Supporting Information

Selective CO oxidation in excess H_2 over copper-ceria catalysts: Identification of active entities/species

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Experimental details.

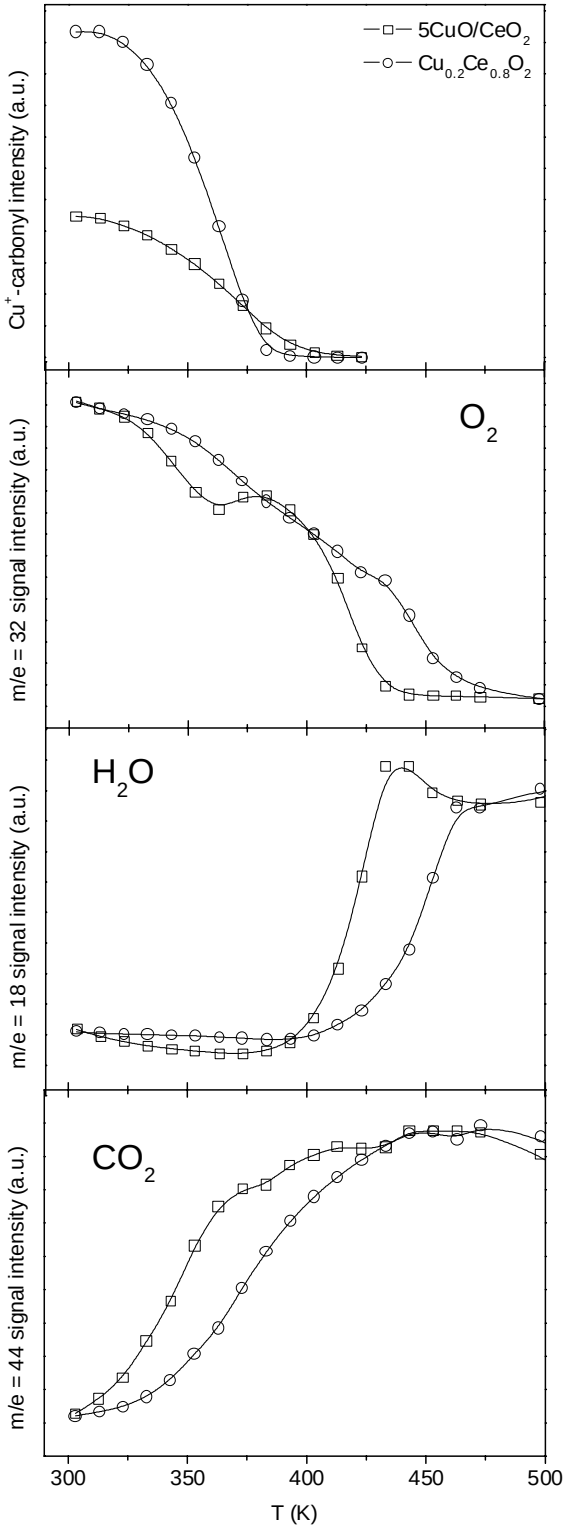
Preparation of the catalysts. Cu-doped ceria samples, labelled as $Ce_{1-x}Cu_xO_2$ (x = 0.05 and 0.2; i.e. with Ce/Cu atomic ratios of 19.0 and 4.0, respectively) were prepared by a modified reverse microemulsion method.[1] Briefly, the precursors were introduced in a reverse microemulsion (water in oil) using *n*-heptane as the organic phase, Triton X-100 (Aldrich) as surfactant, and hexanol as cosurfactant. Then, this suspension was mixed with another similar suspension containing as aqueous phase an alkali solution (TMAH, Aldrich) in order to coprecipitate the cations. The resulting mixtures were stirred for 24 h, centrifuged, decanted, and rinsed with methanol. Finally, the solid portion was dried overnight at 373 K, and the resulting powders were calcined under air at 773 K for 2 h. ICP-AES chemical analysis of these samples confirmed quantitative precipitation of both Cu and Ce cations. Surface area values (S_{BET}) obtained for these samples were observed to increase with the copper content (130 and 151 $m^2\ g^{-1}$ for $Ce_{0.95}Cu_{0.05}O_2$, $Ce_{0.9}Cu_{0.1}O_2$ and $Ce_{0.8}Cu_{0.2}O_2$, respectively), in agreement with a gradual crystal particle size decrease.[2]

Samples of copper supported on CeO_2 (Cu wt % of 0.5, 1.0 and 5.0, denoted as $0.5CuO/CeO_2$, $1CuO/CeO_2$ and $5CuO/CeO_2$, and corresponding to Ce/Cu at. ratios of 90.9, 45.5 and 8.6, respectively) were prepared by incipient wetness impregnation of a CeO_2 support prepared by microemulsion (in a similar manner as described above) with copper nitrate aqueous solutions. Following impregnation, the samples were dried overnight at 373 K and finally calcined under air at 773 K for 2 h. S_{BET} values obtained for these samples were of 116, 107 and 101 $m^2\ g^{-1}$ for $0.5CuO/CeO_2$, $1CuO/CeO_2$ and $5CuO/CeO_2$, respectively, therefore decreasing with the copper loading and in any case resulting lower than that of the parent CeO_2 support (130 $m^2\ g^{-1}$).

