

Electronic Supplementary Information

The structure of Pd-functionalized UiO-67 during CO₂ hydrogenation

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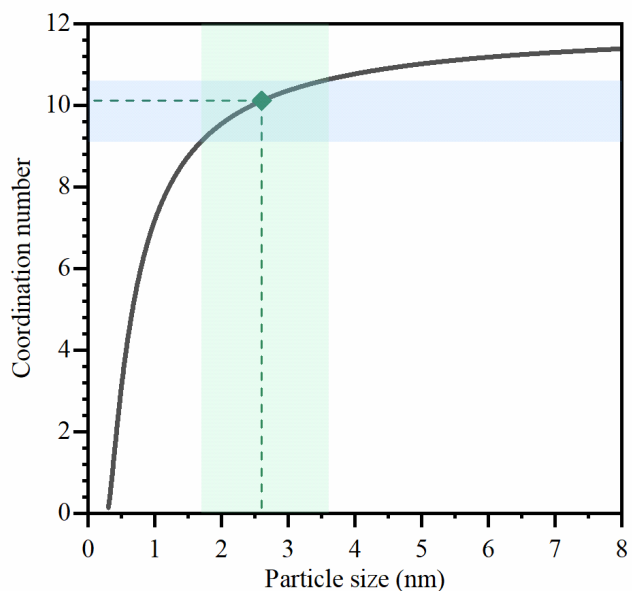


Figure S1. Evolution of coordination numbers of fcc NPs as a function of NP diameter (solid black) [Calvin et al. *J. Appl. Phys.* 2003]. The green scatter shows the average coordination number extracted from EXAFS corresponding to a NP diameter of 2.6 nm. The colored light blue and light green boxes include the margins of the coordination number and, respectively, particle size, based on the error of EXAFS fitting.

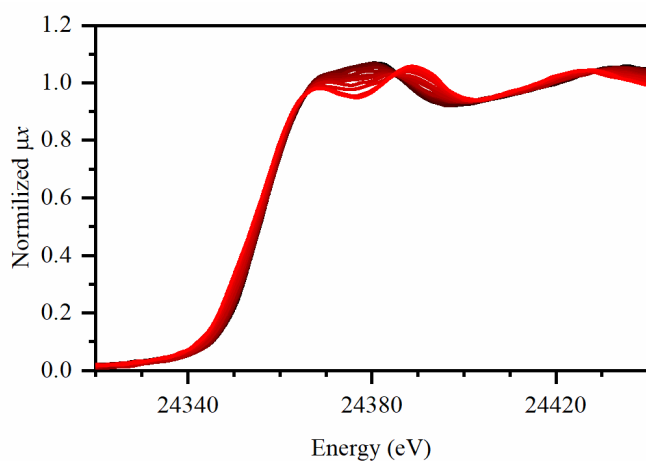


Figure S2. Evolution of Pd *K*-edge XANES spectra (from black to red) upon activation of the sample in H₂.

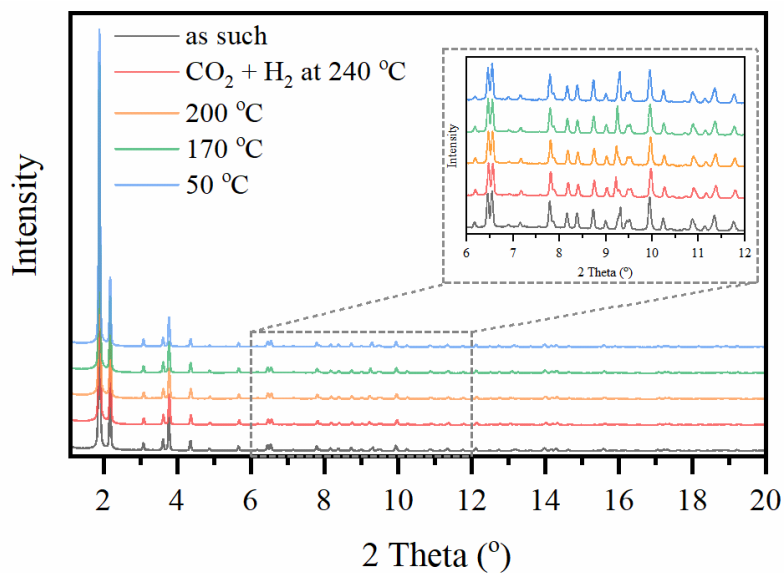


Figure S3. XRPD patterns collected across the lifespan of the investigated catalyst activated in H₂ at 300 °C and exposed to reaction mixture under 8 bar. Inset graph show the zoom-in (6°– 12°) XRPD.

