Supporting Information

Approaching C1 Reaction Mechanisms Using Combined *Operando* and Transient Analysis: A Case Study on Cu/CeO_2 Catalysts During LT-Water-Gas Shift Reaction

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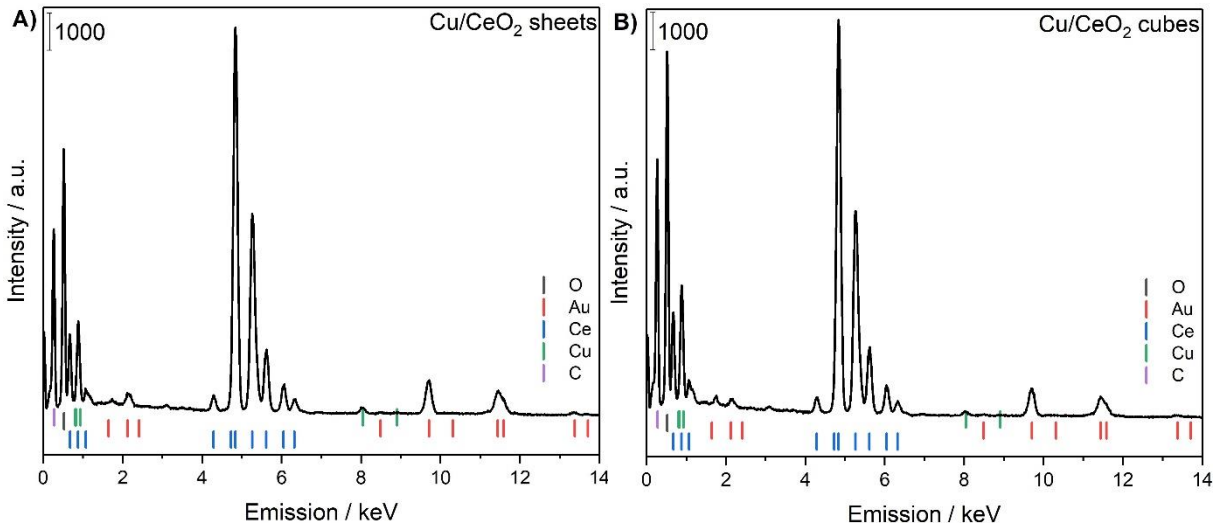

Figure S1. EDX spectra of the Cu/CeO_2 samples for CeO_2 **A)** sheets and **B)** cubes. The gold emissions originate from the TEM grid.