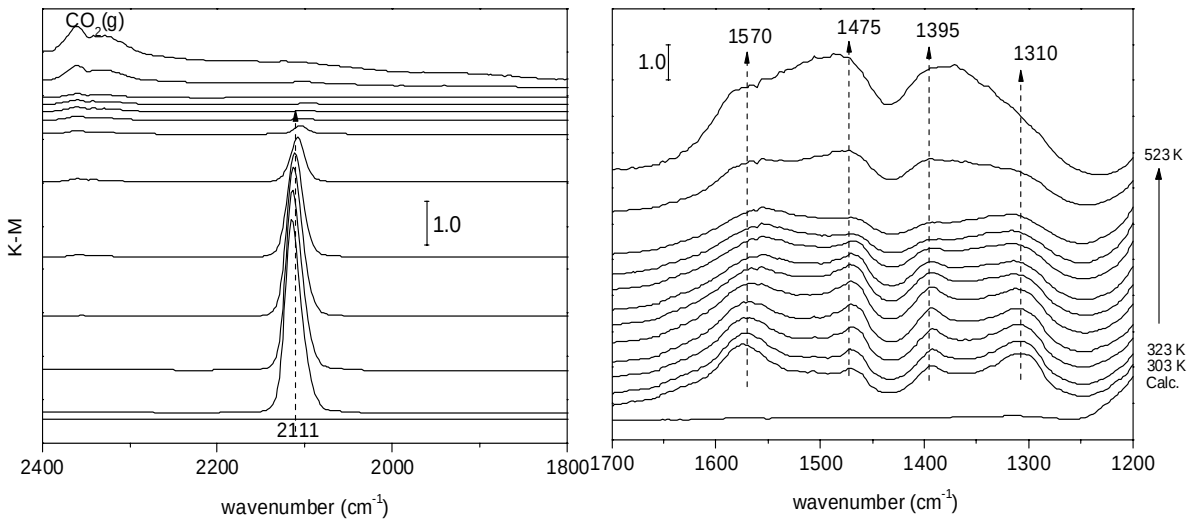
Techniques. Operando-DRIFTS analysis was carried out using a Bruker Equinox 55 FTIR spectrometer fitted with an MCT detector. The DRIFTS cell (Harrick) was fitted with CaF_2 windows and a heating cartridge that allowed samples to be heated to 773 K. Aliquots of *ca*. 100 mg were calcined in situ at 773 K and then cooled to 298 K under diluted oxygen before introducing the reaction mixture and heating in a stepped way, recording one spectrum (average of 50 scans at 4 cm^{-1} resolution) typically every 10 K after the signal of the different monitored gases (analysed on line by means of a quadrupole mass spectrometer Pfeiffer Omnistar) becomes constant (i.e. steady conditions). The gas mixture (1 % CO + 1.25 % O_2 + 50 % H_2 in He) was prepared using mass flow controllers with *ca.* 100 $cm^3\ min^{-1}$ passing through the catalyst bed at atmospheric pressure.

X-ray absorption near edge structure (XANES) experiments at the Cu K- and Ce L_{III}-edges were performed at station 7.1 of the SRS (Daresbury, UK) synchrotron. A

