

Supporting Information

Understanding the Reduction Behavior of VO_x/CeO₂ on a Molecular Level: Combining Temperature-Programmed Reduction with Multiple In Situ Spectroscopies and X-Ray Diffraction

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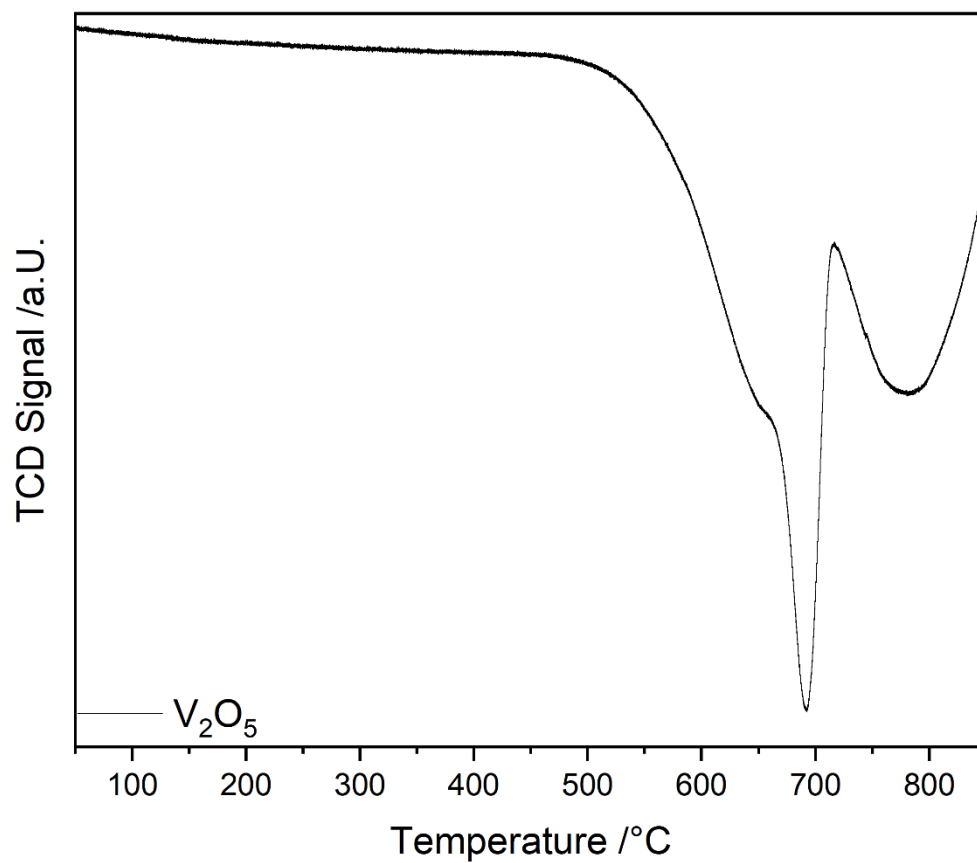


Figure S1: TPR of V_2O_5 used as the temperature calibration reference for the TPR setup. The temperature axis was shifted to the literature known value of the maximum at 690 °C for all other samples.