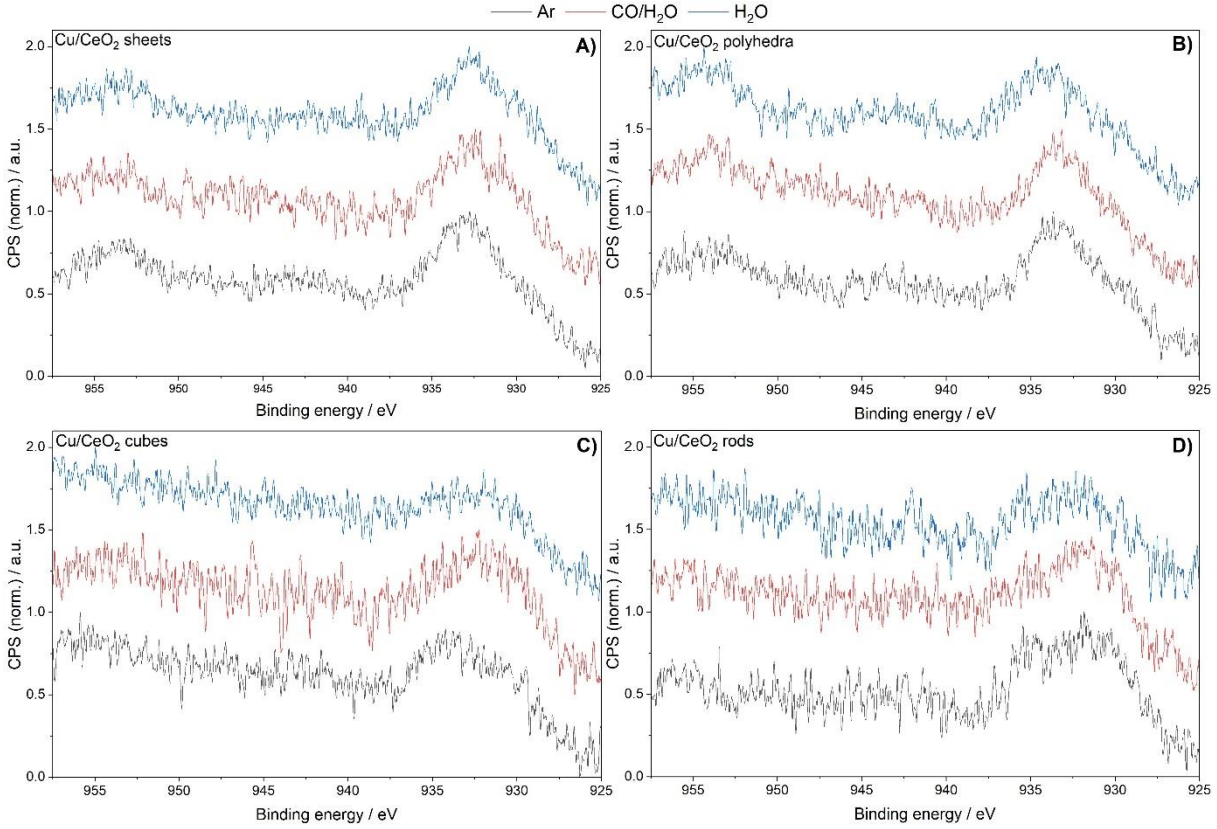

Figure S2. Cu 2p photoemission of the copper-loaded **A)** ceria sheets, **B)** ceria polyhedra, **C)** ceria cubes, and **D)** ceria rods. Spectra were recorded directly after argon (gray), CO/H_2O (red) and H_2O (blue) pretreatment at 190 °C. Spectra are offset and normalized to the Cu $2p_{3/2}$ signal for clarity.

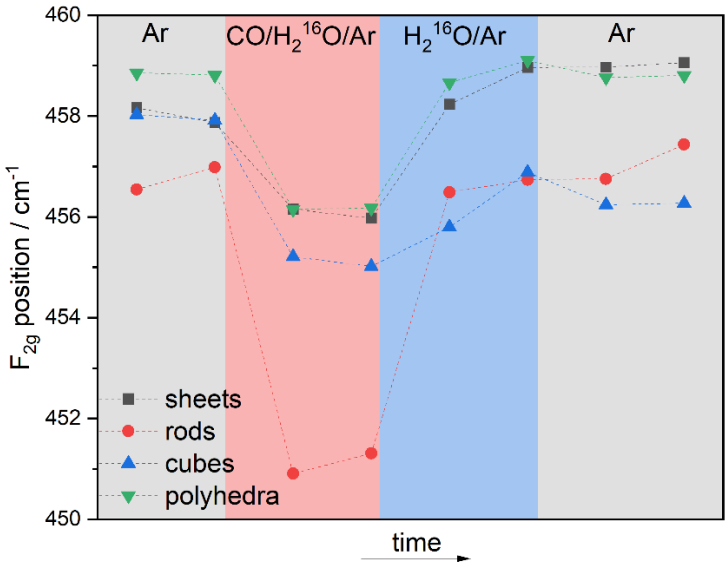

Figure S3. *In situ* / *operando* Raman F_{2g} positions for Cu/CeO_2 catalysts for the indicated gas environments at 190 °C using $H_2{}^{16}O$ (total flow rate: 100 mL/min). The underlying spectra were recorded at 532 nm excitation and after gas-phase exposure for about 30 min and 1 h.

