

Supporting Information

Unraveling the Mechanism of the CO₂-Assisted Oxidative Dehydrogenation of Propane over VO_x/CeO₂: An Operando Spectroscopic Study

Leon Schumacher, Marius Funke, Christian Hess*

Technical University of Darmstadt, Department of Chemistry, Eduard-Zintl-Institut für
Anorganische und Physikalische Chemie, Peter-Grünberg-Str. 8, 64287 Darmstadt,
Germany

*Corresponding Author (E-Mail: christian.hess@tu-darmstadt.de)

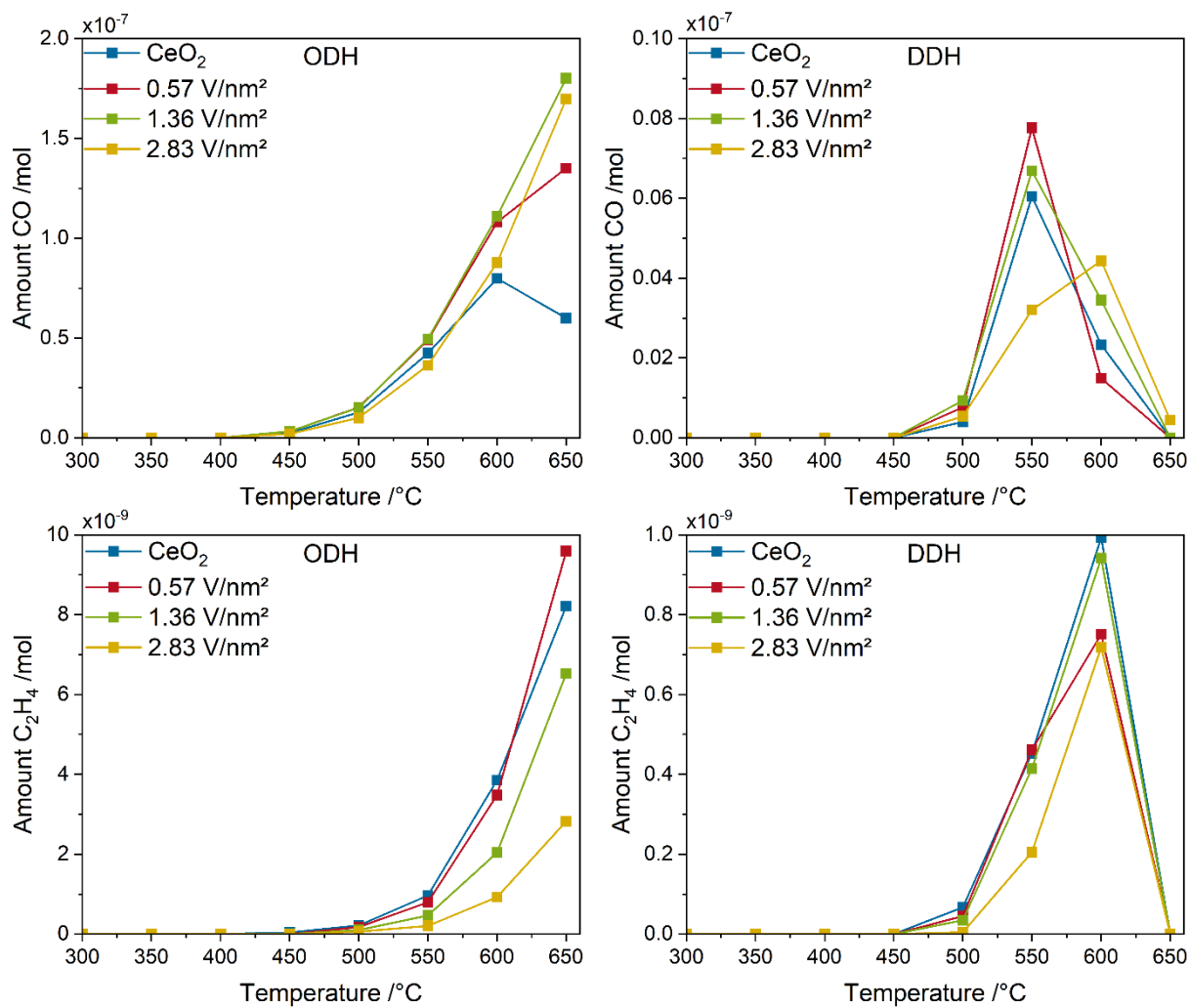


Figure S1: Comparison between the amounts of CO and C_2H_4 created under ODH (12.5% CO_2 /12.5% C_3H_8 /He) and DDH (12.5% C_3H_8 /He) conditions for ceria and vanadia-loaded samples.