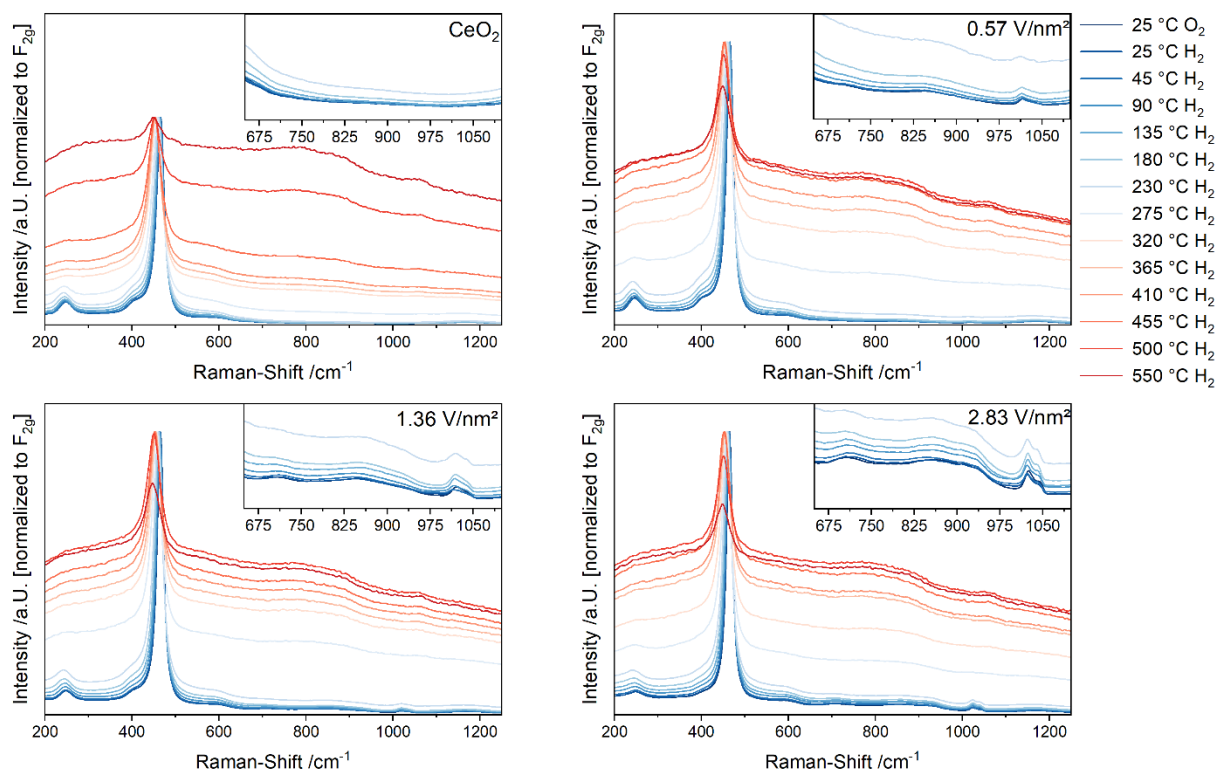


Figure S2: In situ Raman spectra for bare ceria and vanadia-loaded samples recorded at 514 nm excitation in 7.5% H_2/Ar flow between 25 °C and 550 °C. Spectra were normalized to the F_{2g} mode. The inset gives an enlarged view of the region of V-O-Ce/V-O-V and V=O vibrations.

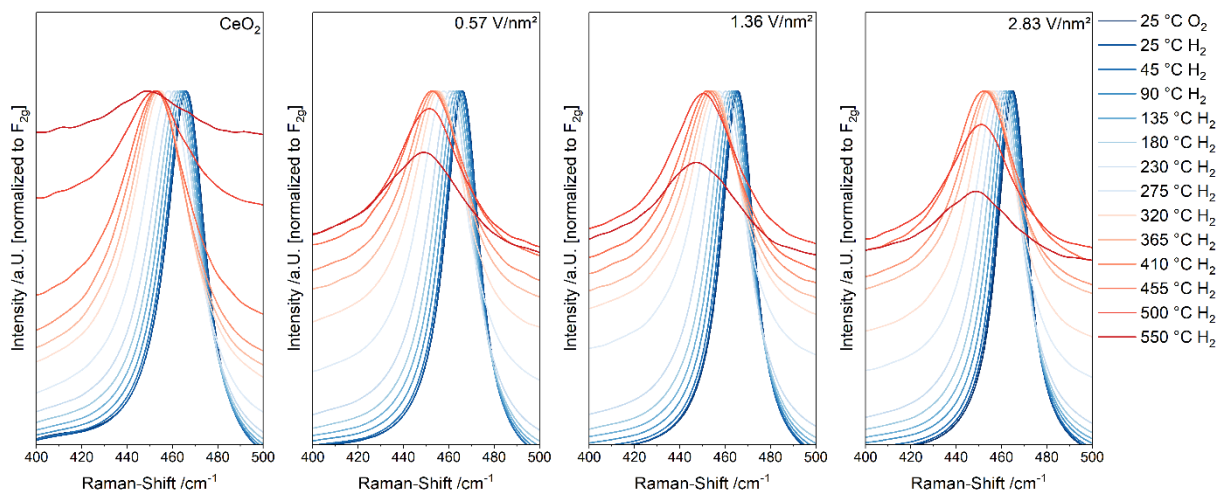


Figure S3: Evolution of the F_{2g} peak position and peak width of bare ceria and vanadia-loaded samples recorded at 514 nm excitation in 7.5% H₂/Ar between 25 °C and 550 °C. The spectra were normalized to the F_{2g} peak intensity. The initial spectrum was recorded at 25 °C in 12.5% O₂/He.