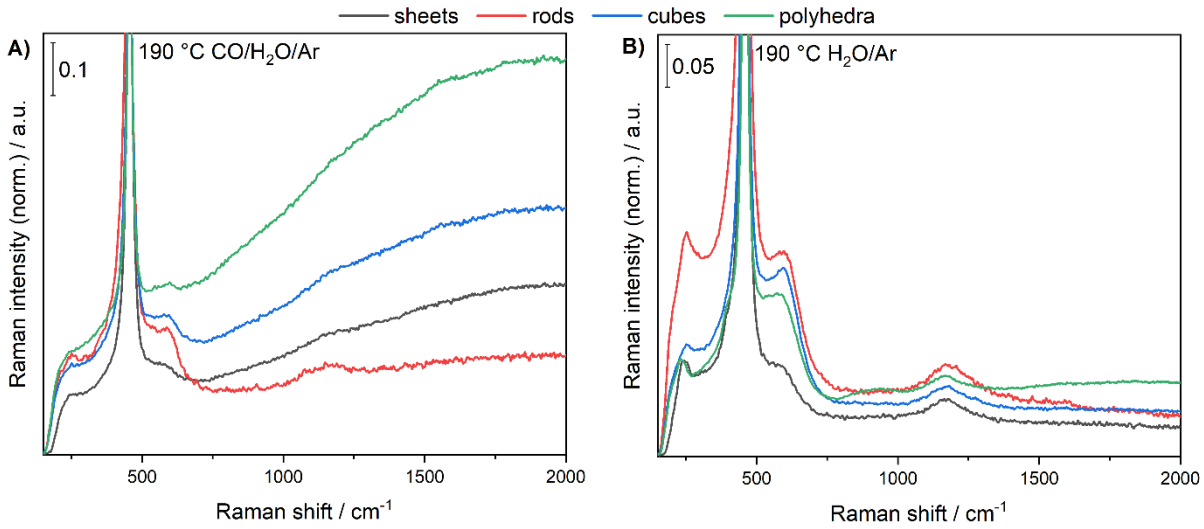

Figure S4. A) *Operando* Raman spectra of the Cu/CeO_2 catalysts recorded under reaction conditions at 190 °C (2 vol% CO/8 vol% H_2O/Ar) and **B)** *in situ* Raman spectra recorded in 8 vol% H_2O/Ar after reaction conditions at 190 °C. The total flow rate was always 100 mL min^{-1}. Spectra were normalized to the F_{2g} Band and the F_{2g} bands were cut off for clarity. Raman spectra were recorded at 532 nm laser excitation.

