

Supplementary Information

Unravelling the mechanism of CO₂ activation over low-loaded Cu/CeO₂(111) catalysts using *operando* and transient spectroscopies

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Experimental Section

XPS. X-ray photoelectron spectroscopy (XPS) was performed using a modified LHS/SPECS EA200/MCD system described previously.^[1–3] Samples can be pretreated in the same reaction cell as that used for the *operando* Raman and UV-Vis measurements and subsequently transferred to the analysis chamber without air exposure (quasi *in situ*). To ensure the comparability of the spectra, the u'' of the Ce 3d signal was shifted to 916.7 eV.^[4] Narrow scans were recorded with a resolution of 0.025 eV. Samples were measured after 1 hour treatments in O₂ (10 vol%), H₂ (2 vol%) and H₂/CO₂ (4 vol%/2 vol%), which were conducted at 250 °C and at a total flow rate of 100 ml/min.

Operando Measurements. Combined *operando* Raman and UV-Vis spectra as well as the catalytic activity were measured with a previously described experimental setup.^[5–8] For the Raman measurements, we used settings identical to those in our previous study.^[9]

UV-Vis spectra were recorded in diffuse reflection using an AvaSpec ULS2048CL-EVO spectrometer (Avantes) equipped with a balanced deuterium lamp and a halogen discharge lamp (AvaLight-D-S-BAL, Avantes). Spectra were taken before and after a Raman spectrum. The total measuring time was 60 s, resulting from 400 runs with an exposure time of 150 ms each. As a white standard, barium sulfate powder (Sigma Aldrich) was employed, which shows no absorption within the range 175–1100 nm.

Transient DRIFTS. Diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) was performed as described previously.^[9] Briefly, the spectra were recorded on a Vertex 70 (Bruker) FTIR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a commercial reaction cell (Praying Mantis™ High Temperature Reaction Chamber, Harrick Scientific Products) with infrared transparent KBr windows, as described previously.^[10,11]

As background, the catalyst itself was employed after a 15 min exposure at 250 °C to H₂ (4 vol%) or CO₂ (2 vol%) or the reaction mixture (4 vol% H₂ and 2 vol% CO₂, balanced with argon; total gas flow: 100 ml/min). Spectra were acquired within the range 850–3800 cm⁻¹, utilizing a resolution of 0.5 cm⁻¹ and an aperture of 8 mm. The mirror speed was set to 40 kHz. In transient DRIFTS experiments, the gas phase was switched immediately after the background spectrum had been recorded, commencing the measurements.

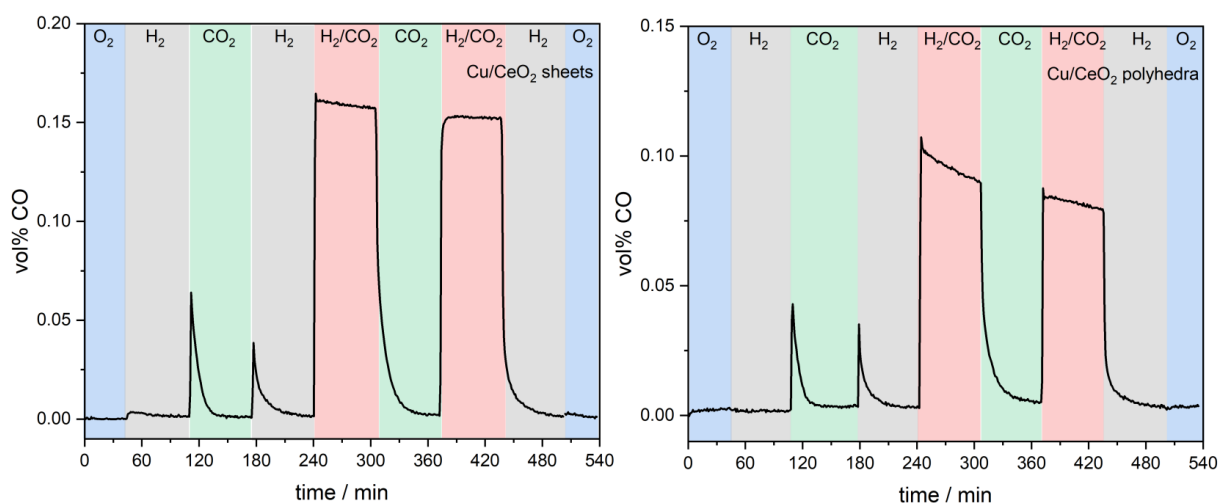


Figure S1. CO concentration (in vol%) from the gas-phase IR analysis during the *operando* Raman and UV-vis measurements for Cu/CeO₂ sheets (left) and polyhedra (right).

