Supporting Information

Structural and mechanistic insights into low-temperature CO oxidation over a prototypical high entropy oxide by Cu L-edge operando soft X-ray Absorption Spectroscopy

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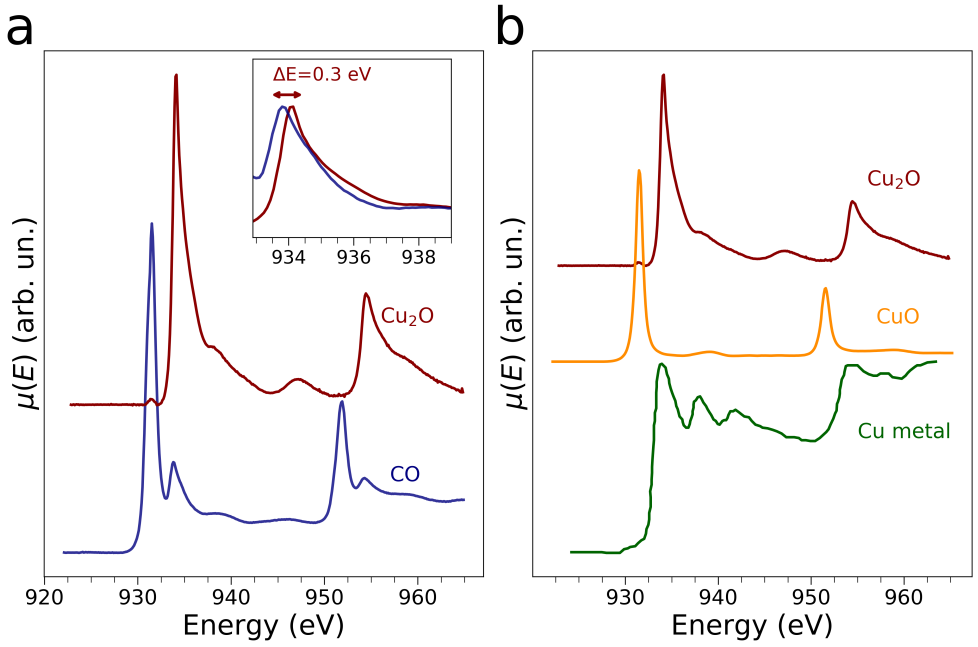

Figure S1: (a) Cu $L_{2,3}$-edge XAS spectra of Cu_2O in He at room temperature (dark red line) and of the $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ HEO upon exposure to CO flux at 235 °C for 50 minutes (blue line). The inset compares the Cu(I) L_3-edge peaks present in the Cu $L_{2,3}$-edge spectra. (b) Cu $L_{2,3}$-edge XAS spectra of Cu_2O (dark red line), CuO (yellow line) and metallic Cu (green line), where all spectra are measured in He at room temperature. The Cu $L_{2,3}$-edge spectra of the Cu_2O, CuO and metallic Cu standards were aligned to the HEO spectra using the L_3-edge of CuO as a reference.

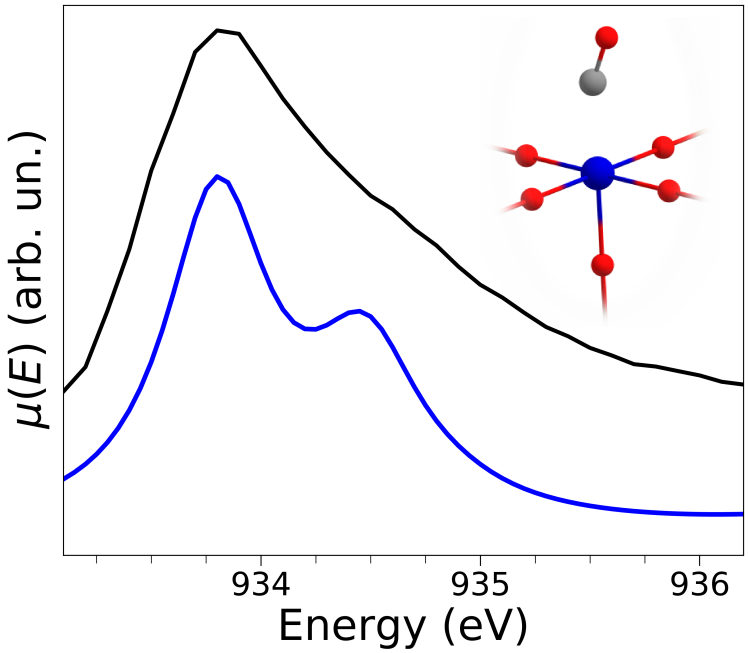

Figure S2: Comparison between the Cu(I) Cu L_3-edge feature measured upon exposure of the HEO surface to CO (50 minutes, 235 °C) and the theoretical Cu L_3-edge spectrum best reproducing the experimental curve (blue) and associated to the global minimum of the residual function Δ. The associated molecular cluster is also shown, with $d = 2.1$ Å, $\theta = 20°$ and $\phi = 20°$, where the Cu(I) cation, the oxygen and carbon atoms are depicted in blue, red and gray, respectively.

