Electronic Supplementary Information (ESI) for the paper entitled:

**Transient structural and catalytic behaviour of Pt-particles probed by operando spectroscopy during a realistic driving cycle.**

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**S1 Detailed Turbo-XAS Data Treatment Procedure**

![Figure S1. Schematic showing: (a) experimental setup; (b) photo of the apparatus at ID24.](image)
The Turbo-XAS analysis strategy can be divided into the following steps:

1) Batch normalisation;
2) Internal reference search;
3) Outlier rejection;
4) Linear combination analysis (LCA);
5) Signal-to-noise optimisation.

1) Normalisation was performed by subtracting a first order polynomial both for the pre-edge and post-edge region to obtain an edge jump of 1. Care was taken to use the same parameters throughout the data set, avoiding errors which may arise from arbitrary choices.

2) In order to enhance the signal-to-noise ratio, referencing for LCA was done internally within each data set. To find the two extremes for LCA fitting we compared the integral of the edge region of each spectrum, selecting the spectrum with the lowest value as the “reduced Pt” reference and the spectrum with the highest value as the “oxidised Pt”. Figure S2 shows the reproducibility of the result for both samples.

![Figure S2. Internal referencing procedure for the samples. The white line intensity is proportional to the Pt oxidation state.](image)

3) A first statistical analysis was performed at this stage with a very broad median filter. A median criterion of 10 was used, meaning that each spectrum with a median value higher
than 10 times the median of all the medians in the data set was substituted with the average of the adjacent spectra. This step was rendered necessary for the sole purpose of discarding the spectra with evident glitches. Less than 0.1% of the spectra were discarded at this stage, at the same time eliminating all the low quality spectra, confirming a very good reproducibility of the beamline setup.

4) LCA was carried out including a region from before the edge to after the first peak (see Figure S3) using the reference parameters found in step 2). In this way a time-resolved relative Pt oxidised fraction, roughly oscillating between 0 and 1, was determined.

![Figure S3. Example of a LCA fit. The green box represents the integration range in point 2) of the data treatment, while the yellow box represents the LCA range, as in point 4).](image)

5) A final statistical filtering was necessary to enhance again the signal-to-noise ratio. For this stage, a Savitsky-Golay\(^1\) filter was employed (window size of 5 points and 3\(^{rd}\) order polynomial). With this stage the signal-to-noise ratio, in its definition of the mean of the signal divided by its standard deviation, increased about 10 to 20 % according to the different data sets. See Figure S4 for a comparison.
Figure S4. Comparison between a filtered and unfiltered data set during one NEDC.

S2 Extended Catalytic Activity Curves

Figure S5 Evolution of CO$_2$ production over 5 consecutive slow cycles.

S3 Quantification of Pt Oxidation State by Linear Combination Fitting

It is important to note that a relatively weak signal was obtained due to the low Pt loading, while the near edge structure can also be affected by small nanoparticle sizes. Therefore only the relative Pt oxidized fraction is presented in the manuscript based on the internal referencing procedure described above. Under reaction conditions Pt does not behave as
pure metal or oxide, having surface Pt sites bound to hydrogen and CO. LCA analysis with \textit{ex situ} Pt species (e.g. Pt foil, PtO$_2$) is considered to contain some systematic error (approx. 5%) due to the low Pt signal, and the presence of Bragg reflections from the microreactor which hinder normalisation of the spectra. The following analysis should therefore be regarded as semi-quantitative.

From the comparison of the “white line” intensity with the reference spectra of Pt foil and PtO$_2$:

**Pt-CeO$_2$/Al$_2$O$_3$** internal references during NEDC:
- Oxidized: Pt$^{+0.52}$ (approx. 13\% of PtO$_2$)
- Reduced: Pt$^0$ (-1\% deviation from the Pt foil)

**Pt-CeO$_2$/Al$_2$O$_3$** internal references during average cycles:
- Oxidized: Pt$^{+0.4}$ (approx. 10\% of PtO$_2$)
- Reduced: Pt$^0$ (-1\% deviation from the Pt foil)

**Pt/Al$_2$O$_3$** internal references during NEDC:
- Oxidized: Pt$^{+1.18}$ (approx. 29\% of PtO$_2$)
- Reduced: Pt$^0$ (-3\% deviation from the Pt foil)

**Pt/Al$_2$O$_3$** internal references during average cycles:
- Oxidized: Pt$^{+0.54}$ (approx. 14\% of PtO$_2$)
- Reduced: Pt$^{+0.1}$

For the fits, the most reduced internal reference spectrum is used as Pt$^0$, and PtO$_2$ reference spectrum as Pt$^{+4}$. The oxidized fraction observed is consistent with estimation of the average Pt particle size by TEM, with oxygen chemisorbed only on the surface.

\textbf{References}