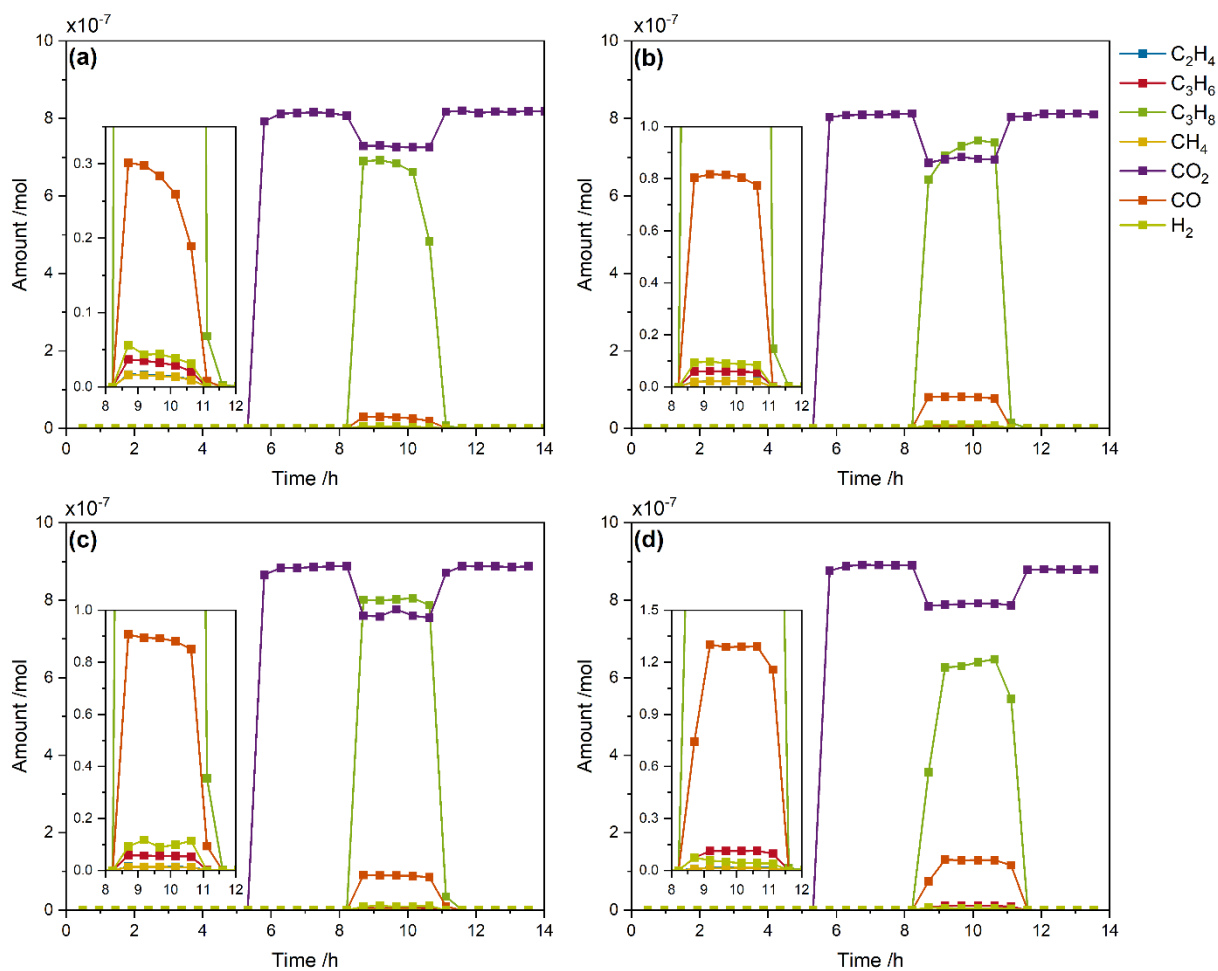


Figure S2: Molar product distributions of all detected reaction products formed by (a) CeO_2 , (b) 0.57, (c) 1.36, and (d) 2.83 V/nm^2 under different gas feeds (see experimental section) at 550 °C. The insets show the product distribution during ODH conditions (12.5% CO_2 /12.5% C_3H_8 /He) in an enlarged view for each sample.