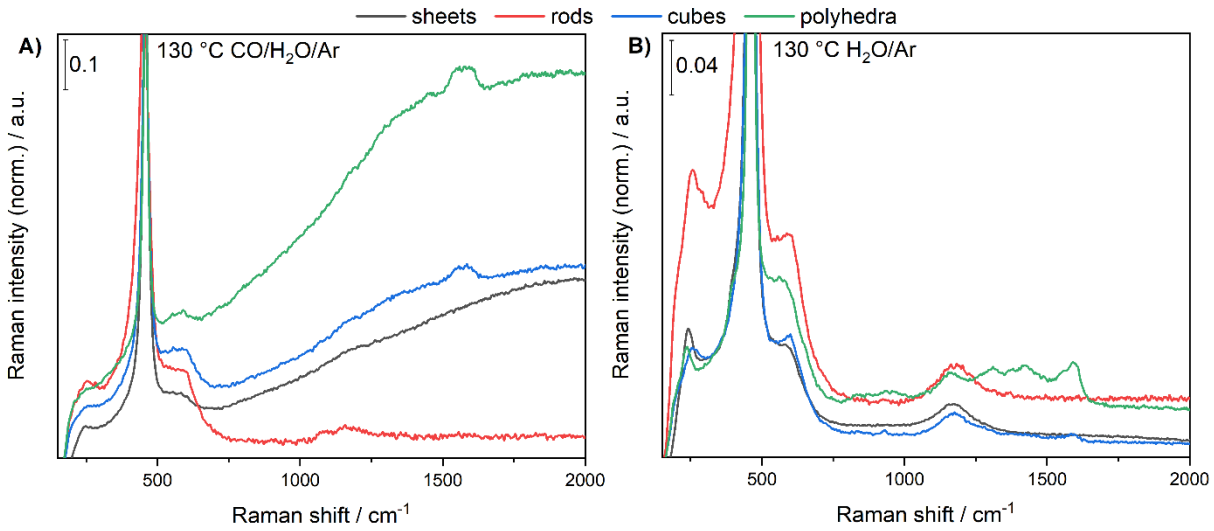

Figure S5. A) *Operando* Raman spectra of the Cu/CeO_2 catalysts recorded under reaction conditions at 130 °C (2 vol% CO/8 vol% H_2O/Ar) and **B)** *in situ* Raman spectra recorded in 8 vol% H_2O/Ar after reaction conditions at 130 °C. The total flow rate was always 100 mL min^{-1}. Spectra were normalized to the F_{2g} Band and the F_{2g} bands were cut off for clarity. Raman spectra were recorded at 532 laser excitation.

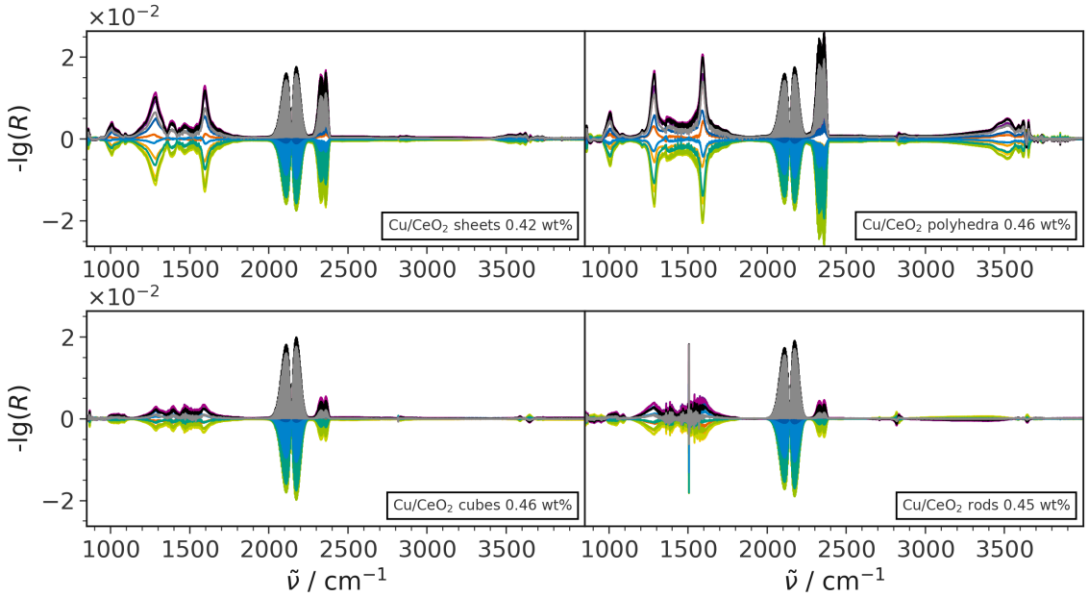

Figure S6. PSD spectra of the Cu/CeO_2 samples at 190 °C. The gas-phase composition was periodically changed from 8 vol% H_2O/Ar to 2 vol% CO/8 vol% H_2O/Ar.

