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Supporting information for article:

**Fluorescence-detected XAS with sub-second time resolution
reveals new details about the redox activity of Pt/CeO₂ catalyst**

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S1. Statistics of the I0 signal measured with avalanche photodiode (APD) and ionization chamber

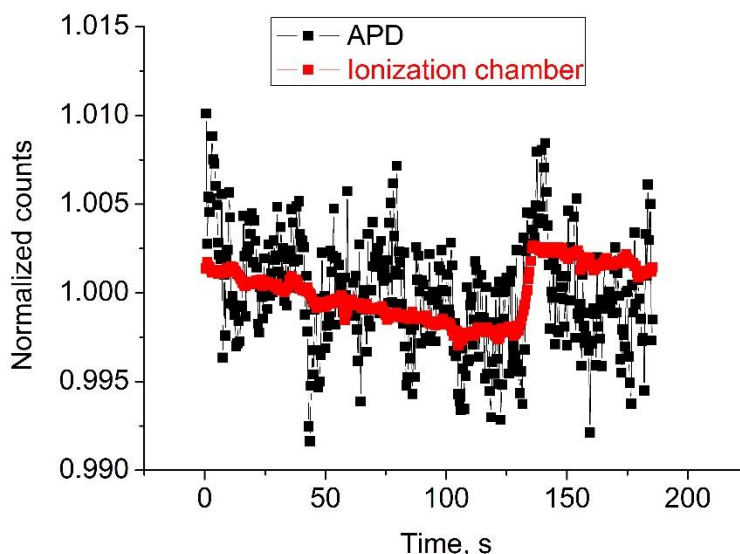


Figure S1 Normalized intensity of the incoming x-ray beam measured with APD and ionization chamber as a function of time. A step at 130s corresponds to the electron injection in the synchrotron ring operating in the top-up mode (occurring approx. every 3 minutes). Signal from the ionization chamber has much better statistics and is preferable for normalization.

S2. Mass-spectrometer data for the CO consumption and CO₂ formation for the studied Pt/CeO₂ catalyst during experiment shown in Figure 6.

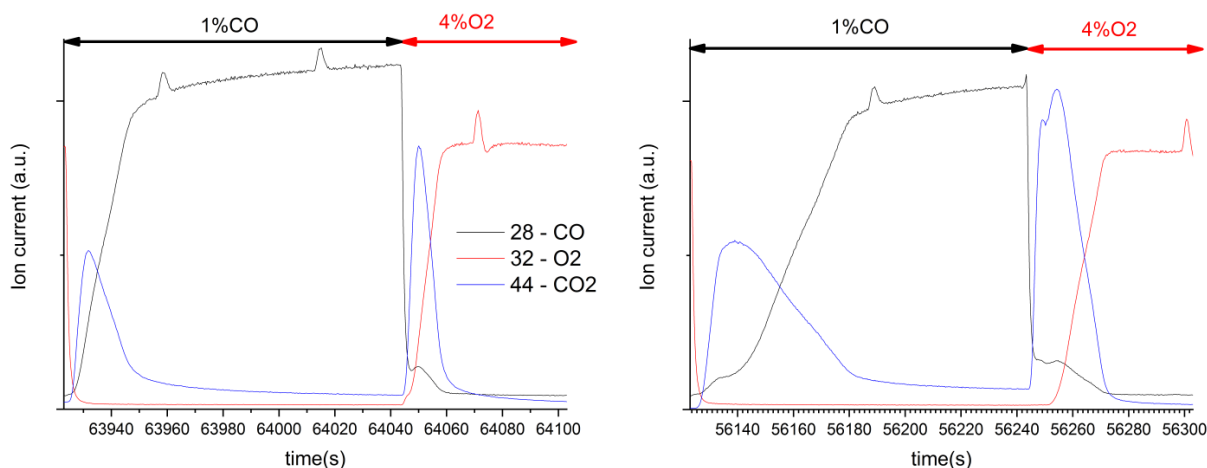


Figure S2 Evolution of the mass-spectrometer signals at the outlet on the cell for the transient experiments shown in the Figure 6: 47 °C (left panel) and 150 °C (right panel). Ion currents registered for fragments with masses 28, 32 and 44 a.u. corresponding to CO, O₂ and CO₂ molecules were normalized to the signal of Ar with the mass of 40.