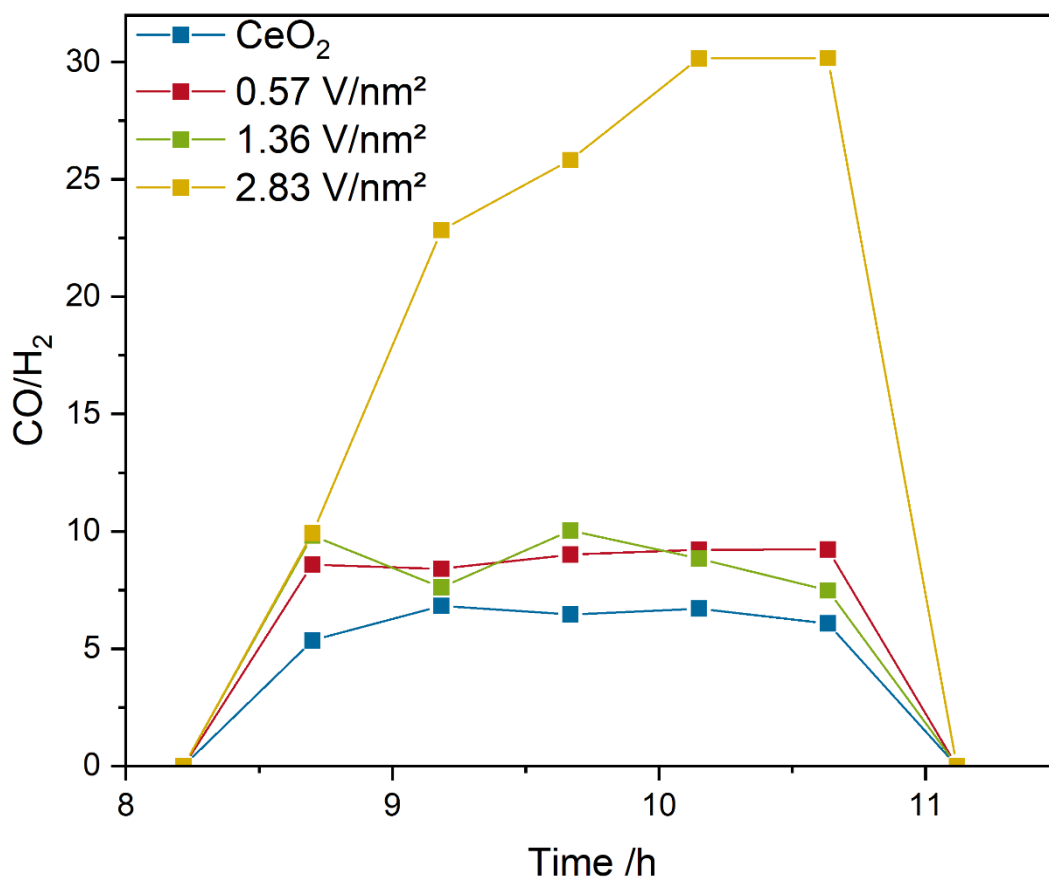


Figure S3: CO/H₂ ratio under ODH conditions (12.5% CO₂/12.5% C₃H₈/He) for ceria and vanadia-loaded samples as an indicator for the ODH/DDH+RWGS ratio.

Table S1: Calculated carbon balances from chromatograms measured during 12.5% CO₂/12.5% C₃H₈/He exposure at 550 °C.

Sample	CeO ₂	0.57 V/nm ²	1.36 V/nm ²	2.83 V/nm ²
Carbon Balance /%	6.6	6.2	6.3	7.2