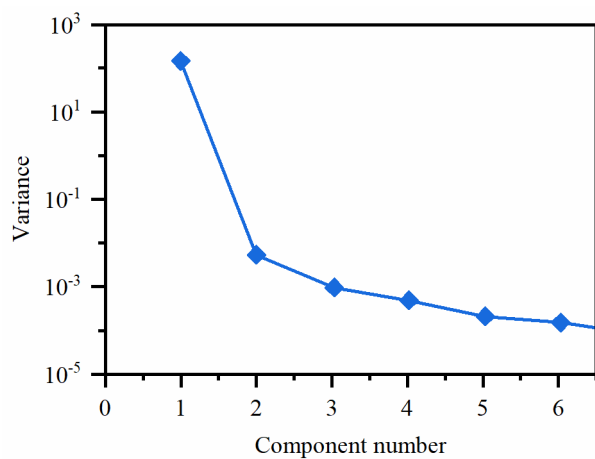


Figure S4. Statistical estimator (scree plot) used to evaluate the number of PCs contributing to Pd K-edge XANES spectra.

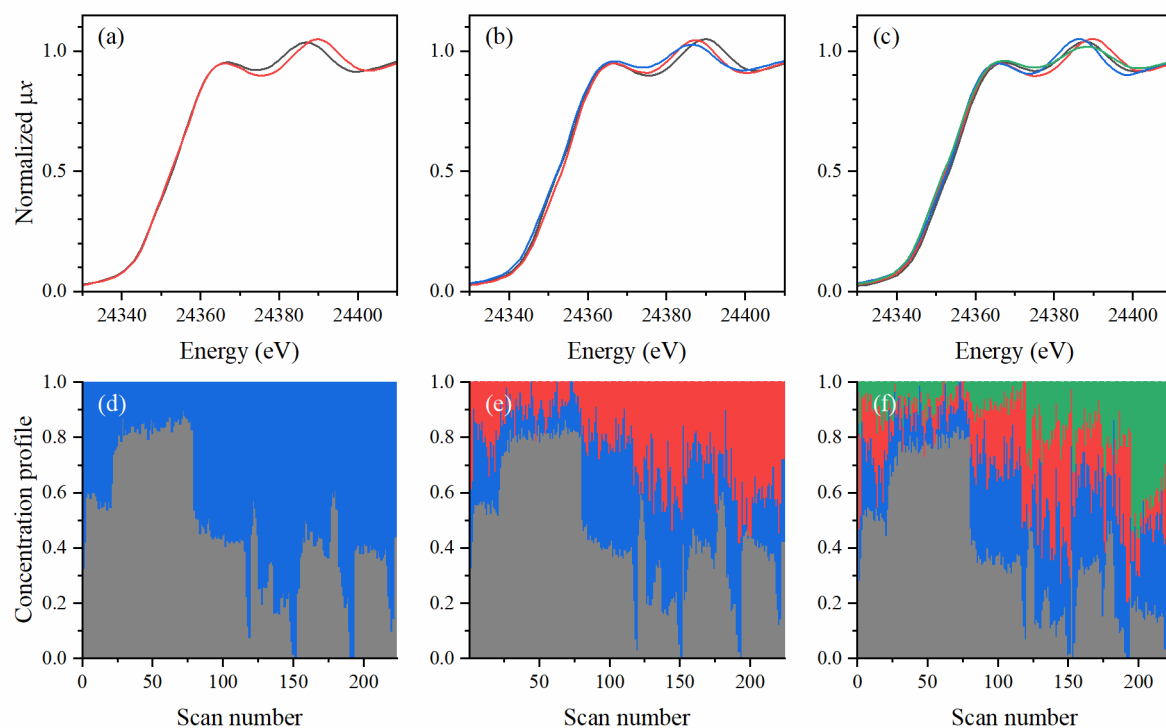


Figure S5. (a-c) Pd *K*-edge XANES spectra extracted from the whole experimental dataset by MCR approach and (d-f) evolution of MCR components using two (a, d), three (b, e) and four (c, f) components.