S3. Fitting of the time-resolved data for Ce L₃ edge.

To fit the changes in the Ce³⁺ concentration during the redox cycling of 1.5 wt% Pt/CeO₂ catalyst in CO and oxygen containing atmospheres (shown in the Fig. 6 of the main text) we used a two-exponent function describing fast and slow components of the reaction process:

$$y(t) = \begin{cases} Sc \cdot \left((1 - C_0) \cdot \left(1 - e^{-\frac{t-t_0}{\tau_1}} \right) + C_0 \cdot \left(1 - e^{-\frac{t-t_0}{\tau_2}} \right) \right), & t \leq 120 + t_1 \\ y(120 + t_1) \cdot \left((1 - C_1) \cdot e^{-\frac{t-t_1-120}{\tau_3}} + C_1 \cdot e^{-\frac{t-t_1-120}{\tau_4}} \right), & t > 120 + t_1 \end{cases}$$

The whole time range was split into two parts corresponding to reduction ($0 < t < 120$) and oxidation ($120 < t < 180$). At $t = 0$ s the gas flow was switched from 4% O₂ in argon to 1% CO in argon and at $t = 120$ s it was switched back. The following parameters were quantified:

Sc (Saturated concentration) - the asymptotic value of the concentration of reduced ceria at $t \rightarrow \infty$, %

C_0 - fraction of the slow component in the fit for reduction

C_1 - fraction of the slow component in the fit for oxidation

t_0 - induction period of reduction, i.e. the delay time from the moment of the gas switch to the start of the exponential-like kinetics, s

t_1 - induction period of oxidation, s

τ_1, τ_2 - time constants for the fast and slow kinetics in the reduction process, s

τ_3, τ_4 - time constants for the fast and slow kinetics in the oxidation process, s

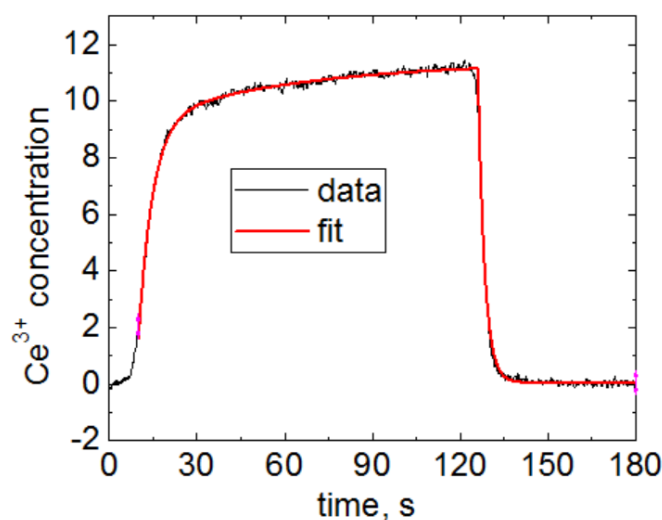


Figure S3 Typical changes in the Ce³⁺ concentration (%) during the redox cycling.

Table S1 Kinetic parameters for the evolution of the Ce³⁺ concentration during the redox cycling of 1.5 wt% Pt/CeO₂ catalyst at 47 °C in the beginning, in the middle, and at the end of the catalyst bed with respect to the reactor inlet (z corresponds to distance in millimeters from the reactor inlet).

	z=0	z=0.3	z=0.6	z=0	z=0.3	z=0.6
	47 °C reduction			47 °C oxidation		
Saturated Ce ³⁺ concentration (%)	2.1	2.5	4.5	-	-	-
Induction period (s)	0.5	1.2	2.3	0.4	0.6	0.7
Fast time constant (s)	4.1	5.0	4.8	2.0	1.8	1.7
Slow time constant (s)	- ^a	29	55	9	12	10