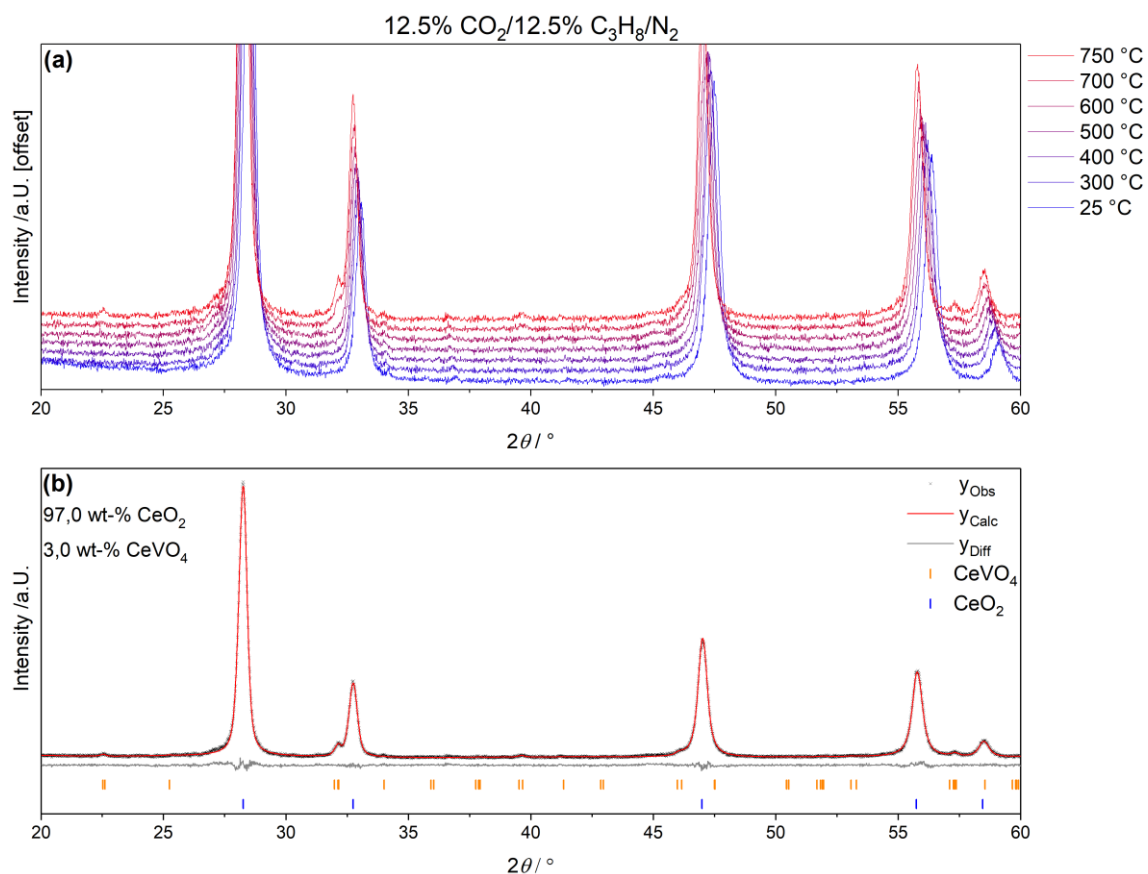


Figure S4: (a) In situ XRD patterns of the 2.83 V/nm² sample under ODH conditions (12.5% CO₂/12.5% C₃H₈/N₂) between 25 and 750 °C and (b) Rietveld analysis of the diffraction pattern recorded at 750 °C to quantify CeVO₄.

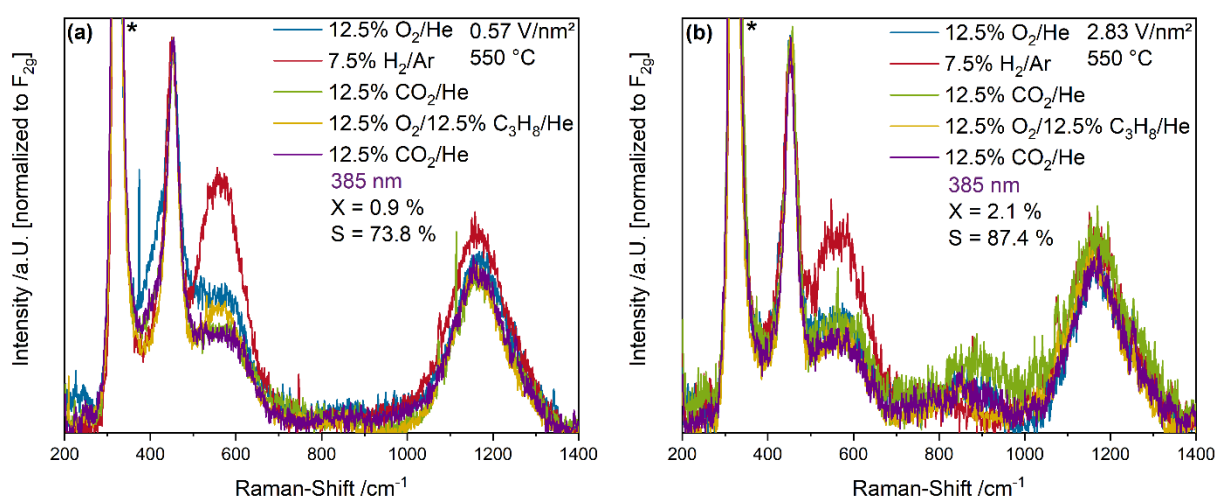


Figure S5: Operando UV-Raman spectra (385 nm excitation) of (a) the 0.57 and (b) the 2.83 V/nm² sample recorded under different gas feeds at 550 °C. The spectra are normalized to the F_{2g} mode and the peak caused by the CaF₂ window is marked with an asterisk. The conversions and selectivities are given.