Figure S6 illustrates the dataset of XANES spectra utilized in the MCR analysis. As highlighted by the dashed lines, significant structural changes are evident in the spectra subjected to analysis. The transition from dark blue to dark red spectra reveals notable alterations: the A maximum broadened, the intensity of the B minimum increased significantly, and the position of the C maximum shifted towards lower energies. These, among various other variations in the spectra, underscore the occurrence of genuine structural changes during the reaction.

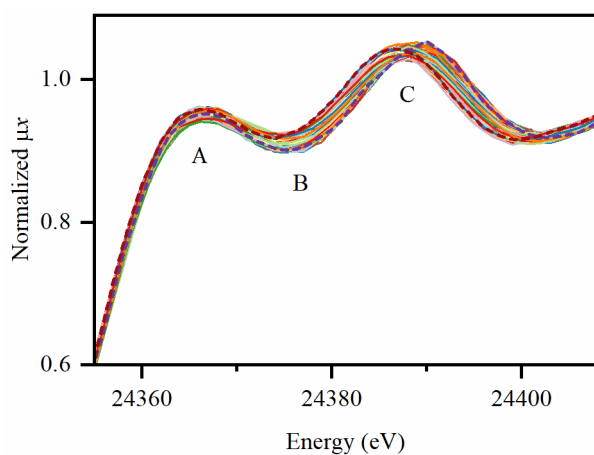


Figure S6. Experimental Pd *K*-edge XANES spectra of all samples presented in the manuscript as input dataset for MCR analysis. A, B and C highlights first two maximums and a minimum of the activated sample before its interaction with the reaction mixture (dashed dark-blue). The dashed dark-red line represents one of the spectra of the sample in the reaction mixture.

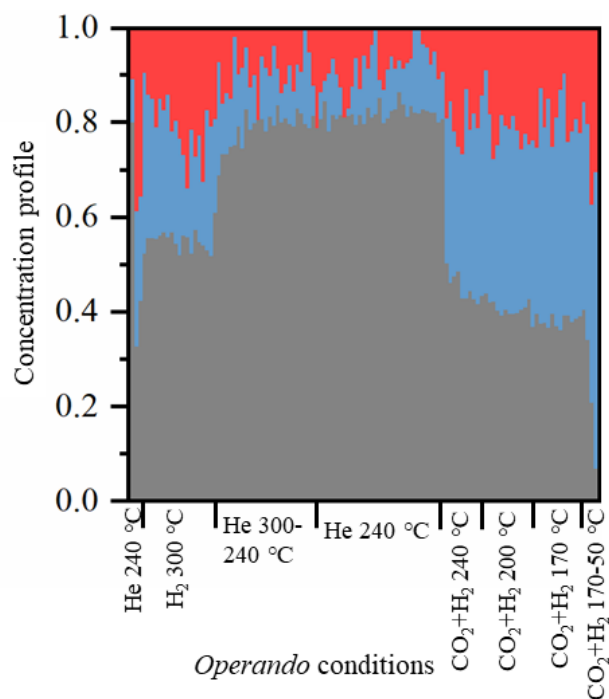


Figure S7. Evolution of MCR components (the color code is the same as for spectra presented in Figure 5a of the main text) for the sample activated in H₂ at 300 °C and exposed to reaction mixture under 1 bar.