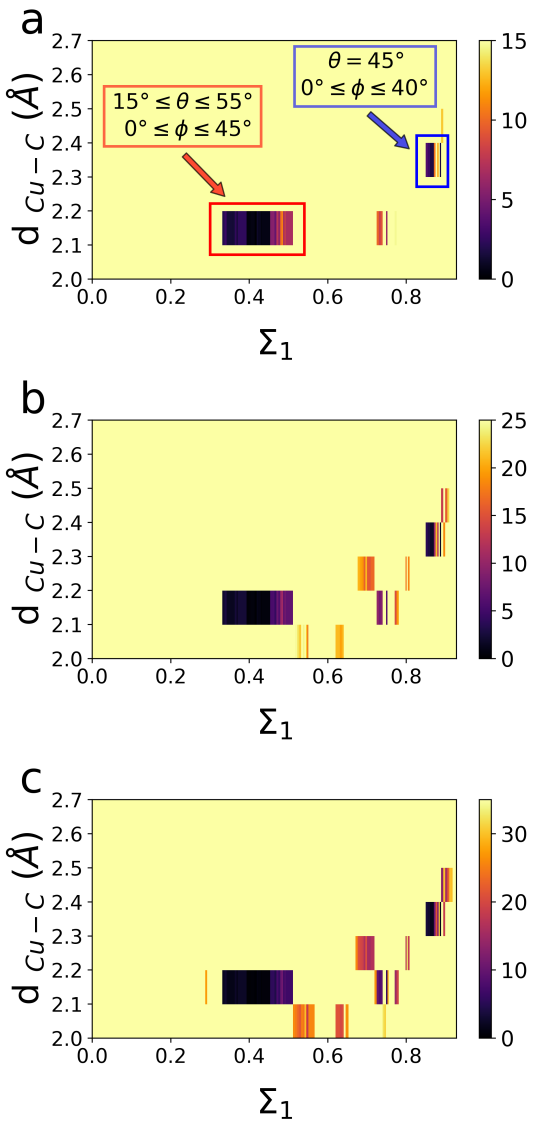

Figure S3: Distribution of the theoretical Cu L_3-edge spectra of the clusters modeling the interaction between the HEO surface and CO as a function of the distance between the Cu(I) cation and the CO carbon atom (d_{Cu-C}) and of Σ_1. The values of Δ within 15%, 25% and 35% of the global minimum of Δ are shown in panels a, b and c, respectively.

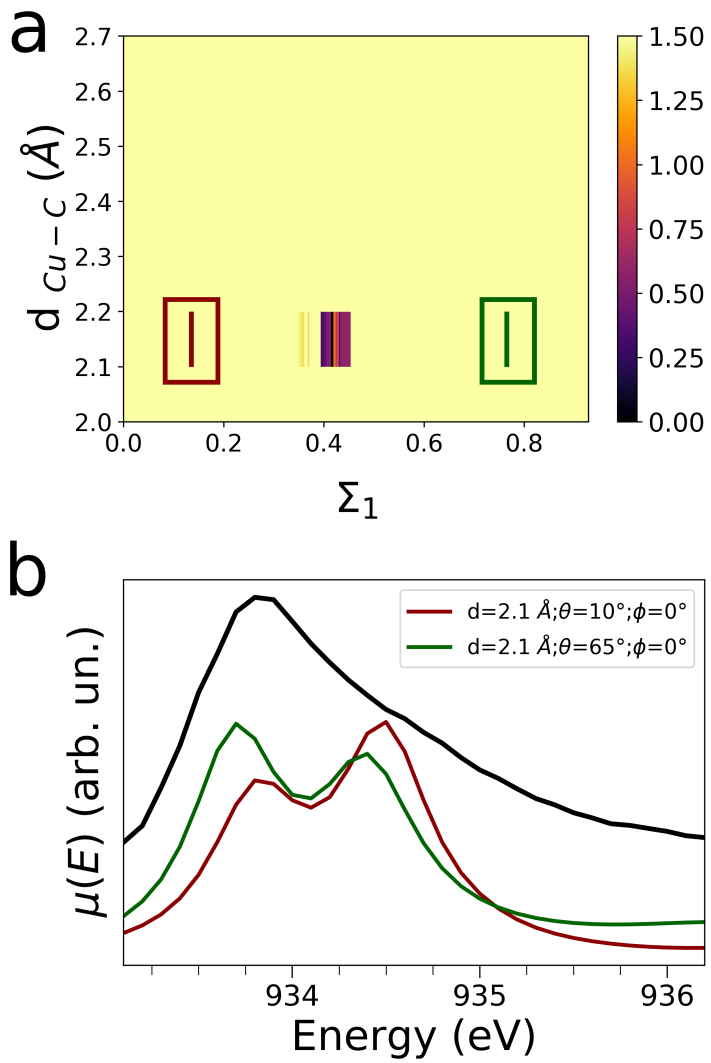

Figure S4: (a) Distribution of the theoretical Cu L_3-edge spectra of the clusters modeling the interaction between the HEO surface and CO as a function of the distance between the Cu(I) cation and the CO carbon atom (d_{Cu-C}) and of Σ_1. The values of Δ within 1.5% of the global minimum of Δ are shown on the color scale, while two ulterior selected spectral regions are evidenced in green and dark red lines, respectively. (b) Theoretical Cu L_3-edge spectra of two selected CO adsorbtion geometries (green and dark red lines) compared to the experimental curve (black line). The values of Δ associated to each theoretical spectrum are highlighted in panel a with the same green and dark red colors.