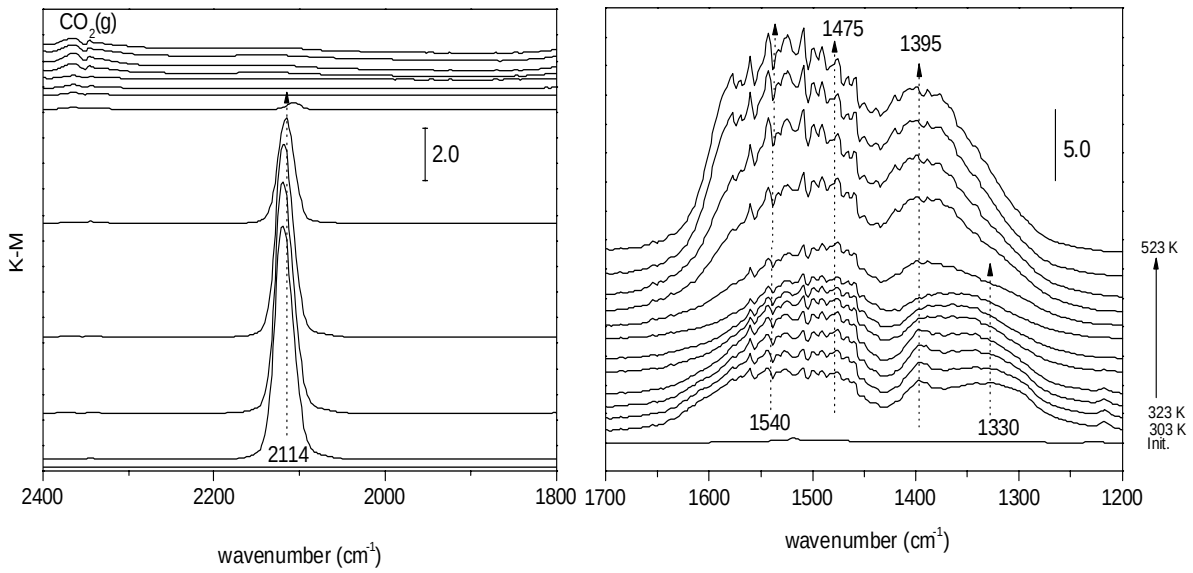
Si(111) double-crystal monochromator was used in conjunction with a rejection mirror to minimise the harmonic content of the beam. Transmission experiments were carried out using noble gas- or N_2/O_2-filled ionisation chambers as detector. The energy scale was simultaneously calibrated by measuring a Cu foil or a pure CeO_2 disc using a third ionisation chamber. Self-supporting discs were employed (absorbance 0.5-1.0) and placed in a controlled-atmosphere home made cell for *in situ* treatment. Gases analyses were performed on line by means of a quadrupole mass spectrometer Pfeiffer Omnistar. The samples were pretreated under diluted oxygen at 773 K and XANES spectra were taken in the presence of a $CO + O_2 + H_2$ flowing mixture (similar to the one employed for the DRIFTS experiments) during a 2 K min^{-1} temperature ramp up to 573 K. The series of spectra were analyzed by using principal factor analysis (PCA), details of which can be found elsewhere.[3] Raman spectra were collected using a single monochromator Renishaw System 1000 equipped with a cooled CCD detector and holographic super-notch filter. The samples were excited with the green laser line (514 nm); the spectral resolution was ca. 3 cm^{-1} and spectrum acquisition consisted of 3 accumulations with a total of ca. 15 min acquisition time. An in situ cell (Linkam, TS-1500), which allows thermal treatments under flowing gases, was employed to hold the samples in powder form. The as-prepared samples were pretreated in flowing 20 % O_2/He at 773 K for 1 h before any further treatment. The $Cu_{0.2}Ce_{0.8}O_2$ catalyst and the CeO_2 support employed as reference were examined under a $CO + O_2 + H_2$ flowing mixture similar to the one employed for the DRIFTS and XANES experiments and after stabilization at any determinate reaction temperature during ca. 10 min.



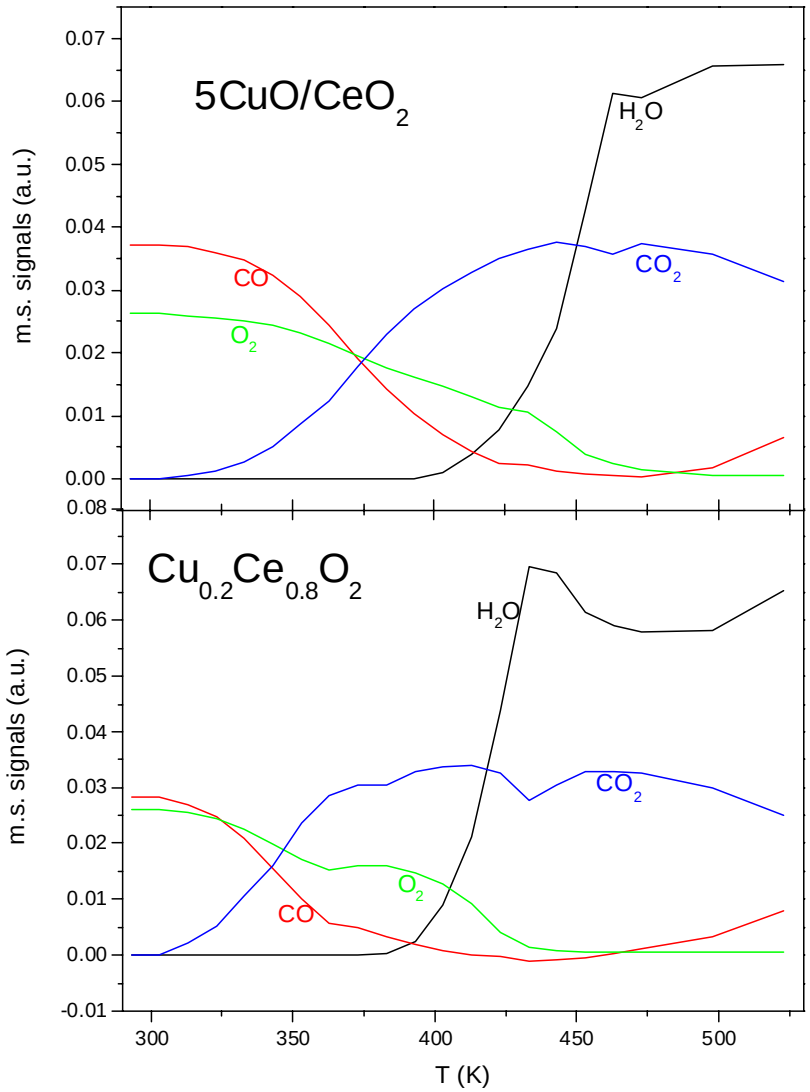
Supporting Information Figure 1. Evolution of the indicated gases during *Operando* DRIFTS experiments under CO-PROX conditions over the indicated catalysts. The top graphic displays the evolution of the Cu^{+}-carbonyl species during the run. Note the decrease of this latter upon increasing reaction temperature is affected by thermal desorption.[4,5]