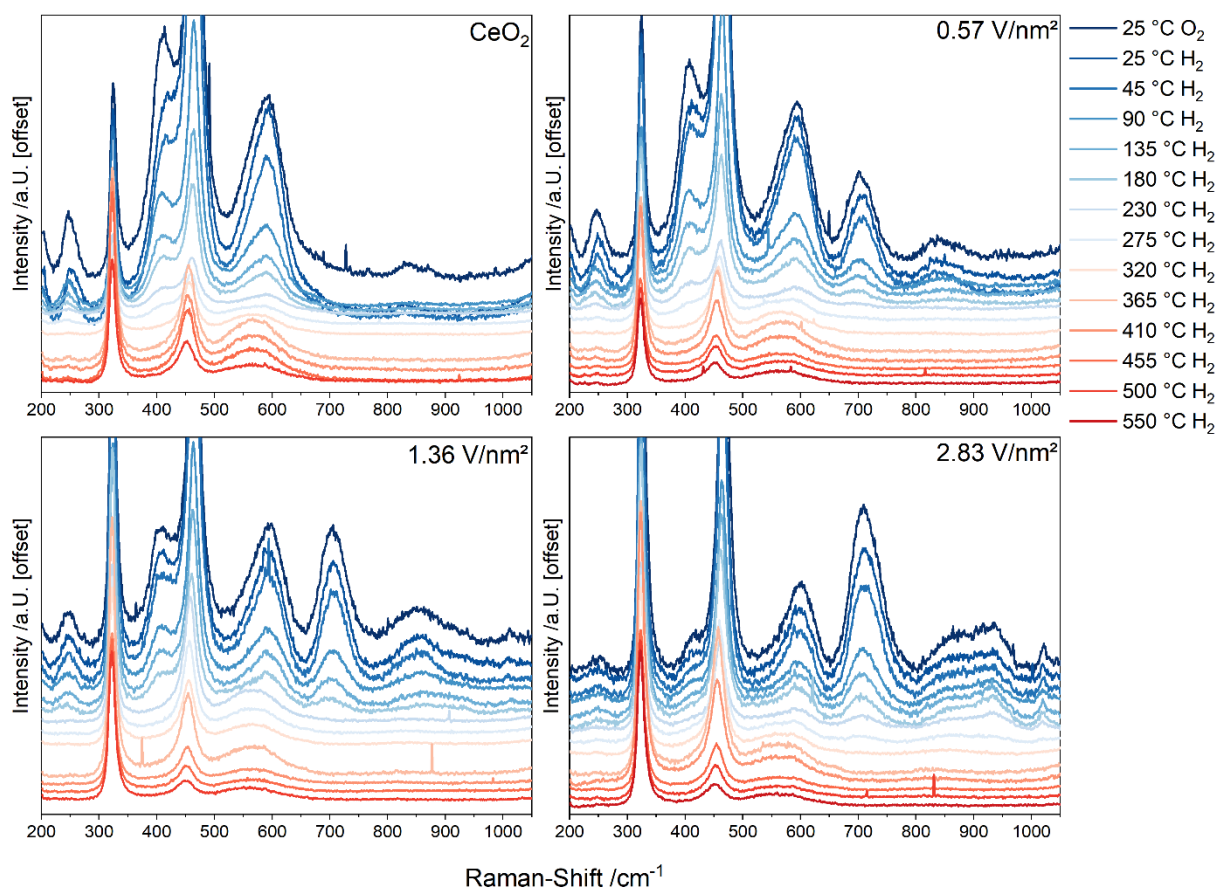


Figure S4: In situ Raman spectra for bare ceria and vanadia-loaded samples recorded at 385 nm Raman excitation in 7.5% H_2/Ar between 25°C and 550°C . Spectra are offset for clarity.