^aValues not contributing to the fit

Table S2 Kinetic parameters for the evolution of the Ce³⁺ concentration during the redox cycling of 1.5 wt% Pt/CeO₂ catalyst at 150 °C in the beginning, in the middle, and at the end of the catalyst bed with respect to the reactor inlet (z corresponds to distance in millimeters from the reactor inlet)

	z=0	z=0.3	z=0.6	z=0	z=0.3	z=0.6
	150 °C reduction			150 °C oxidation		
Saturated Ce ³⁺ concentration (%)	10.8	11.0	11.4	-	-	-
Induction period (s)	1.0	5.3	9.1	1.5	3.6	6.1
Fast time constant (s)	5.0	4.3	4.9	1.5	2.1	2.3
Slow time constant (s)	63	53	53	26	- ^a	-

^aValues not contributing to the fit

S4. Fitting of the time-resolved data for Pt L₃ edge.

To fit the changes in the platinum coverage by oxygen during the redox cycling of Pt/CeO₂ catalyst in CO and oxygen containing atmospheres (shown in the Fig. 6 of the main text) we used a two-exponent function describing fast and slow components of the reaction process:

$$y(t) = \begin{cases} 100 - Sc \cdot \left((1 - C_0) \cdot \left(1 - e^{-\frac{t-t_0}{\tau_1}} \right) + C_0 \cdot \left(1 - e^{-\frac{t-t_0}{\tau_2}} \right) \right), & t \leq 120 + t_1 \\ y(120 + t_1) \cdot \left((1 - C_1) \cdot e^{-\frac{t-t_1-120}{\tau_3}} + C_1 \cdot e^{-\frac{t-t_1-120}{\tau_4}} \right), & t > 120 + t_1 \end{cases}$$

The whole time range was split into two parts corresponding to reduction ($0 < t < 120$) and oxidation ($120 < t < 180$). At $t = 0$ s the gas flow was switched from 4% O₂ in argon to 1% CO in argon and at $t = 120$ s it was switched back. The following parameters were quantified:

Sc – amplitude of changes in platinum coverage by oxygen %

C_0 - fraction of the slow component in the fit for reduction

C_1 - fraction of the slow component in the fit for oxidation

t_0 - induction period of reduction, i.e. the delay time from the moment of the gas switch to the start of the exponential-like kinetics, s

t_1 - induction period of oxidation, s

τ_1, τ_2 - time constants for the fast and slow kinetics in the reduction process, s

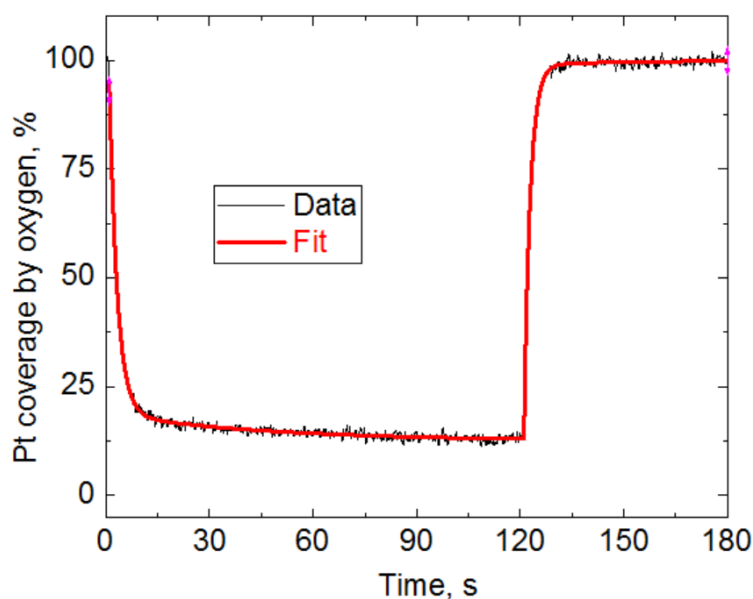


Figure S4 Typical changes in the coverage of platinum by oxygen (%) during the redox cycling.