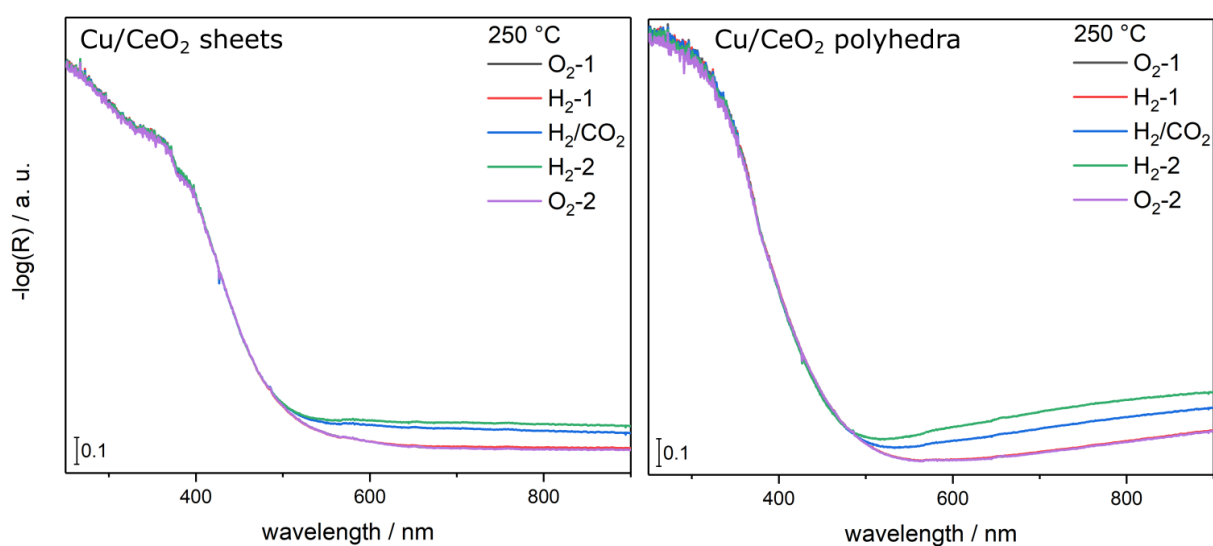


Figure S2. *In situ* / *operando* UV-Vis reflectance spectra of CeO₂ sheets (left) and polyhedra (right) at 250 °C for the indicated gas atmospheres.

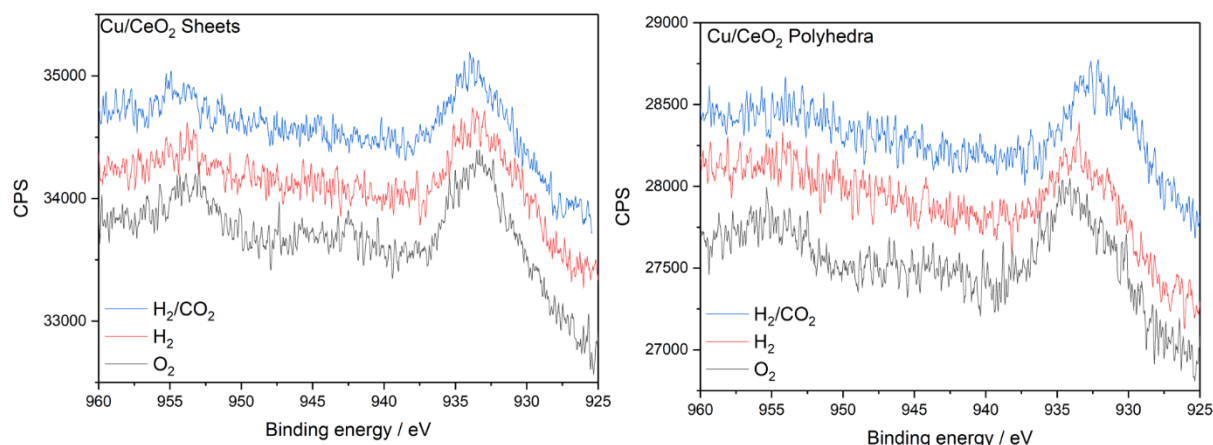


Figure S3. Cu 2p photoemissions of Cu/CeO₂ sheets (left) and polyhedra (right) after exposure to the indicated gas atmospheres at 250 °C (total flow rate: 100 ml min⁻¹). The black spectrum was obtained after O₂ (10 vol%) pretreatment, the red one after H₂ (4 vol%), and the blue one after H₂/CO₂ (4 vol%/2 vol%) pretreatment.

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