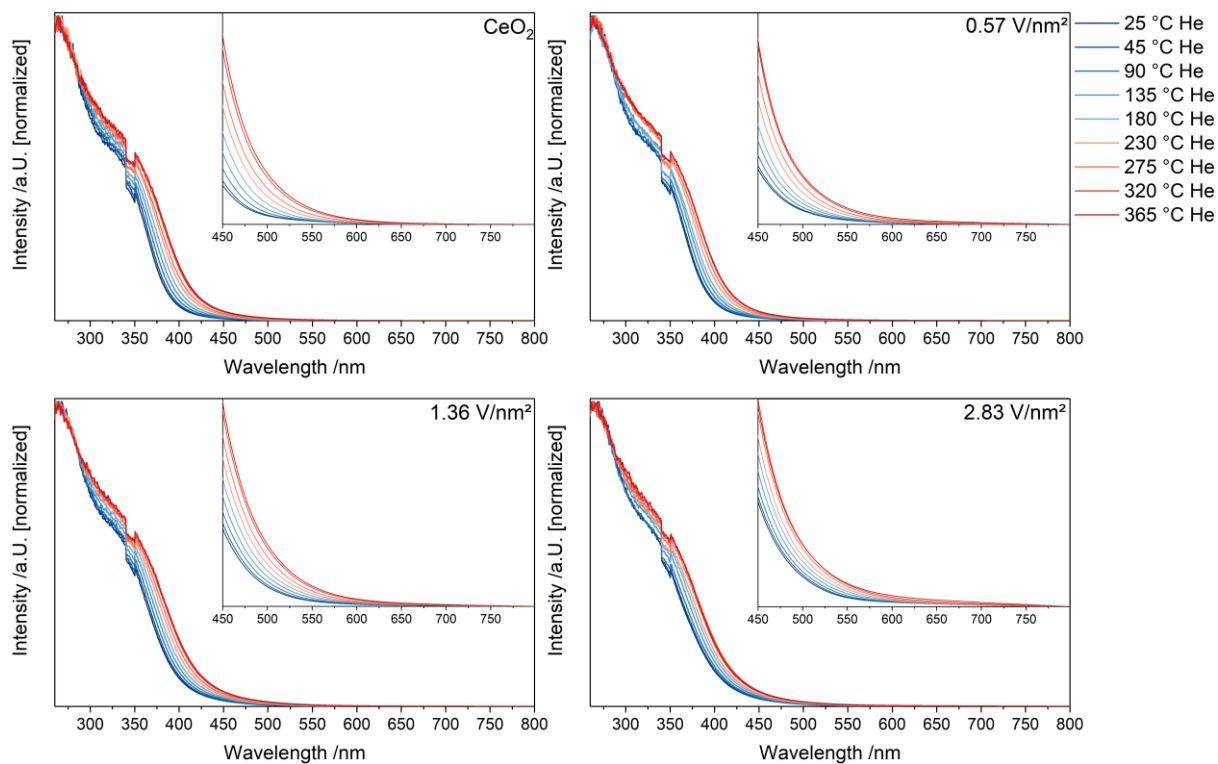


Figure S5: In situ UV-Vis spectra of bare ceria and vanadia-loaded samples recorded between 25 °C and 365 °C in the range between 260 and 800 nm in pure helium as a temperature background for band gap determination in comparison to UV-Vis spectra in 7.5 % H₂/Ar (see Figure S6). The insets highlight the absorption between 450 and 800 nm.

