.0050±0.0010 | 2.71±0.10 | -1.4±0.8 |
| Above ignition      | Pt-Pt      | 2.4±0.3 | 0.0025±0.0010 | 1.99±0.01 | 3.2±2.0 |
|                     | Pt-O       |        |              |        |         |

*Pt-Pt could also be fitted with two contributions from a short Pt-Pt at 2.60 Å and of a long Pt-O-Pt at 3.15 Å.

The oxidation of the platinum particles is likely limited to the surface. The EXAFS fit showed a Pt-Pt contribution remaining above ignition having a Pt-Pt distance shorter than that in a typical PtO₂ but resembling that of metallic platinum. This translates to a structure of a metallic core surrounded by surface platinum oxide. In view of measurements by SXRD where the surface oxide structure on a Pt(110) surface during reaction conditions was found to be a thin distorted α-PtO₂, having compressive and tensile strain relative to bulk α-PtO₂ [2], the subtle post-edge features of the EXAFS spectra we obtained are not comparable to those of α- or β-PtO₂ [19]. This is attributed to a lack of long-range order of the oxide. The low Pt-O coordination number, 2.4, suggests coordination geometry lower than octahedral. The platinum oxides α- and β-PtO₂ are octahedral in Pt-O, while Pt₃O₄ and PtO are square planar [18]. The Pt₃O₄ configuration was predicted to be active for oxidation due to the undercoordinated sites where CO can bind. Bulk platinum oxide is inactive [20]; however, PtO₂ can be active when surface defects are present [21]. Combined metallic, PtO, and Pt₃O₄ clusters were found present by in situ XRD on oxygen covered particles during CO oxidation [22]. Thus, the presence of defect sites and undercoordination may be a feature of the surface oxide that makes it catalytically active above ignition.

To keep track of the adsorption and desorption of CO on the surface of platinum particles during the reaction, and especially to probe the surface above ignition, infrared measurements were performed. Figure 2 shows the infrared spectra recorded during heating and cooling of Pt/Al₂O₃ at 2 °C/min and O₂/CO=5. Spectra are normally shown at intervals of 5 °C, but at intervals of 1 or 2 °C in the immediate vicinity of ignition and extinction, at 151 °C and 100 °C, respectively. During heating, the peaks at 2060 cm⁻¹ and 1820 cm⁻¹, corresponding to linearly and bridge-bonded CO [23,24] abruptly decreased in intensity at 151 °C, which exactly corresponds to the temperature of ignition. In parallel, the peaks between 2300 to 2400 cm⁻¹, attributed to gaseous carbon dioxide [24], increased sharply upon ignition, while the double band centered around 2140 cm⁻¹, corresponding to gaseous CO [23] abruptly decreased. Additional peaks between 1200 to 1700 cm⁻¹ that are attributed to carbonates and bicarbonates [25] appeared after ignition. During cooling, the linear- and bridge-bonded carbon monoxide peaks appeared slowly approaching extinction and returned to almost full intensity at the
temperature of extinction, while the gaseous carbon dioxide peak decreased sharply. The surface of the platinum particles below ignition is CO-covered, while that above ignition is free of adsorbed CO.

The adsorbed CO on metallic platinum at the low activity regime, as seen in the broadened whiteline of the XANES and the linear- and bridged-CO infrared peaks, inhibits oxygen from interacting with the catalyst surface and so limits the rate of the reaction [3]. CO keeps the particles reduced. With increasing temperature, CO desorbs, which allows oxygen to interact with the sites previously occupied by CO and increases the reaction rate. With increasing CO conversion and temperature, the concentration of absorbed CO species decreases to the point of ignition where conversion increases very rapidly and causes the surface to oxidize [7]. CO has less affinity for adsorption to an oxidic surface and the infrared spectra show no CO adsorbed after ignition. The discontinuity in the conversion curve indicates a possible change in the reaction mechanism from Langmuir-Hinshelwood [26] below ignition, where CO and O$_2$ adsorb on the metallic surface and react to CO$_2$ and so is rate-limited by the strong adsorption of CO, to a Mars-van Krevelen type [2] at above ignition, where the activated oxygen is available from the surface oxide layer, which is replenished from the gas phase, and is thus not hindered by CO adsorption. However, our data cannot distinguish this mechanism from one that occurs on the surface of the oxide.

Figure 2. Infrared spectra during a) heating and b) cooling at 2 °C/min of Pt/Al$_2$O$_3$ in O$_2$/CO=5; ignition and extinction occurred at 151 and 100 °C, respectively.

4. Conclusion
The high activity regime for carbon monoxide oxidation on supported platinum catalysts occurs at low CO concentration and high temperature with partially oxidized platinum as the active phase. The switch from low to high activity is characterized by a sudden increase in CO conversion accompanied by oxidation of the platinum particles, as supported by the increasing intensity of the XANES. There is breaking of Pt-Pt bonds and the appearance of a Pt-O scatterer after ignition as indicated by the EXAFS fits. CO poisons the catalyst surface at low activity. The depletion of CO from the surface during ignition, as seen in the infrared data, enables oxygen to react, which increases conversion and causes the surface to oxidize. A disordered surface oxide is formed, which is defect-rich.
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