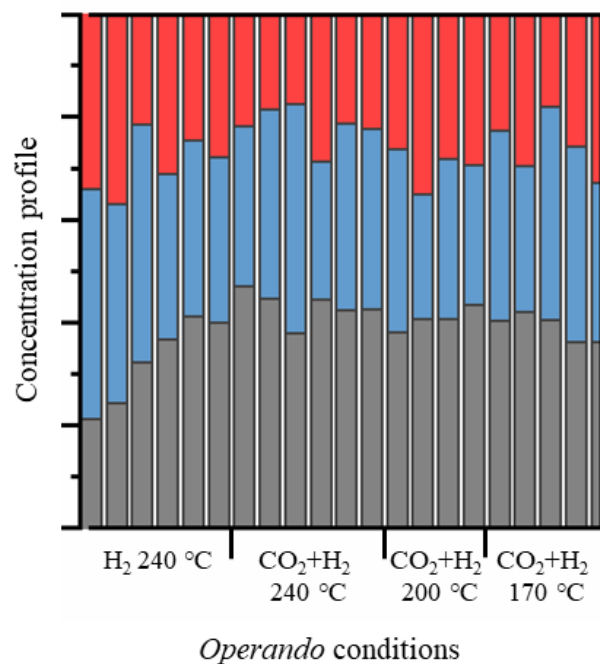


Figure S8. Evolution of MCR components (the color code is the same as for spectra presented in Figure 5a of the main text) for the sample activated in H₂ at 240 °C and exposed to reaction mixture under 1 bar.

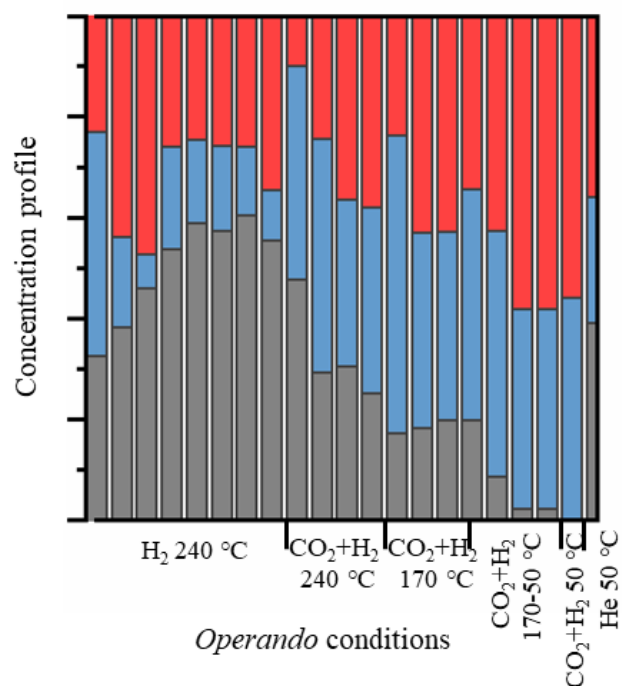


Figure S9. Evolution of MCR components (the color code is the same as for spectra presented in Figure 4a of the main text) for the sample activated in H₂ at 240 °C and exposed to reaction mixture under 8 bar.

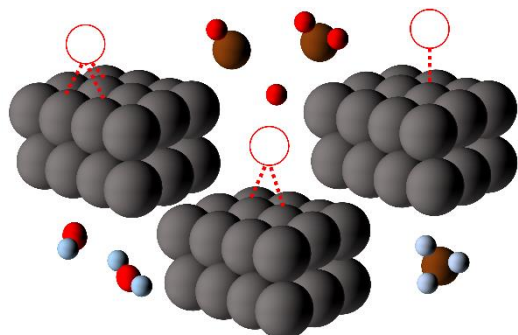


Figure S10. Schematic illustration of palladium surfaces with possible positions (red circles) (top, bridge, hollow) for adsorbed species (CO₂, CO, CH_x, H₂O, O, OH) used for theoretical XANES calculation.

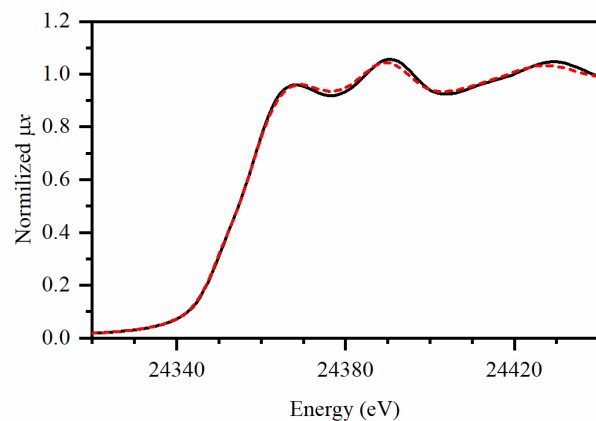


Figure S11. Experimental Pd K-edge XANES spectra for activated Pd@ γ -Al₂O₃ NPs in He at room temperature (solid black) and in a gas flow of 5 ml/min CO and 45 ml/min He at 350 °C (dashed red) collected at ALBA synchrotron.