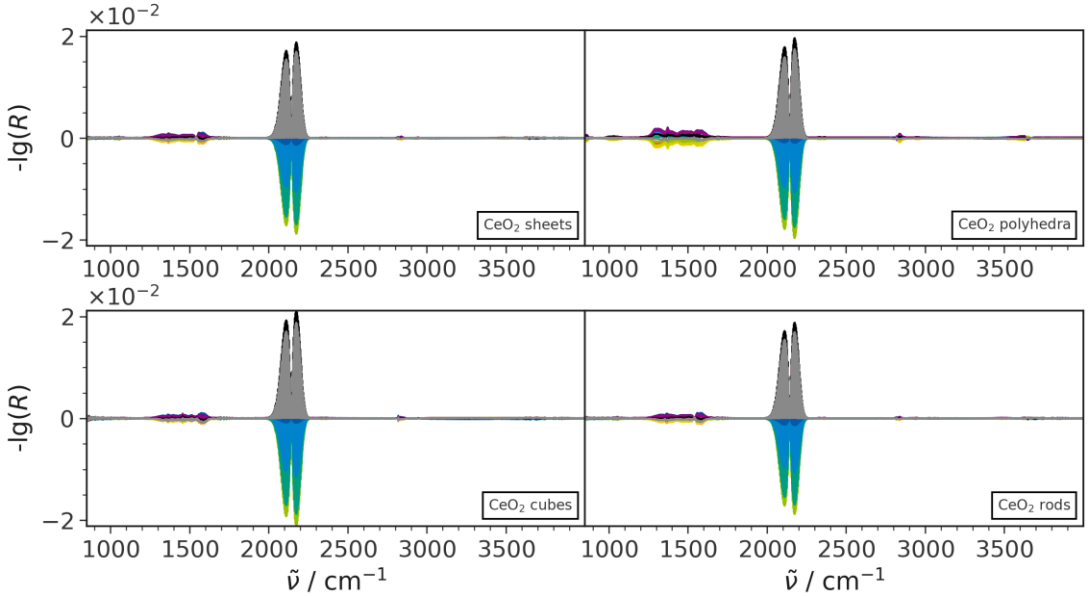

Figure S7. PSD spectra of the bare CeO_2 samples at 190 °C. The gas-phase composition was periodically changed from 8 vol% H_2O/Ar to 2 vol% CO/8 vol% H_2O/Ar.

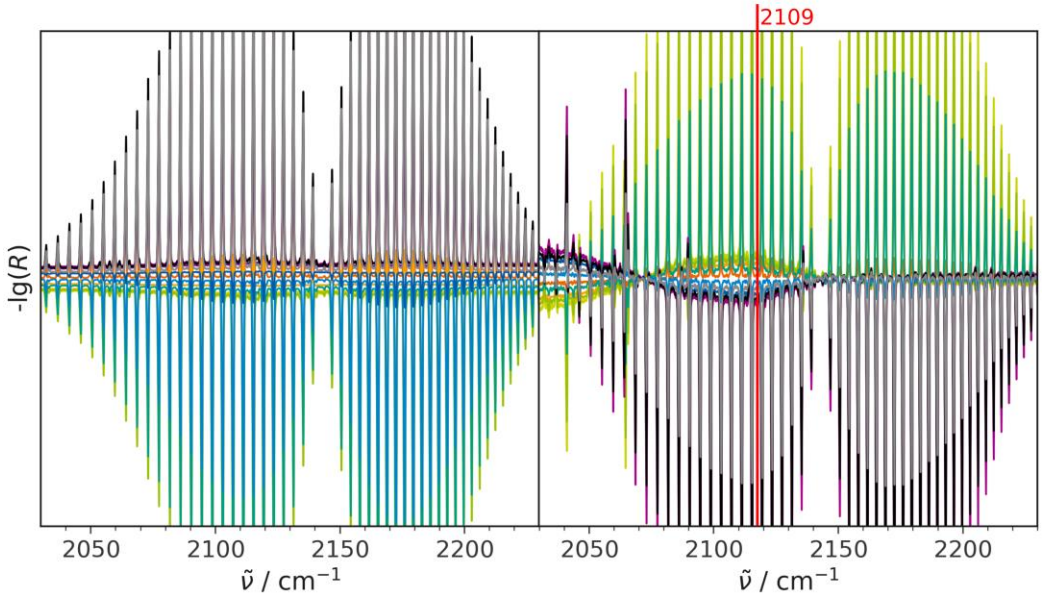

Figure S8. PSD spectra of the CO region of Cu/CeO_2 sheets at 190 °C. **Left:** The gas-phase composition was periodically changed from 8 vol% H_2O/Ar to 2 vol% CO/8 vol% H_2O/Ar, corresponding to the conditions applied in Figure 6. **Right:** The gas-phase composition was periodically changed from 2 vol% CO/Ar to 2 vol% CO/8 vol% H_2O/Ar. The presence of a potential CO adsorbate in the right panel is marked in red.

