Supporting Information

Nontrivial redox behavior of nanosized cobalt: new insights from *ambient pressure* x-ray photoelectron and absorption spectroscopies.

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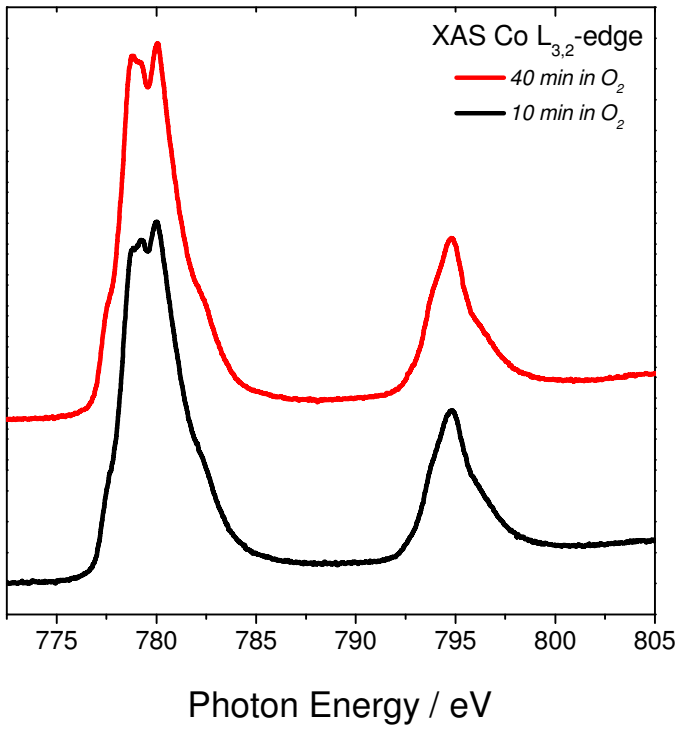

Figure S1. XAS Co L-edge spectra for 3.5 nm Co NPs after 10 min (bottom) and 40 min (top) exposure at 0.2 mbar O_2 at 570 K.

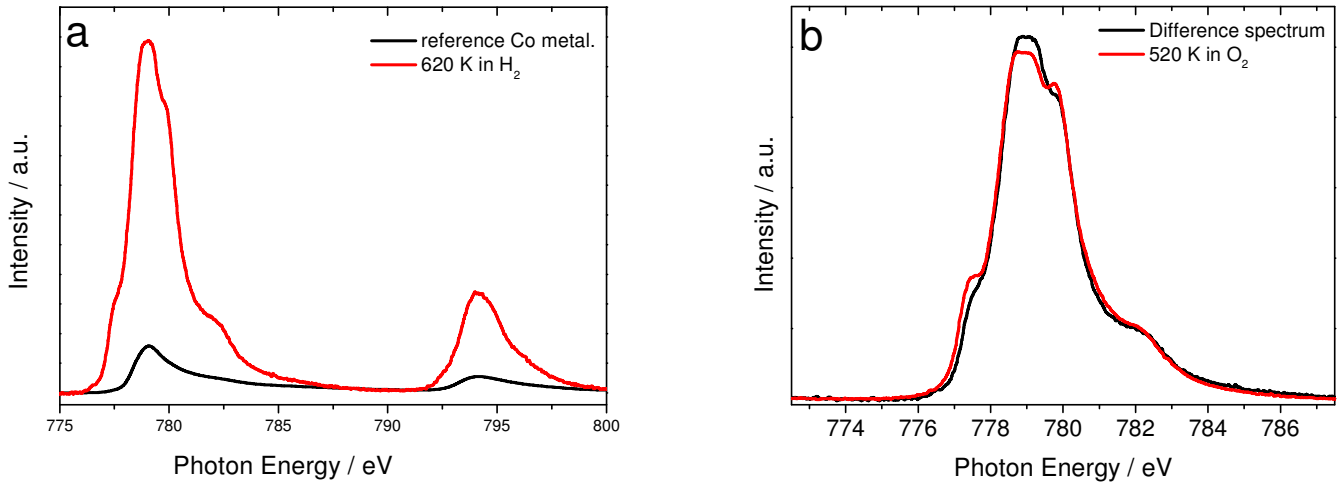

Figure S2.a) The Co $L_{3,2}$ absorption edge of 3.5 nm Co NPs at 620 K under 0.2 mbar H_2 (*red line*) and the reference spectrum metallic Co $L_{3,2}$-edge recorded on a completely reduced Co (0001) crystal (*black line*). The spectra are presented after liner background subtraction and intensity normalization, so as no negative intensity is produced after subtraction **b)** The difference curve remain after subtraction of the spectra showed in (a) (*black line*), the spectrum of the CoO-type oxide formed on Co NPs at 520 K in 0.2 mbar O_2 is added in the graph for comparison (*red line*).