Table S3 Kinetic parameters for the evolution of the platinum coverage by oxygen during the redox cycling of 1.5 wt% Pt/CeO₂ catalyst at 47 °C in the beginning, in the middle, and at the end of the catalyst bed with respect to the reactor inlet (z corresponds to distance in millimeters from the reactor inlet).

	z=0	z=0.3	z=0.6	z=0	z=0.3	z=0.6
	47 °C reduction			47 °C oxidation		
Induction period (s)	0.7	1.5	2.4	1.2	1.4	2.1
Fast time constant (s)	1.2	1.6	2.1	1.2	1.2	1.4
Slow time constant (s)	15	29	28	- ^a	-	-

^aValues not contributing to the fit

Table S4 Kinetic parameters for the evolution of the platinum coverage by oxygen during the redox cycling at 150 °C of 1.5 wt% Pt/CeO₂ catalyst in the beginning, in the middle, and at the end of the catalyst bed with respect to the reactor inlet (z corresponds to distance in millimeters from the reactor inlet).

	z=0	z=0.4	z=0.8	z=0	z=0.4	z=0.8
	150 °C reduction			150 °C oxidation		
Induction period (s)	0.8	5.1	10.4	1.1	3.6	6.8
Fast time constant (s)	2.3	3.2	4.0	1.8	2.1	2.3
Slow time constant (s)	45	35	52	- ^a	-	-