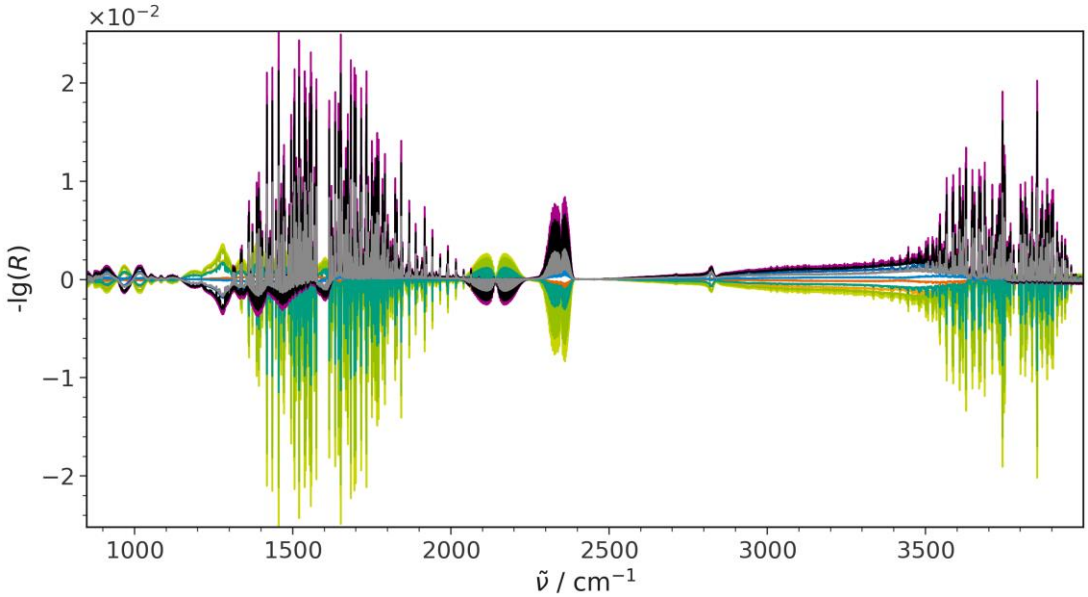

Figure S9. PSD spectra of Cu/CeO_2 sheets at 190 °C. The gas-phase composition was periodically changed from 2 vol% CO/Ar to 2 vol% CO/8 vol% H_2O/Ar.