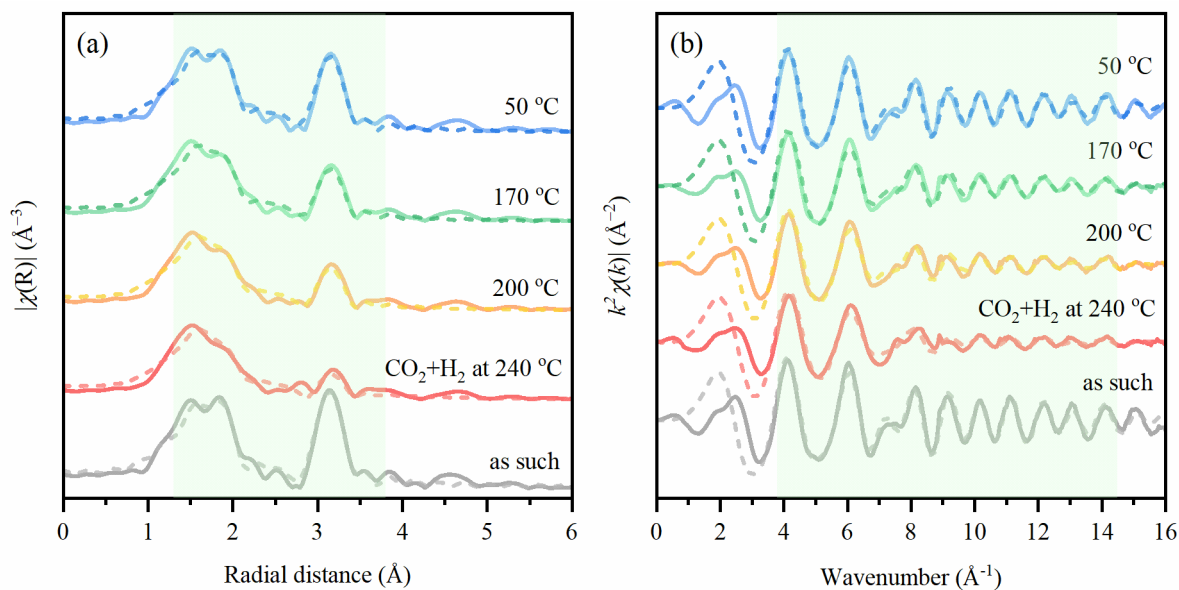


Figure S12. Experimental FT-EXAFS spectra in R -space (a) and k -space (b) (solid) and best fits (dashed) of Zr K -edge collected for the sample activated in H_2 at $300\text{ }^\circ\text{C}$ and exposed to reaction mixture under 8 bar. The highlighted area shows the interval in the R - and k -space accordingly where the fits were performed.