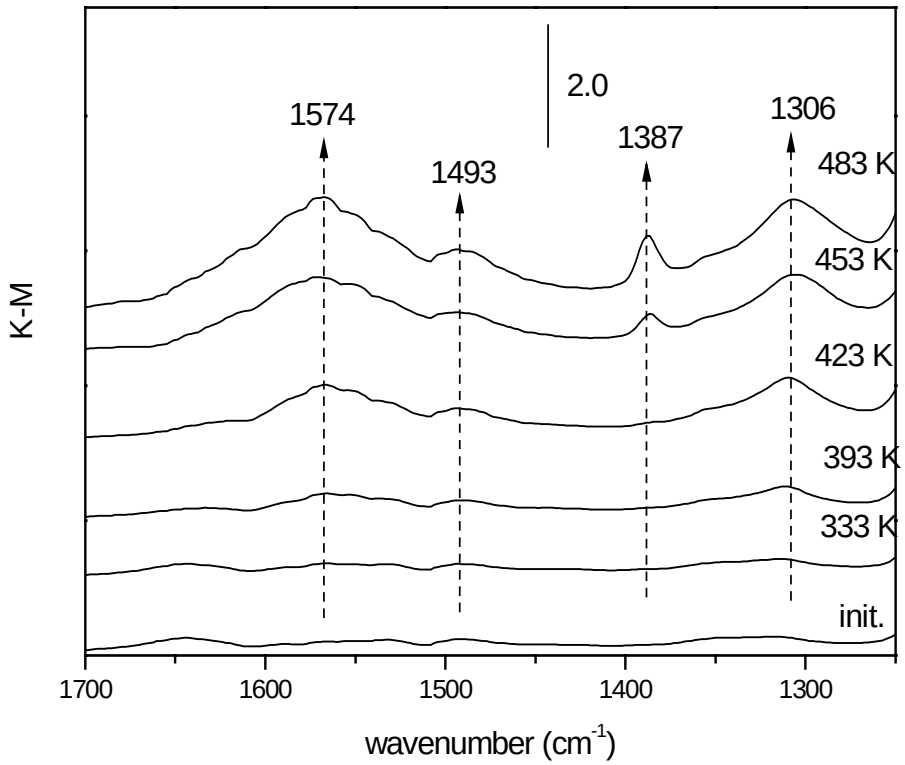
Supporting Information Figure 2. DRIFTS spectra recorded for $5CuO/CeO_2$ under CO-PROX conditions. The bottom one was recorded prior to introduction of the reaction mixture. The rest were recorded every 20 K from 303 to 523 K, from bottom to top. Bands of carbonate-type species are attributed as follows:[6] 1570 and 1310 cm^{-1}: bidentate carbonates; 1395 cm^{-1} along with a shoulder at ca. 1610 cm^{-1} and a band at 3620 cm^{-1} (not shown): hydrogencarbonates; 1475 cm^{-1} along with a shoulder at ca. 1350 cm^{-1}: polydentate carbonates.