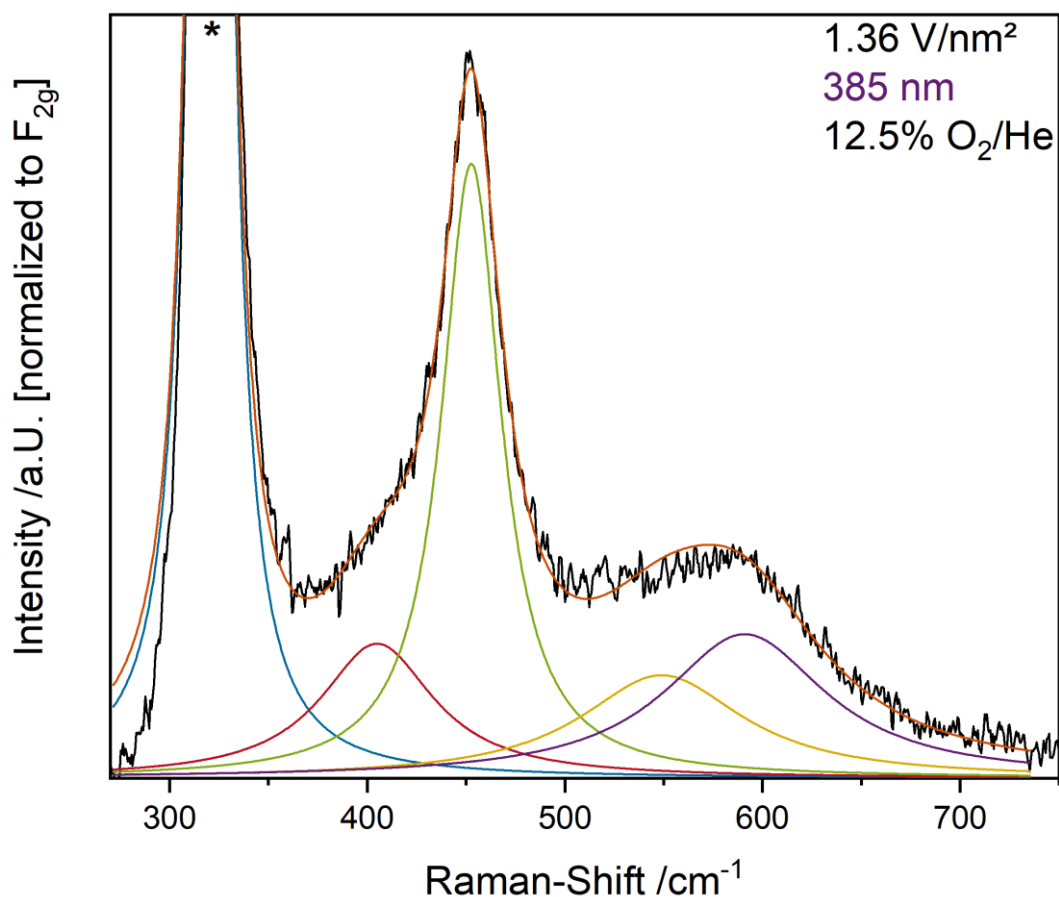


Figure S6: Exemplary fit of the 1.36 V/nm² sample under 12.5% O₂/He at 550 °C. The spectrum was normalized to the F_{2g} peak and the peak caused by the CaF₂ peak is marked with an asterisk. Two components were used to fit the defect region in agreement with previous literature. The CaF₂ peak was also fitted as it overlapped notably with the other signals.