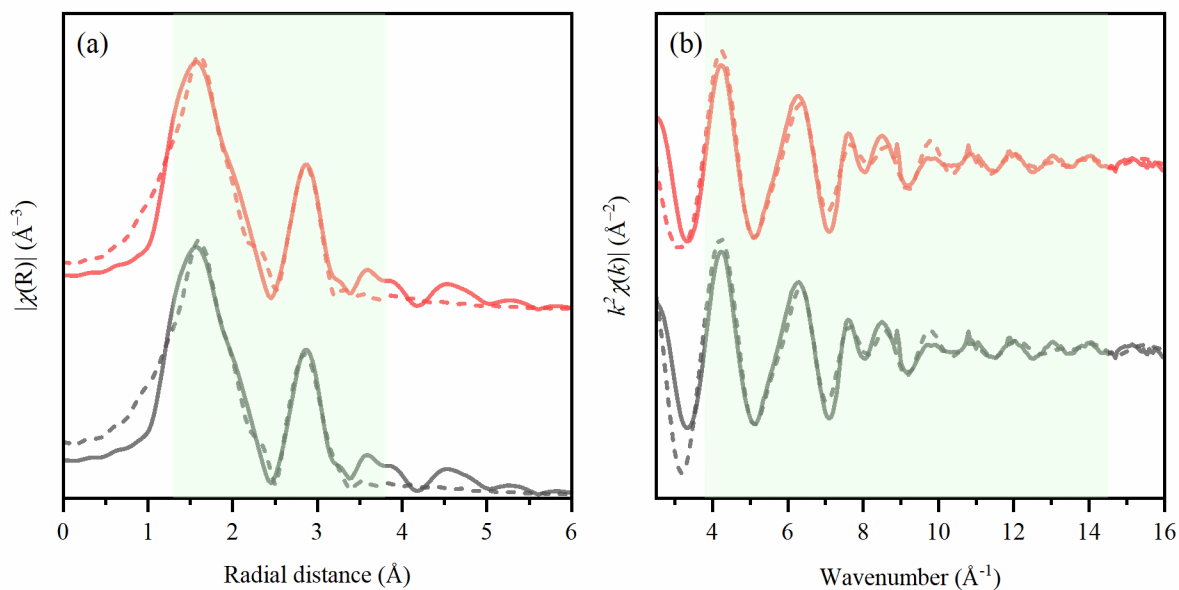


Figure S13. Experimental FT-EXAFS spectra in R -space (a) and k -space (b) (solid) and best fits (dashed) of Zr K -edge collected for the sample activated directly in the reaction mixture under 1 bar at $240\text{ }^\circ\text{C}$. The highlighted area shows the interval in the R - and k -space accordingly where the fits were performed. Grey dashed line represents fit with both Zr-Pd and Zr-Zr scattering paths, red dashed line – only Zr-Pd.

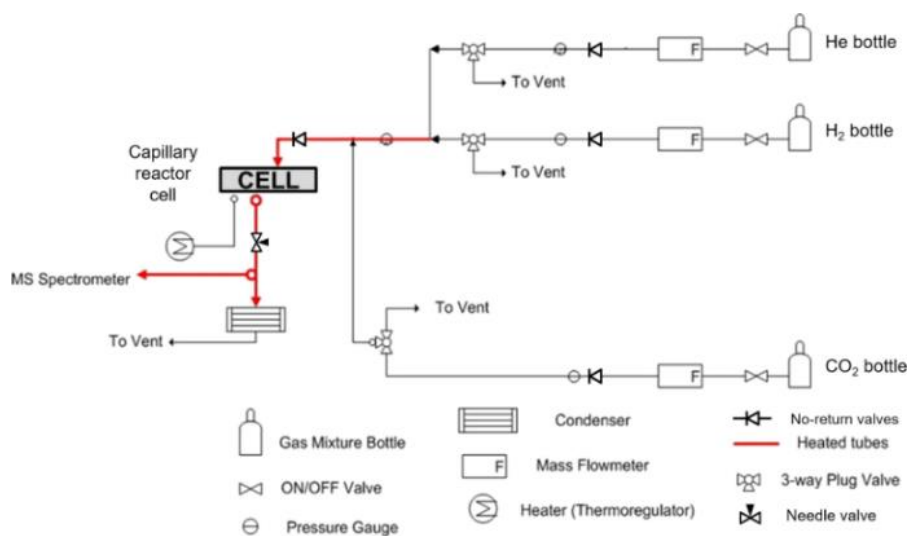


Figure S14. Schematic illustration of the experimental setup used for operando XAS measurements.

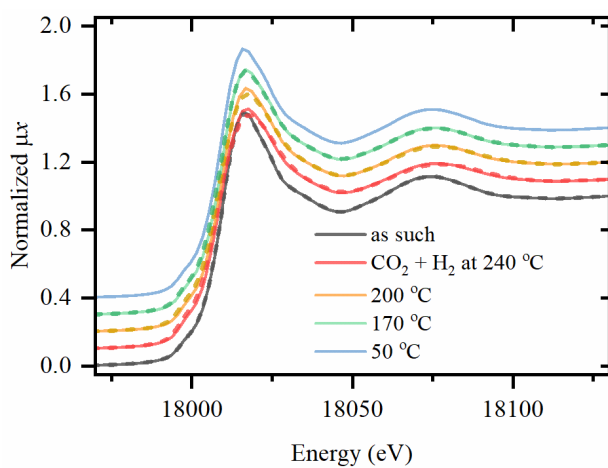


Figure S15. Experimental Zr *K*-edge XANES spectra for the sample activated in H₂ at 300 °C and exposed to reaction mixture under 8 bar (solid lines); activated directly in the reaction mixture under 1 bar at 240 °C (dashed lines).