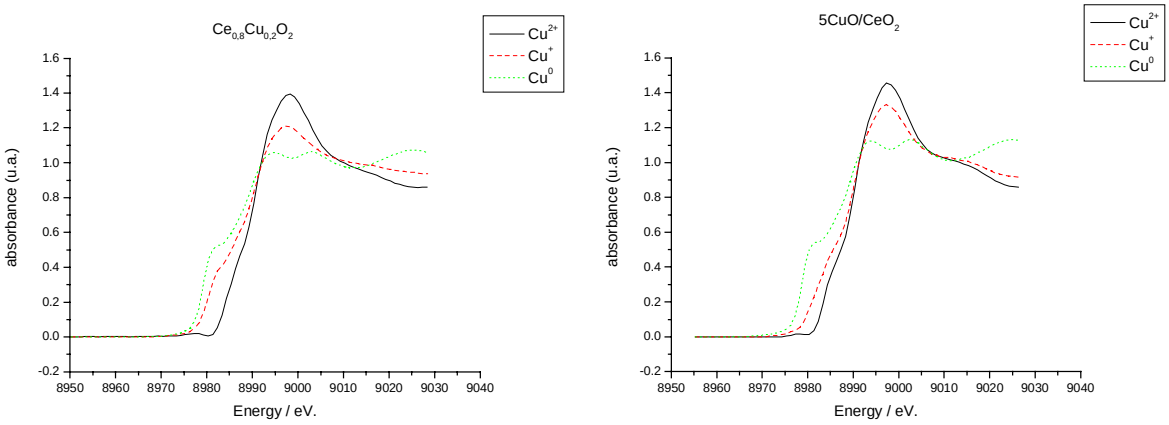
Supporting Information Figure 3. DRIFTS spectra recorded for $Cu_{0.2}Ce_{0.8}O_2$ under CO-PROX conditions. The bottom one was recorded prior to introduction of the reaction mixture. The rest were recorded every 20 K from 303 to 523 K, from bottom to top. The nature of the carbonate species appears similar to those detected in $5CuO/CeO_2$ although their frequency can be modified due to the different nature of the supports in each case, as detailed elsewhere.[6]



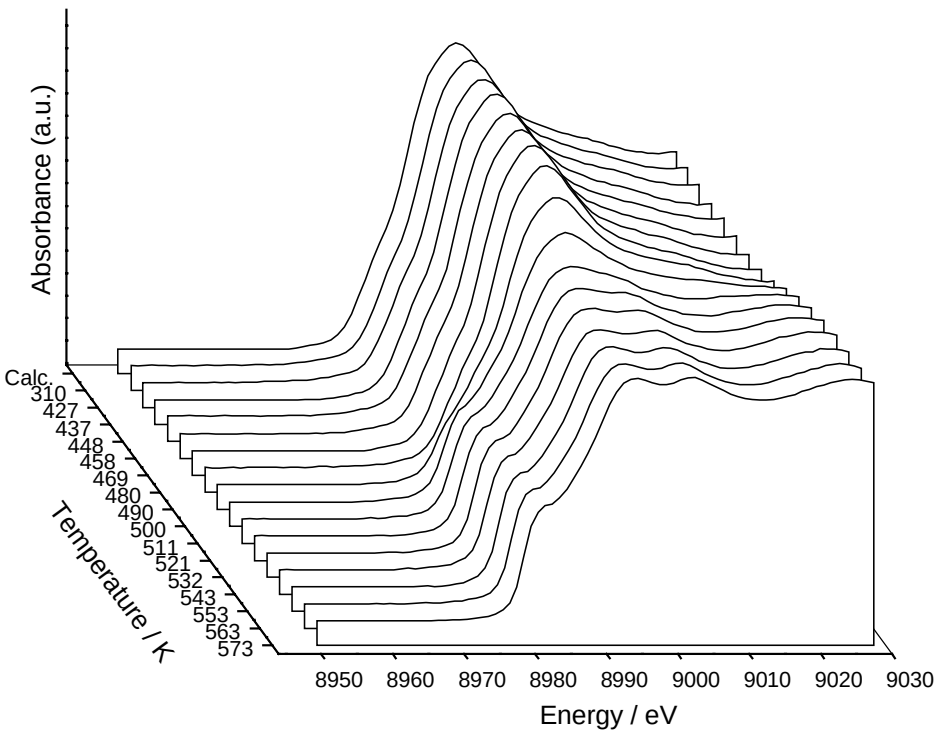
Supporting Information Figure 4. Evolution of the indicated gases during *Operando*-DRIFTS experiments under CO-PROX conditions over the indicated catalysts.