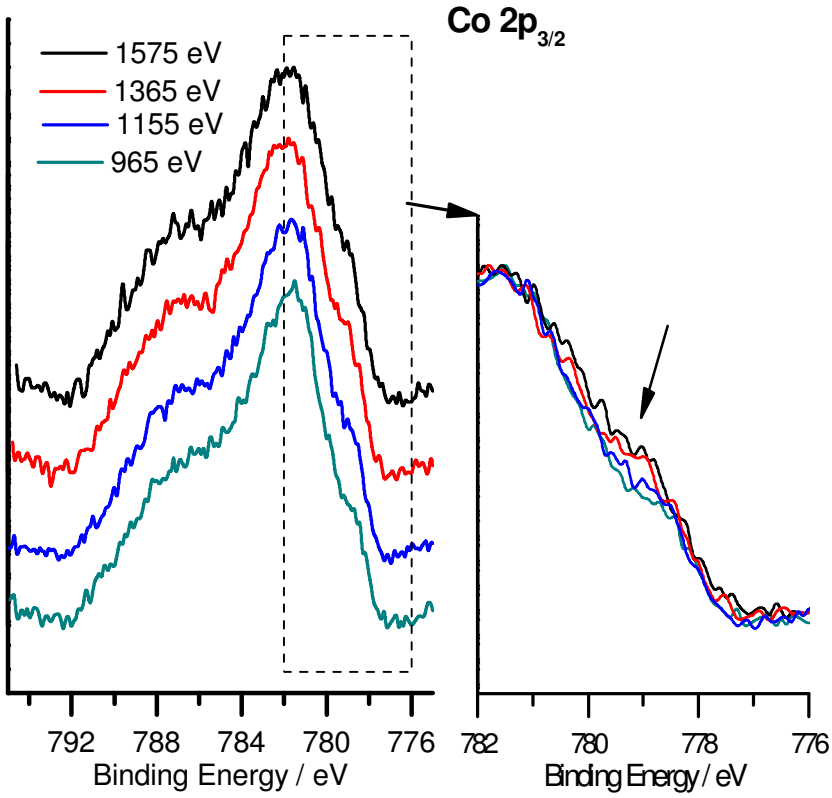

Figure S3. The Co 2p3/2 core level photoelectron peaks of 3.5 nm Co NPs in 0.2 mbar H_2 at 520 K recorded by 4 different photon energies.

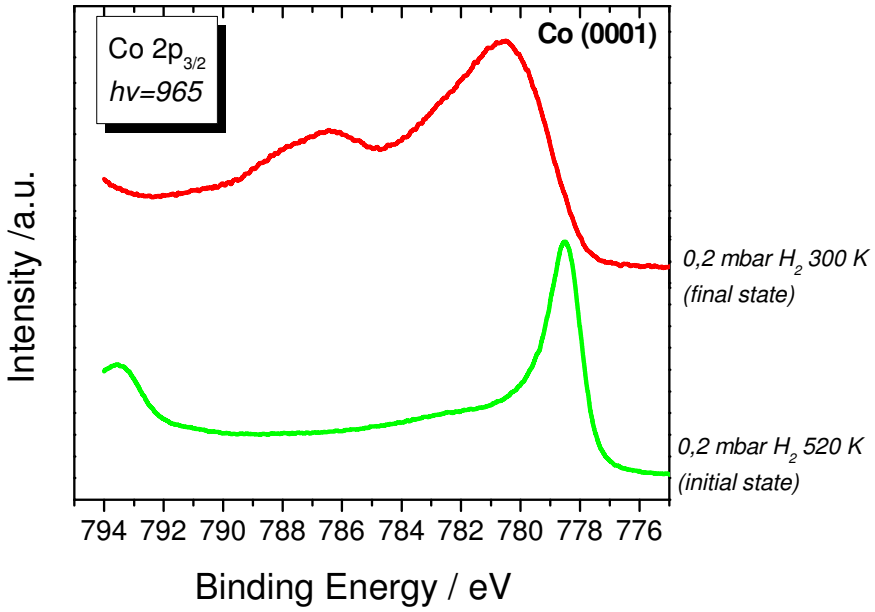

Figure S4. The Co 2p3/2 core level photoelectron peaks of Co (0001) crystal in 0.2 mbar H_2 at 520 K and after cooling at 300 K without changing the gas atmosphere. Traces of oxidative agents in the chamber or surface segregation of bulk diluted oxygen might be responsible for the oxidation.

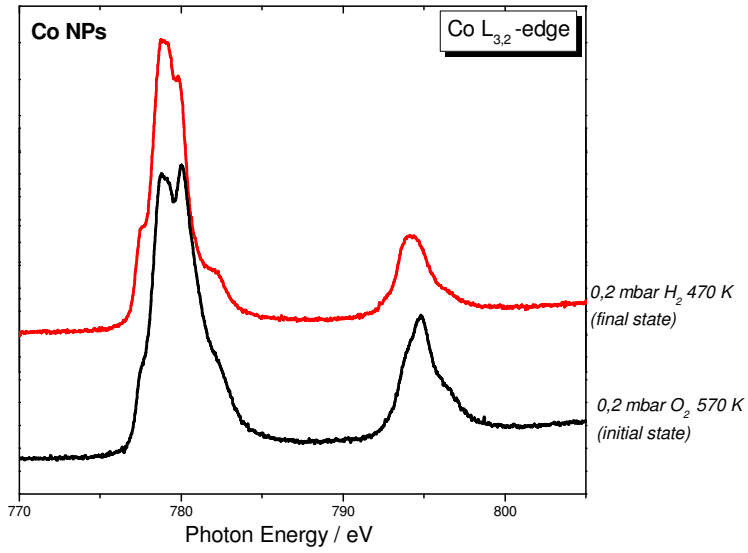

Figure S5. XAS Co L-edge spectra for 3.5 nm Co NPs in oxidative conditions (0.2 mbar O_2 at 570 K) (bottom spectrum) and mild reducing condition (0.2 mbar H_2 at 470 K) (top spectrum).