^aValues not contributing to the fit

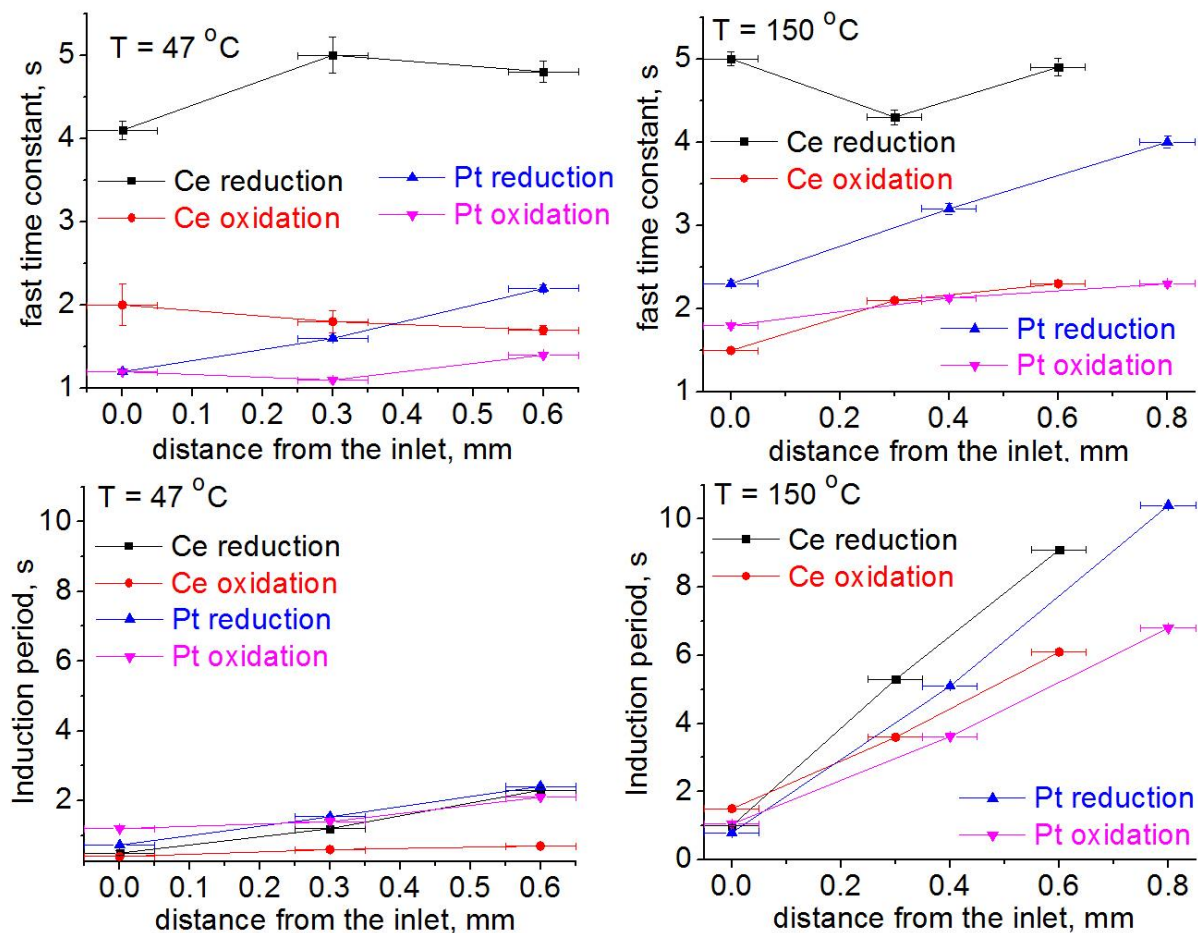


Figure S5 Evolution of the kinetic parameters shown in Tables S1-S4 as a function of distance from the reactor inlet (z). The error bars for the x-axis correspond to a half width of the X-ray beam in the vertical direction. The error bars for the y-axis were estimated from the fitting procedure. The error bars for the induction period are smaller than the symbols.

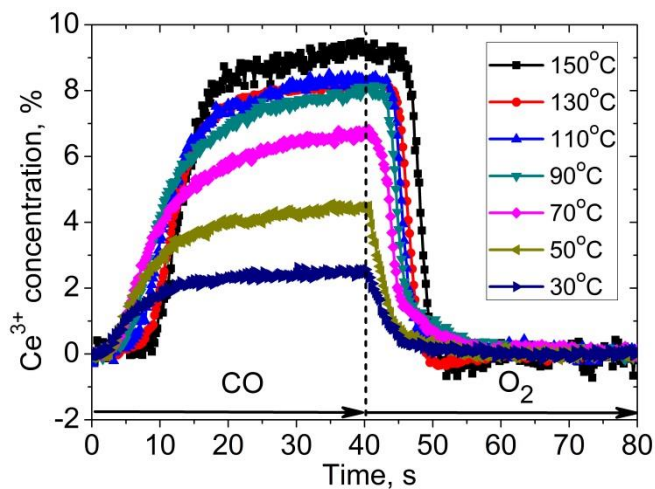


Figure S6 Evolution of the Ce^{3+} concentration as a function of time at different temperatures at a fixed position (z) in the reactor.

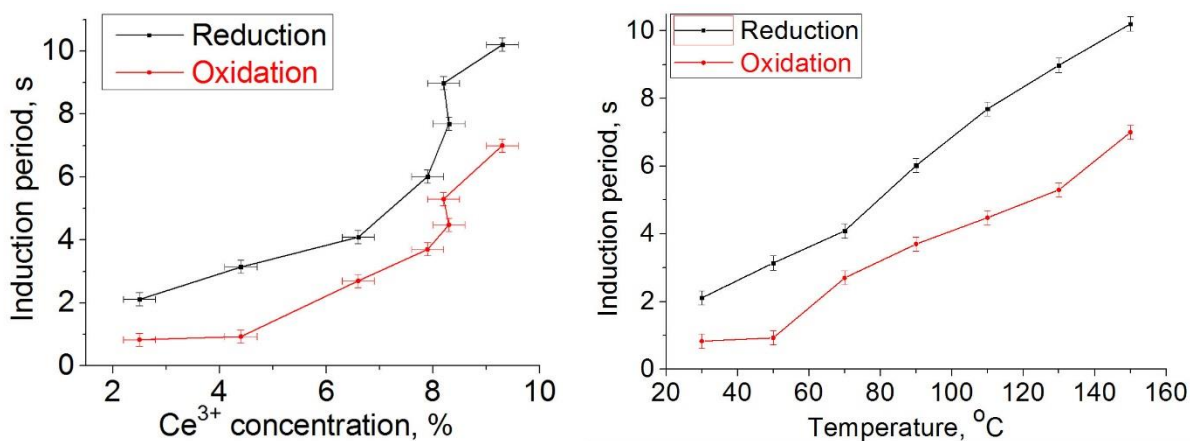


Figure S7 The induction period for Ce^{3+} formation (reduction) and Ce^{3+} decay (oxidation) as a function of the maximal Ce^{3+} concentration and the temperature. The error bars were estimated from the fitting procedure. Larger errors for Ce^{3+} concentration in comparison to Figure S5 are related to shorter time of experiments.

S5. Quality and details of all fits