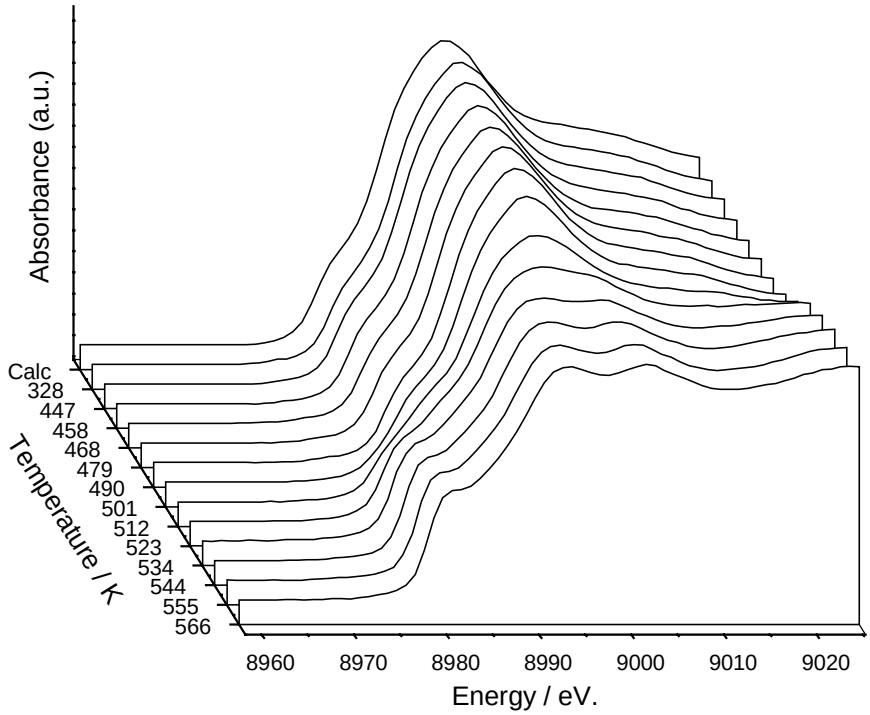
Supporting Information Figure 5. DRIFTS spectra recorded under CO-PROX conditions for the CeO_2 support. The bottom one was recorded just prior to introduction of the CO-PROX mixture and the rest were recorded at the indicated temperatures.



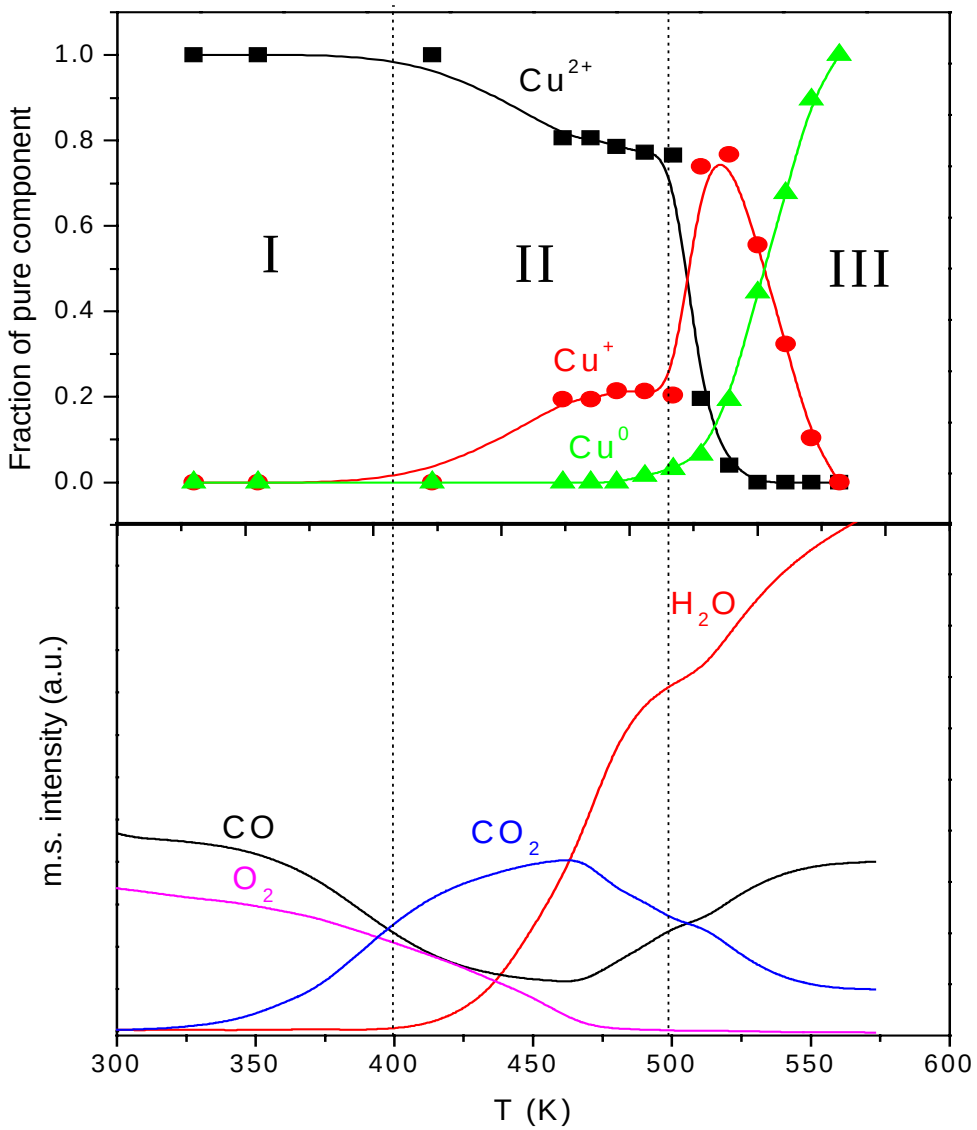
Supporting information Figure 6. Spectra for the Cu-containing species extracted from Principal Component analysis of the *Operando*-XANES spectra. Left: $Ce_{0.8}Cu_{0.2}O_2$. Right:$5CuO/CeO_2$



