



	Experiment title: Further operando studies of Pt-based Diesel Oxidation Catalysts by Energy Dispersive EXAFS: performance and stability under rapid temperature transient conditions	Experiment number: CH-4953
Beamline: ID24	Date of experiment: from: 9 th Feb 2017 to: 14 th Feb 2017	Date of report: 27/07/2017
Shifts: 15	Local contact(s): Debora Motta Meira	<i>Received at ESRF:</i>
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Report:

Automotive catalysts experience a complex range of environmental conditions during use, including transient temperature changes, changes in gas environment and gas flow rate [1]. In order to provide essential information on the behaviour of working catalysts, it is critical to expose the catalyst to experimental conditions representative of real-world use during *in situ* or *operando* studies [1,2]. Of the examples given above, the application of rapid transient temperature changes has proven uniquely difficult to reproduce in practise, except in large-scale specialised engine test bench setups. The combination of *operando* spectroscopy with transient temperature changes and catalytic data is therefore unexplored in the literature.

The aim of this proposal was to investigate a series of Pt-based Diesel Oxidation Catalysts (DOC) for CO oxidation by *operando* XAS, while applying rapid transient temperature conditions extracted from a real automotive driving cycle [3]. The effects of temperature ramp rate and catalyst response were therefore determined in relation to the catalyst composition. Experiments were performed with the aid of a silicon microreactor optimised for rapid temperature transitions combined with simultaneous spectroscopic and activity measurements [4,5]. Synchrotron radiation measurements were performed at beamline ID24 of the ESRF. This experiment was a continuation of a previous study also performed at ID24 (CH4577), which has recently been published with co-authorship including ESRF staff [6]. Further publication is expected based on the extensive results obtained in the previous and current proposal.

A series of alumina-supported Pt (1 wt.%) and Pt/CeO₂ (1/5 wt.%) catalysts were placed in silicon microreactor chips and subjected to repeated rapid heating and cooling ramps (5, 20, 40, 70, 110, 180, 290 °C/min). Two distinct gas environments were applied during the temperature treatments to simulate the emissions of a diesel exhaust, a CO only composition (1000 ppm CO, 10% O₂, He balance), and a CO/NO mix composition (as before including 1000 ppm NO). Data was recorded in fluorescence mode using the Turbo-XAS methodology [7]. A pair of diodes were used to measure the background (I₀) and fluorescence

signal from the sample (I), while scanning from 11470 to 11700 eV (Pt L₃ edge 11564 keV). Internal reference states were obtained by heating each catalyst in a flow of synthetic air, followed by hydrogen (5% in He) to obtain oxidised and reduced forms, respectively. A customised data treatment methodology was employed to process the Turbo-XAS data. This consisted of: (i) batch normalisation (I₀), (ii) internal referencing of whitenline intensity, (iii) outlier rejection to remove noisy spectra, (iv) Linear Combination Fitting (LCF) based on the internal references to assess catalyst response, (v) signal-to-noise optimisation. The XAS data obtained were correlated with on-line mass spectrometry to assess catalyst performance in terms of CO₂ production, and relate this to the oxidation state observed and hysteresis behaviour (Figure 1).

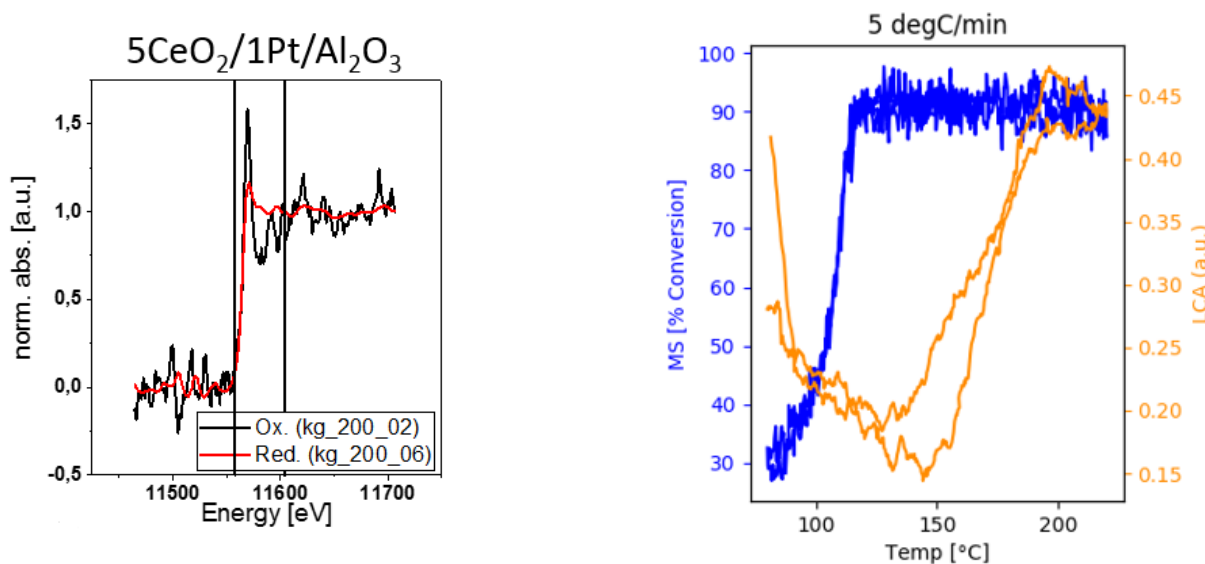


Figure 1. (Left) Internal referencing procedure. (Right) Typical hysteresis curves observed during a ‘slow’ cycle of 5 °C/min, showing CO₂ yield (MS conversion) and fraction of oxidised Pt determined by LCA.

Data analysis is currently still in progress, but as an example of the information which will be gained from this experiment, we expect to see: (i) differences in CO oxidation ‘light-off’ (ignition point) as a function of temperature ramp rate, (ii) hysteresis profile differences, including reverse or normal behaviour, as a function of temperature, (iii) catalyst stability (consistent oxidation state change and CO₂ yield) over multiple temperature cycles, (iv) all of the above with respect to catalyst structure (including presence of ceria, Pt nanoparticle size, preparation method, among other factors). The results obtained will provide information on catalyst performance, stability, surface chemistry and may be used to build basic kinetic profiles of the CO oxidation reaction at various temperature ramp rates. Such data has not previously been measured under rapid transient temperature conditions, therefore providing novel insights.

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