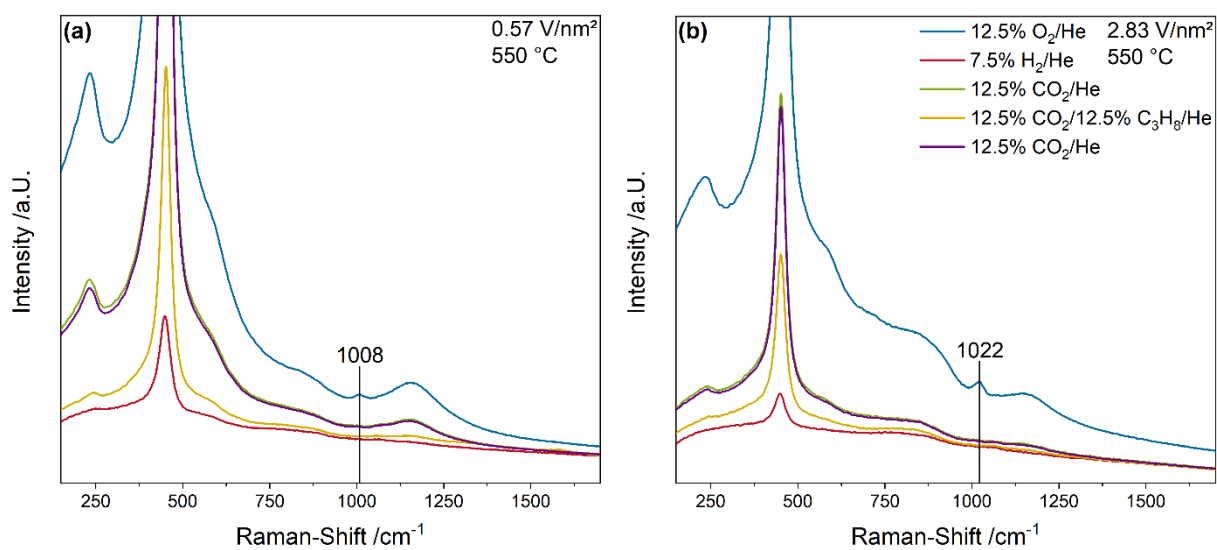


Figure S7: Operando Vis-Raman spectra (514 nm excitation) of (a) the 0.57 and (b) the 2.83 V/nm² samples under different gas feeds recorded at 550 °C. The vanadyl peak is highlighted.

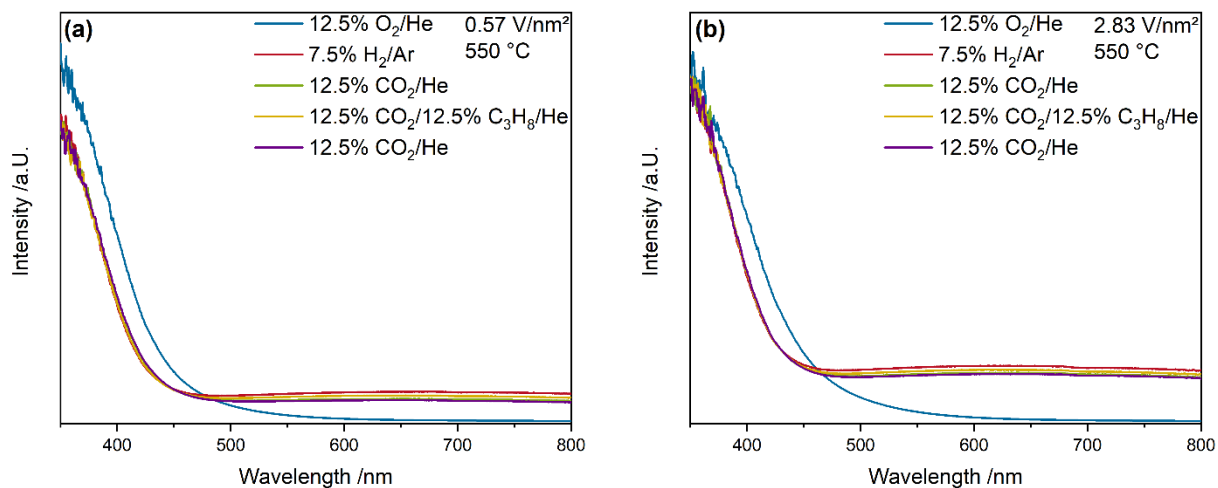


Figure S8: Operando UV-Vis spectra (385 nm excitation) of **(a)** the 0.57 and **(b)** the 2.83 V/nm² sample recorded under different gas feeds at 550 °C.