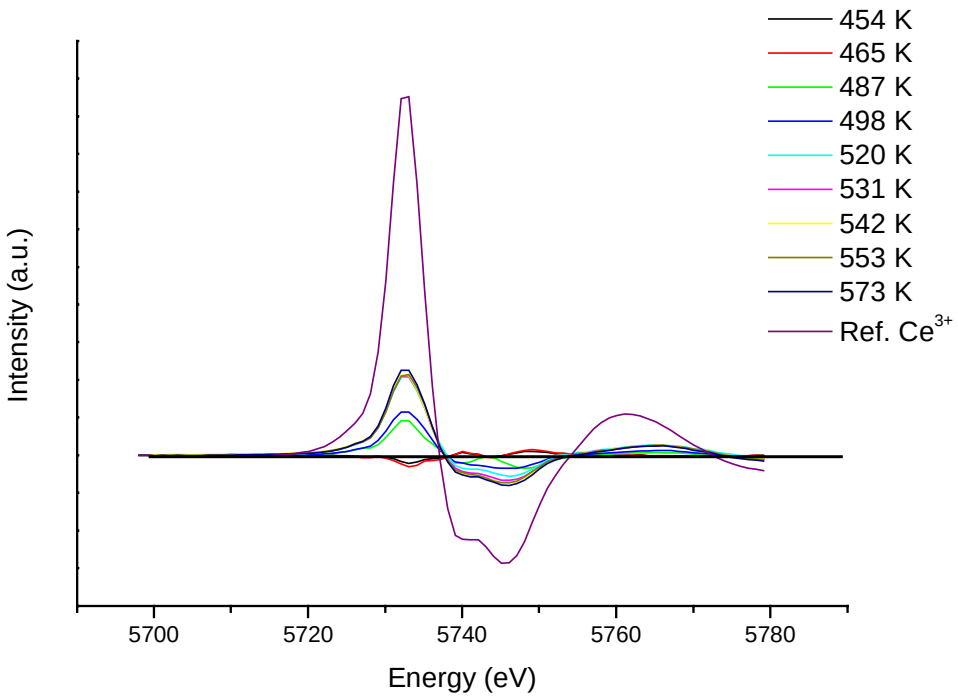
Supporting information Figure 7. XANES spectra obtained under CO-PROX conditions at the indicated temperatures over $Cu_{0.2}Ce_{0.8}O_2$



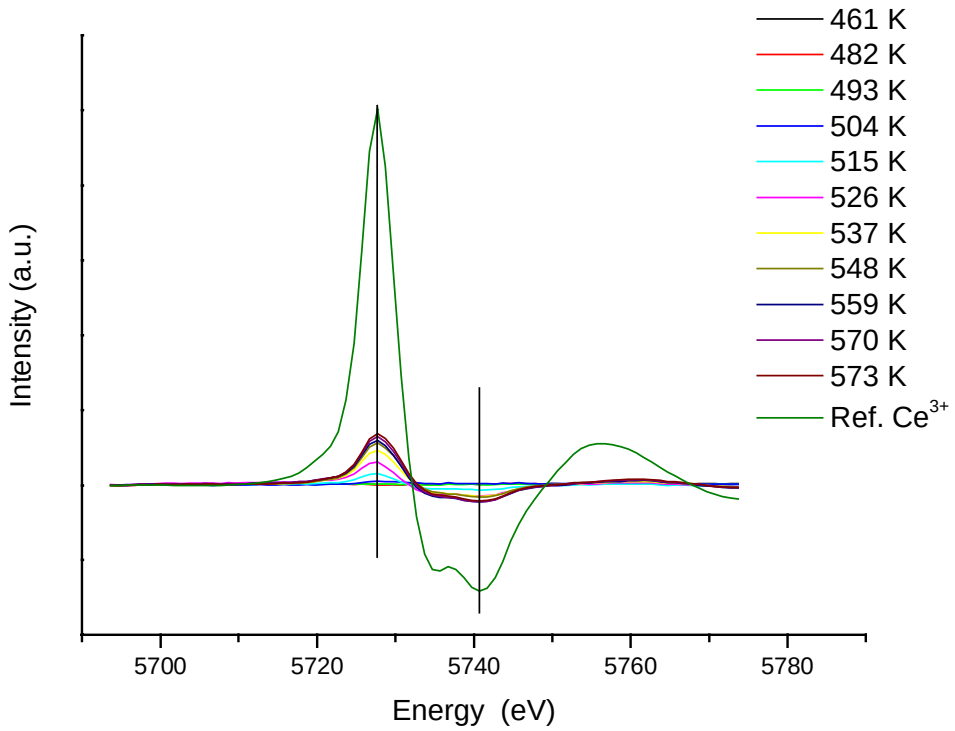
Supporting information Figure 8. XANES spectra obtained under CO-PROX conditions at the indicated temperatures over $5CuO/CeO_2$