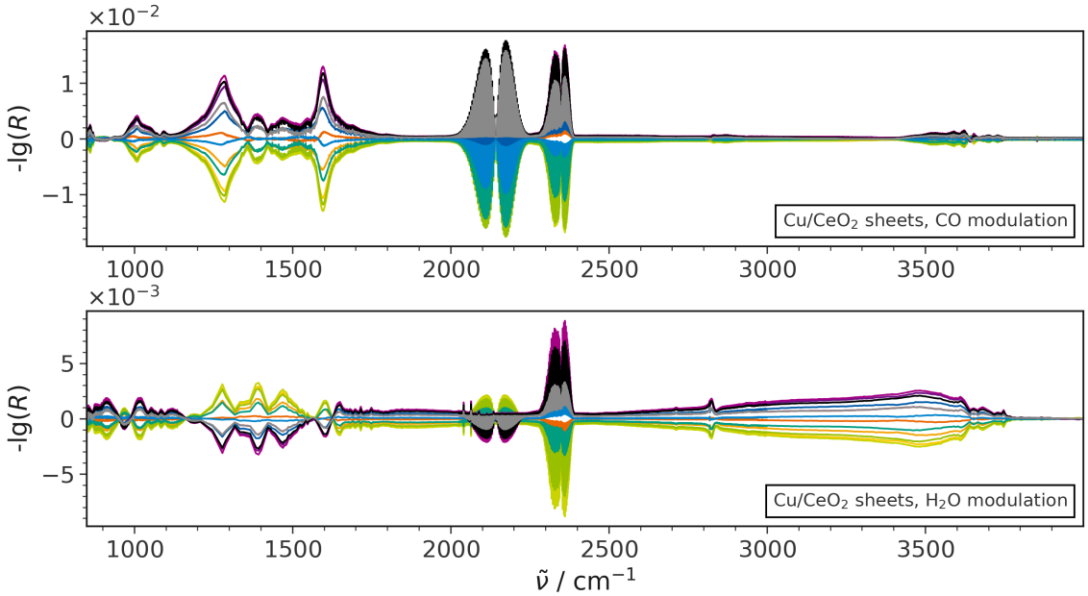

Figure S10. Comparison of PSD spectra of Cu/CeO_2 sheets at 190 °C. **Top:** Spectra taken from Figure 6. The gas-phase composition was periodically changed from 8 vol% H_2O/Ar to 2 vol% CO/8 vol% H_2O/Ar. **Bottom:** Spectra taken from Figure S9. The gas-phase composition was periodically changed from 2 vol% CO/Ar to 2 vol% CO/8 vol% H_2O/Ar. Contributions of gaseous water at 1180–2025 cm^{-1} and 3000–4000 cm^{-1} were removed by plotting only the minima between the single rotational contributions.

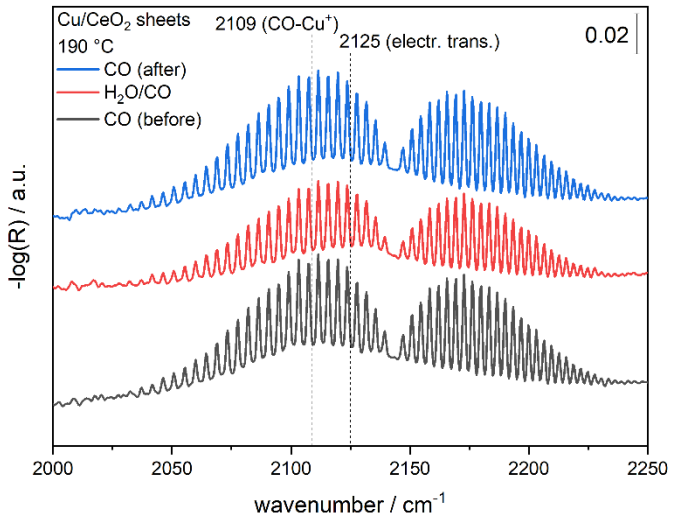

Figure S11. Steady-state DRIFT spectra of Cu/CeO_2 sheets at 190 °C. The sample itself was used as the background spectrum under argon at 190 °C. Subsequently, the sample was exposed to 2 vol% CO/Ar, 2 vol% CO/8 vol% H_2O/Ar and 2 vol% CO/Ar. All spectra were recorded after approximately 30 min under the corresponding gas flow (total flow rate: 100 mL/min).

Table S1. Results from transient IR-PSD analysis of Cu/CeO_2 sheets. Time values correspond to the signal onset and signals of decreasing bands are marked with (-). Refer to Figure S9 for the underlying PSD spectra.

Position / cm^{-1}	$t(Cu/CeO_2)$ / s	Assignment
3471	54	Weakly adsorbed H_2O
2824	47	Formate C-H
2368	56	CO_2
2183	50 (-)	CO_g
2109	54 (-)	CO_{ads}
1942	51	H_2O_g
1605	51 (-)	Carbonate species
1469	52 (-)	Carbonate species
1392	51 (-)	Carbonate species
1280	50 (-)	Carbonate species
1017	52	Carbonate species
968	49 (-)	Carbonate species
912	54	Carbonate species