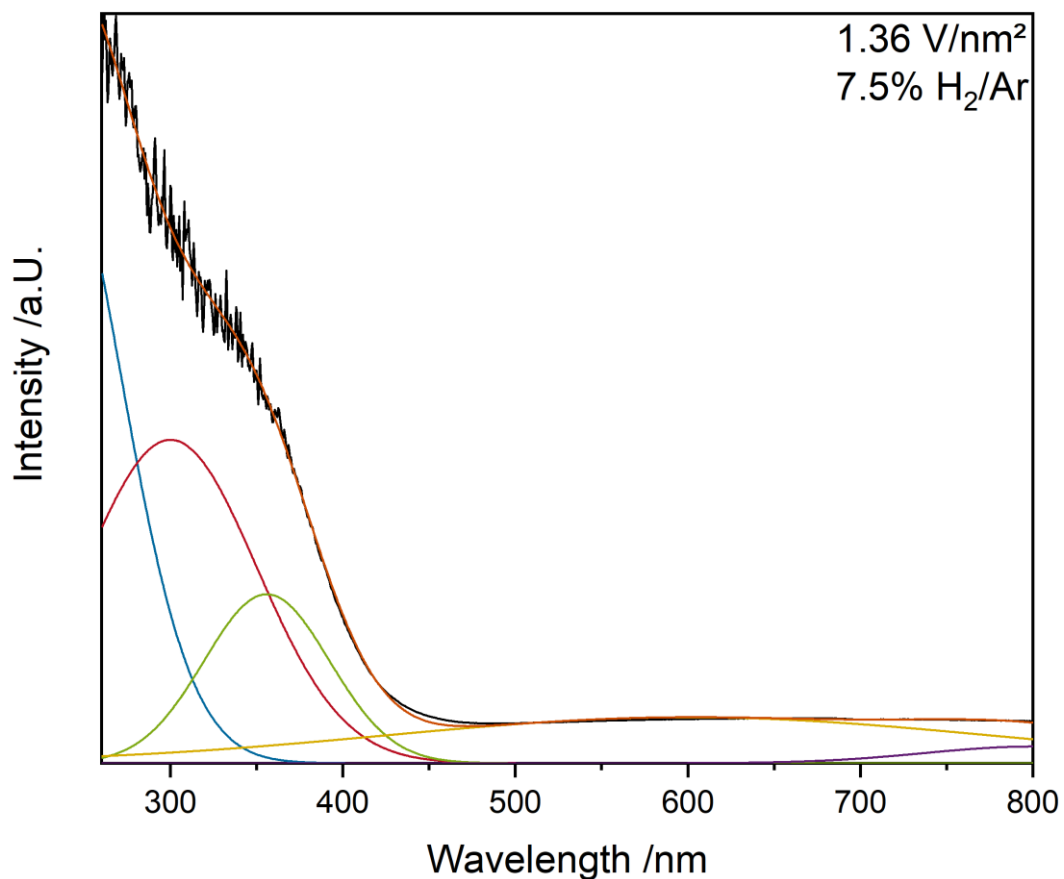


Figure S9: Exemplary fit of the UV-Vis spectrum of the 1.36 V/nm² sample under reductive conditions at 550 °C using five Gaussian-Lorentzian product functions (see experimental section).

