



	Experiment title: Studying the dynamic changes of alumina supported Pt nanoparticles during a New European Driving Cycle by Energy Dispersive EXAFS	Experiment number: CH4577
Beamline: ID24	Date of experiment: from: 27/10/2015 to: 03/11/2015	Date of report: <i>Received at ESRF:</i>
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Report:

A major concern in modern automotive catalysis research is the development of more efficient technologies for exhaust gas aftertreatment. In particular, environmental and health issues render it important to proactively reduce pollution from vehicles, such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxide (NO_x) emissions. Supported Pt-based Diesel Oxidation Catalysts (DOC) are currently one of the most efficient methods for pollution control, particularly for CO removal. However, further improvements are required in modern catalyst systems, in particular to lower the noble metal content, the temperature of conversion, and the long and short-term stability under realistic conditions.

The NEDC is a driving cycle designed to assess the emission levels of road vehicles. It consists of four phases representative of urban driving (low temperatures), followed by one phase at higher speed for motorway driving (higher temperatures) [1]. Catalysts tested under such conditions follow the temperature profile presented in Fig. 1 (black curve) with fast heating and cooling periods (up to ~120 °C/min). In order to improve future catalyst design and to provide better knowledge of the material, it is essential to study the catalysts under realistic, and often harsh, operating conditions [2,3] such as those experienced during NEDC. However, in conventional laboratory setups, test cycles with such rapid heating/cooling ramps are not easily attainable. Up to now only engine bench test setups and special setups for studying monolith catalysts can be used (e.g. [4]) to validate catalyst performance in the NEDC. These expensive systems are difficult to maintain and to operate. In addition, obtaining complementary spectroscopic information *in situ* with such systems is a difficult task.

By contrast, studying such transient processes in microreactors presents a number of key advantages. Due to their high surface to volume ratio, they possess favourable heat transfer properties compared to classical reactors, thus also under exothermic reactions, isothermal reaction conditions can be easily achieved. The application of fast heating and cooling is also possible, which is a prerequisite for catalyst testing under transient regimes. In addition, detailed structural and mechanistic profiling of the catalyst is feasible, as microreactors can be designed to allow for various complementary characterisation techniques [5]. Our group has recently developed a purpose-built, lithographically-fabricated, silicon microreactor [6], optimised for catalytic studies with high spatial and time resolution. Previously, we have applied this microreactor in studies of Catalytic Partial Oxidation (CPO) of methane [6] and Selective Catalytic Reduction (SCR) of NO_x with ammonia [7].

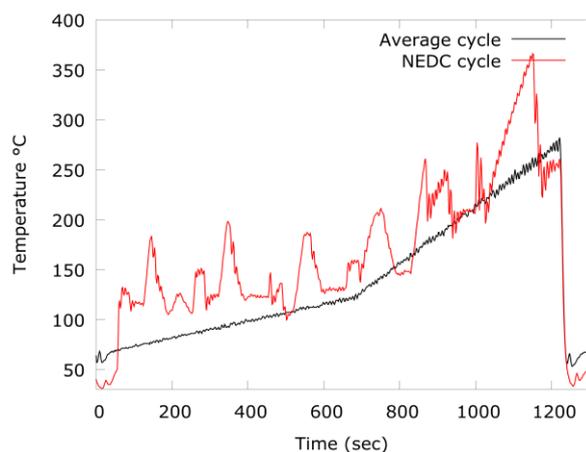


Figure 1. Temperature profile of NEDC and average 'slow' cycle applied during CO oxidation in the microreactor.

Here we present a study on CO oxidation under NEDC temperature transient conditions over Pt/Al₂O₃ and Pt/CeO₂-Al₂O₃ catalysts. The microreactor is specifically designed for analysis by X-ray methods, and allows fast heating and cooling cycles while dosing realistic gas mixtures. In the present study we applied time-resolved, fluorescence-detected, energy dispersive XAS (technique known as Turbo-XAS [8]) to investigate rapid structural dynamics of the active Pt sites during the temperature profile of a NEDC. This was coupled with Mass Spectrometry (MS) and IR thermography. This integrated *operando* approach allowed

simultaneous acquisition of the catalyst temperature profile, product formation, and spectroscopic information with high time resolution.

Synchrotron radiation measurements were performed at beamline ID24 of the ESRF in Grenoble, France. We measured on a set of alumina-supported Pt catalysts with a range of metal loadings (1, 2 and 4 wt.%), and with or without the presence of 5% CeO₂ as promoter. A gas composition of CO (1000 ppm in He), O₂ (5% in He) with He balance was used for DOC, with gases regulated using mass flow controllers. Two temperature protocols were applied: NEDC conditions with the temperature steps described previously [1]; and a constant temperature ramp (Fig. 1). Temperature was controlled with a Pt100 resistance thermometer on the microreactor surface and its profile was monitored by infrared thermography. The system response was studied by Turbo-XAS [8] along with the catalytic activity by means of a MS.

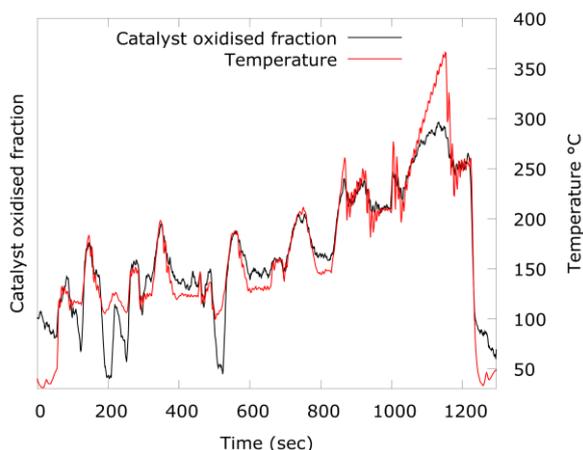


Figure 2. Temperature profile and catalyst oxidized fraction (calculated by LCA) during NEDC cycling.

The catalyst oxidised fraction, obtained by a Linear Combination Analysis (LCA) method, is shown as an example in Fig. 2 along with the NEDC temperature profile. It can be observed how the catalyst response closely matched the fast temperature changes applied. By correlating the temperature profile, the catalyst oxidation state and the MS signal of the reactant (CO) and products (CO₂) it is possible to assess the catalyst performance, including the light-off temperature and the stability over time. Here we report on the differences between a real driving cycle, represented by the NEDC, and test laboratory conditions, represented by a constant heat ramp during CO oxidation. The different thermal treatments experienced by the catalyst are shown in Fig. 1. The analysis carried out shows that the heating rate does in fact influence the catalyst performance and the light off temperature of the

reaction.

Several key observations were made during NEDC and ‘slow’ cycling experiments. The influence of metal loading and the presence of ceria as promoter influenced both the system response and stability over several reaction cycles. This also affected the reproducibility of the catalyst, in terms of the reduced fraction between cycles, or in the ‘resting’ state. In addition, the application of harsh fast transient NEDC conditions was observed to affect the light-off point of the reaction, compared to more mild ‘slow’ cycling conditions. Although the experiment was performed at a single ‘inlet’ position on the catalyst bed (ie. not spatially resolved), due to the time resolution we were able to observe evidence of a mobile oxidation state gradient [3], closely related to the temperature of the bed. Using the combined *operando* approach presented, together with our custom-designed microreactor, we could successfully apply rapid temperature transient conditions and perform spectroscopic and physical measurements on the working catalyst simultaneously. This represents an important step towards understanding a complex catalytic system with high time resolution and under working conditions. The approach presented here may be furthermore adapted for investigation of other transient exhaust gas treatment processes.

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