Electronic Supplementary Information of:

Modulated excitation extended X-ray absorption fine structure spectroscopy

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Figure S1. Simulated sinusoidal temporal variation of coordination number N (from 12 to 6) within a modulation period of 100 s.
**Figure S2.** Simulated sinusoidal temporal variation of Debye-Waller factor $\sigma^2$ (from 0.003 Å$^2$ to 0.005 Å$^2$) within a period of 100 s.

**Figure S3.** Effect of variation of Debye-Waller factor $\sigma^2$ (according to Fig. S2) of a single Pd-Pd first coordination shell on (left panel) the simulated $k^2$-weighted $\chi(k)$ EXAFS spectra, (central panel) the FT-magnitude $|\chi(R)|$ and (right panel) the FT-real part $\text{Re}[\chi(R)]$. Top panels: simulated time-resolved spectra where $\sigma^2$ varies from 0.003 Å$^2$ (blue curve) to 0.005 Å$^2$ (red curve) with a phase lag $\phi = 0^\circ$ ($R = 2.758$ Å, $N = 12$, $\Delta E^\circ = 0$ eV). Bottom panels: corresponding phase-resolved spectra, where the red curve corresponds to the “in-phase angle” ($\phi_{PSD} = \phi = 0^\circ$).
Figure S4. Effect of the variation of N (red line) or $\sigma^2$ (blue line) on the phase resolved (in-phase demodulation angle) normalized (divided by the maximum value) FT-real part with respect to that of initial state (o). Because N effects only the magnitude of $\chi(k)$ the normalized phase resolved $\text{Re}[\chi(R)]$ overlaps with that of the initial state. By contrast, because of the $k$-dependent effect of $\sigma^2$ on the amplitude of $\chi(k)$ a variation of $\sigma^2$ leads to a distortion of the corresponding phase resolved $\text{Re}[\chi(R)]$. 
**Figure S5.** Simulated sinusoidal temporal variation of interatomic distance R increasing from 2.7577 Å to 2.8577 Å within a period of 100 s.

**Figure S6.** Effect of variation of interatomic distance R (according to Fig. S5) of a single Pd-Pd first coordination shell on (left panel) the simulated k²-weighted χ(k) EXAFS spectra, (central panel) the FT-magnitude |χ(R)| and (right panel) the FT-real part Re[χ(R)]. Top panels: simulated time-resolved spectra where R varies from 2.7577 Å (blue curve) to 2.8577 Å (red curve) with a phase lag φ = 0° (σ²= 0.003 Å², N= 12, ΔE°= 0 eV). Bottom panels: corresponding phase-resolved spectra, where the red curve corresponds to the “in-phase angle” (φPSD = φ = 0°).
**Figure S7.** Simulated sinusoidal temporal variation of coordination number N (from 12 to 6) while the interatomic distance R increases from 2.7577 Å to 2.8577 Å, within a period of 100 s. Both parameters have the same phase lag ($\phi_N = \phi_R = 0^\circ$).

**Figure S8.** Effect of simultaneous variation of coordination number N and interatomic distance R (according to Fig. S7) of a single Pd-Pd first coordination shell on (left panel) the simulated $k^2$-weighted $\chi(k)$ EXAFS spectra, (central panel) the FT-magnitude $|\chi(R)|$ and (right panel) the FT-real part $\text{Re}[\chi(R)]$. The upper plots show the simulated time resolved spectra where N and R vary from 12 and 2.7577 Å (red curve) to 6 and 2.8577 Å (blue curve) with a phase lag $\phi = 0^\circ$ ($\sigma^2 = 0.003$ Å$^2$ and $\Delta E^\circ = 0$ eV). The lower plots show the phase resolved spectra, where the red curve corresponds to the “in phase angle” ($\phi^{\text{PSD}} = \phi = 0^\circ$, in this case).
Figure S9. Simulated sinusoidal temporal variation of coordination number N (from 12 to 6) while the interatomic distance R increases from 2.7577 Å to 2.8577 Å, within a period of 100 s. The two parameters vary with different phase lag ($\phi_N = 0^\circ$, $\phi_R = 320^\circ$).
Figure S10. Effect on the simulated phase-resolved EXAFS spectra of a single Pd-Pd first coordination shell at the Pd K-edge (0°<φ<360°) of the variation of (A) the coordination number N only; (B) coordination number N and interatomic distance R with the same phase lag, (C) coordination number N and interatomic distance R with different phase lag. Left panels: $k^2$-weighted $\chi(k)$. Middle panels: FT-magnitude, $|\chi(R)|$. Right panels: FT real part, Re[\chi(R)].
Figure S11. Comparison of the first time-resolved k³-weighted FT-EXAFS spectra at the Pd K-edge of 1.6 wt% Pd/Al₂O₃ recorded at the beginning of the modulation experiment at 573 K showing the structure of the catalyst after the heating pre-treatment in 1 vol% O₂/He (green curve) with the last averaged (over 28 cycles, after deleting the first 2 cycles) time-resolved k³-weighted FT-EXAFS recorded in 1 vol% H₂/He (reed curve) and in 1 vol% O₂/He (blue curve).
Figure S12. Experimental ME-EXAFS data at the Pd K-edge obtained on 1.6 wt% Pd/Al$_2$O$_3$ during a 1 vol% O$_2$/He to 1 vol% H$_2$/He modulation experiment at 573 K. (A) $k^3$-weighted $\chi(k)$ EXAFS spectra of reference PdO and Pd foil; (B) averaged time-resolved $k^3$-weighted $\chi(k)$ EXAFS spectra recorded (blue) in 1 vol% O$_2$/He and (red) in 1 vol% H$_2$/He; (C) phase-resolved $k^3$-weighted $\chi(k)$ EXAFS spectra ($0^\circ < \phi < 360^\circ$; red is $\phi^{PSD} = \phi_{Pd-Pd} = 160^\circ$; green curves are $170^\circ < \phi^{PSD} < 340^\circ$, gray curves are remaining angles).