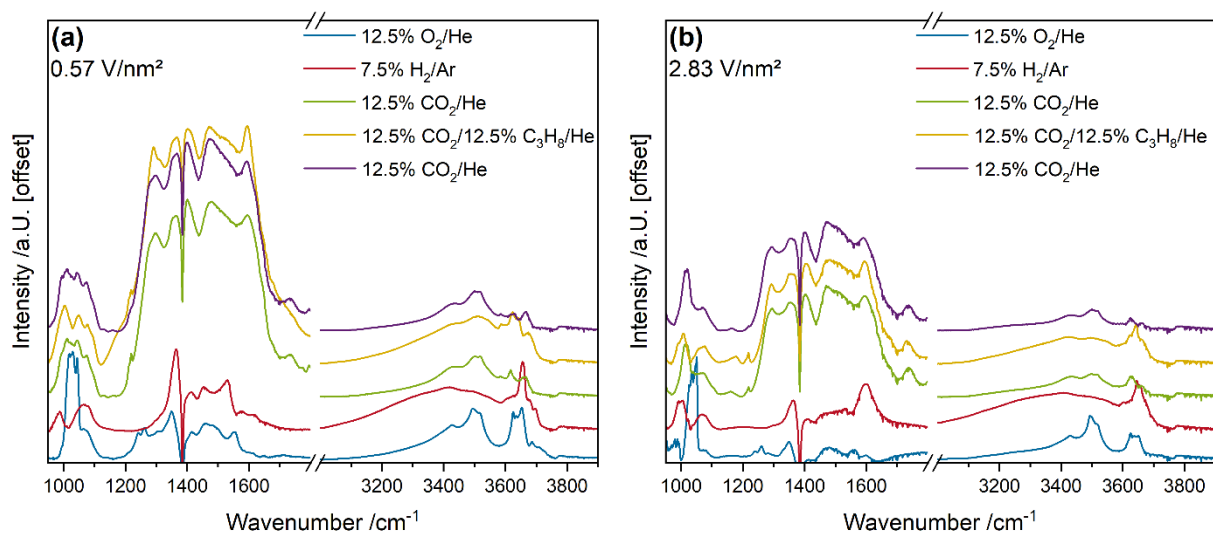


Figure S10: Quasi in situ DRIFT spectra of (a) the 0.57 and (b) the 2.83 V/nm² sample recorded after pre-treatment under the indicated gas feeds at 550 °C and subsequent rapid cooling (200 °C/min) to room temperature under helium.

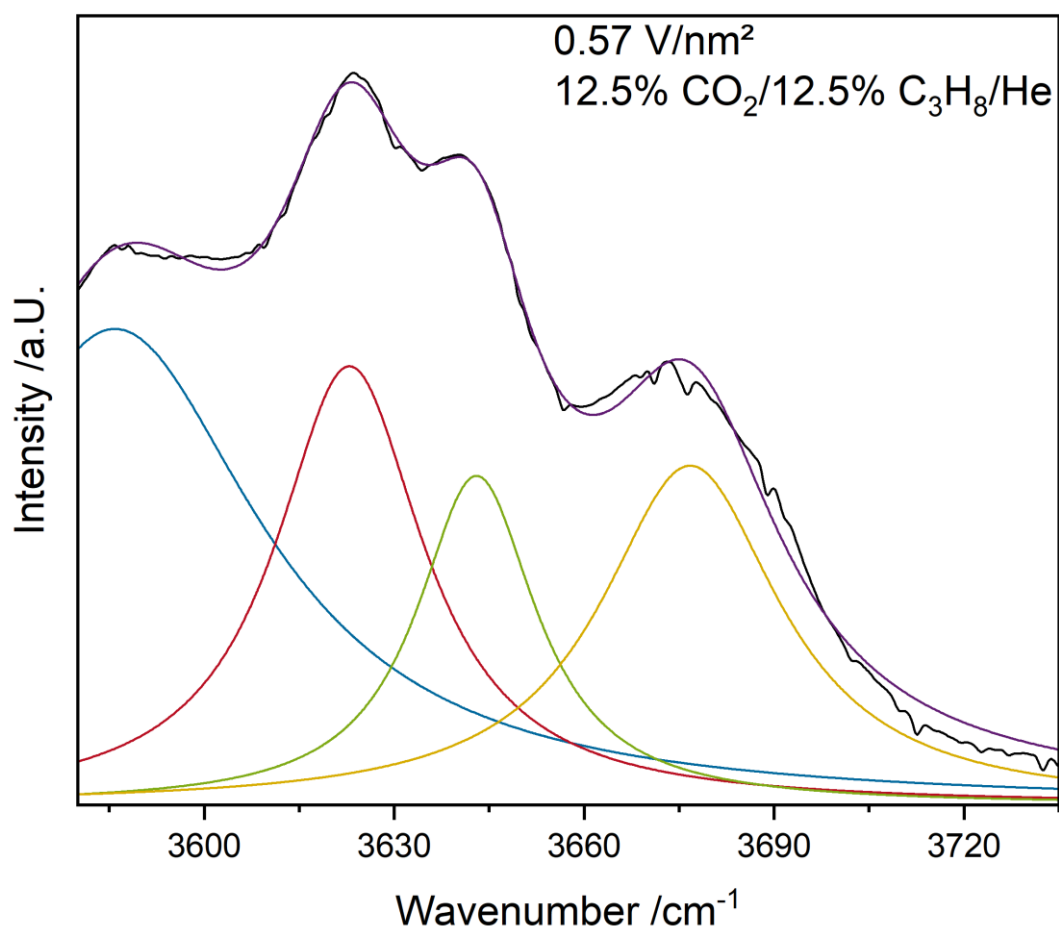


Figure S11: Exemplary fit of the Ce-OH region of the 0.57 V/nm² sample under ODH conditions using four Lorentzian functions.