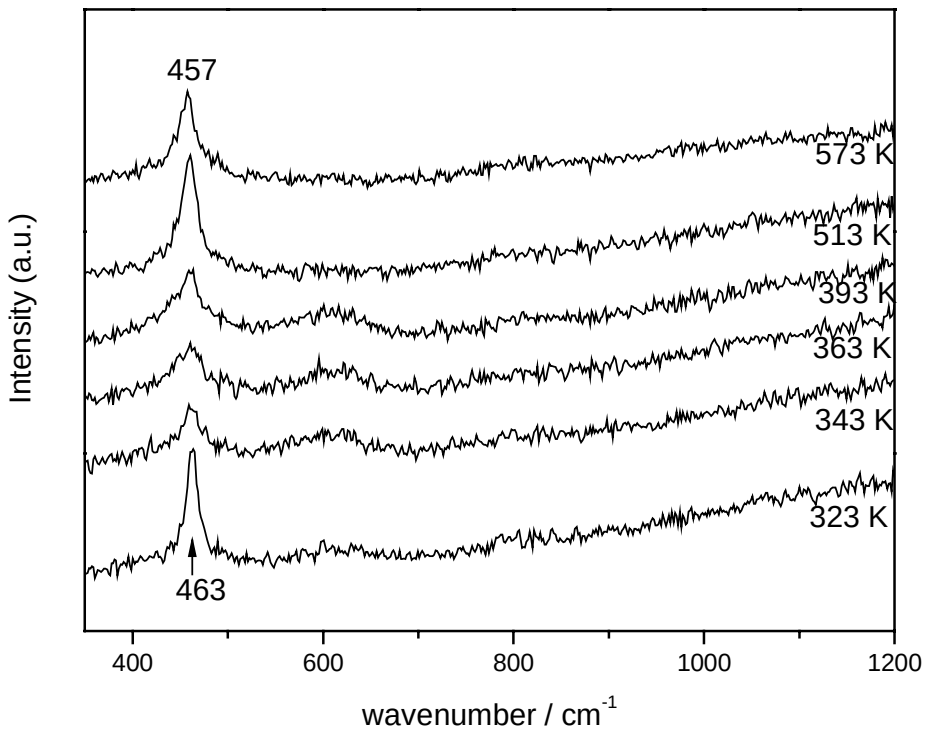
Supporting Information Figure 9. Evolution of principal components obtained from analysis of the *Operando*-XANES spectra for 5CuO/CeO_2 under CO-PROX conditions and evolution of the gases during the run.



Supporting Information Figure 10. XANES difference spectra at the Ce L_{III} edge for $Cu_{0.2}Ce_{0.8}O_2$ under CO-PROX conditions at the indicated temperature. The spectrum of a pure CeO_2 reference was subtracted from the experimental spectra. The spectrum of a Ce^{3+} reference is shown for comparative purpose.



Supporting Information Figure 11. XANES difference spectra at the Ce L_{III} edge for $5CuO/CeO_2$ under CO-PROX conditions at the indicated temperatures. The spectrum of a pure CeO_2 reference was subtracted from the experimental spectra. The spectrum of a Ce^{3+} reference is shown for comparative purpose.



Supporting Information Figure 12. Raman spectra obtained for $Cu_{0.2}Ce_{0.8}O_2$ under CO-PROX conditions at the indicated temperatures. The shift of the F_{2g} mode band at ca. 460 cm^{-1} is in agreement with thermal expansion of the fluorite lattice (in accordance with spectra simultaneously recorded under the same conditions for CeO_2) and reduction at the highest temperatures,[7,8] while the decrease of the band at ca. 600 cm^{-1} at the highest reaction temperatures is consistent with copper migration to the surface as a consequence of reduction to metallic copper.[2] Note that peroxide or superoxide species would be expected to give bands at ca. 840 and 1125 cm^{-1}, respectively.[7,9]

Supporting Information references

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