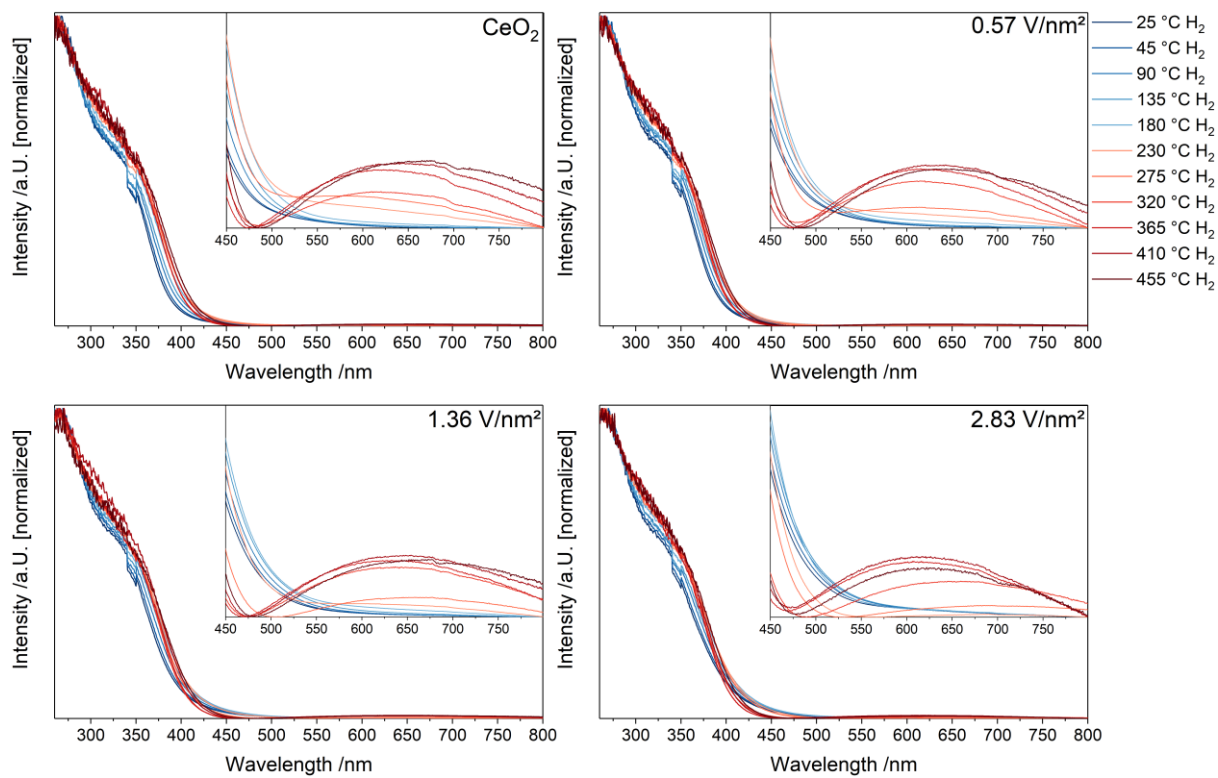


Figure S6: In situ UV-Vis spectra of ceria and vanadia-loaded samples recorded between 25 °C and 455 °C in the range between 260 and 800 nm in 7.5 % H_2/Ar . The insets highlight the absorption between 450 and 800 nm.

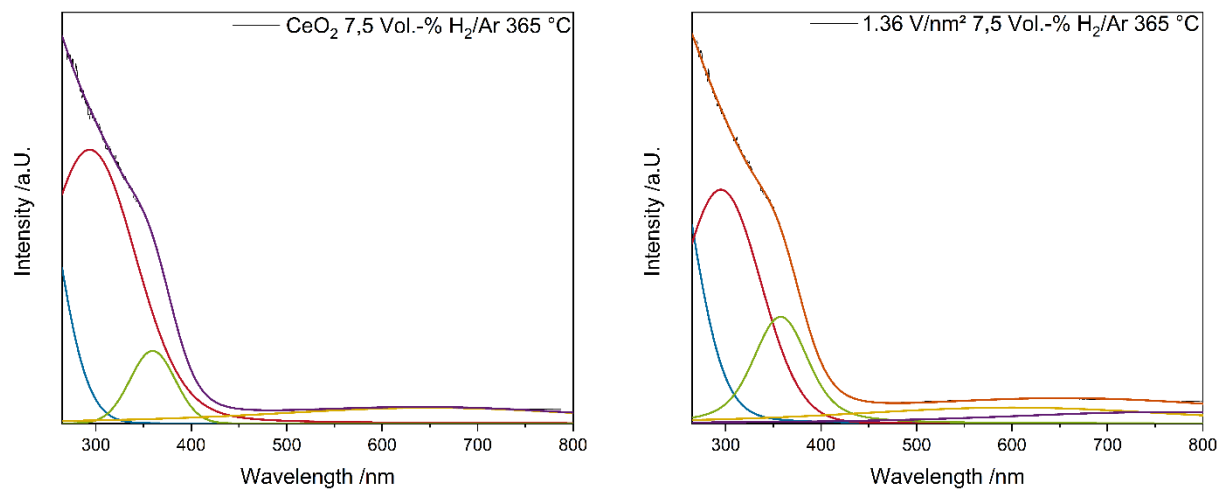


Figure S7: Exemplary fit analysis of UV-Vis spectra for bare ceria and the 1.36 V/nm² sample recorded in 7.5% H₂/Ar at 365 °C. The spectra were fitted using four and five Voigt functions, respectively. For details refer to the experimental section.

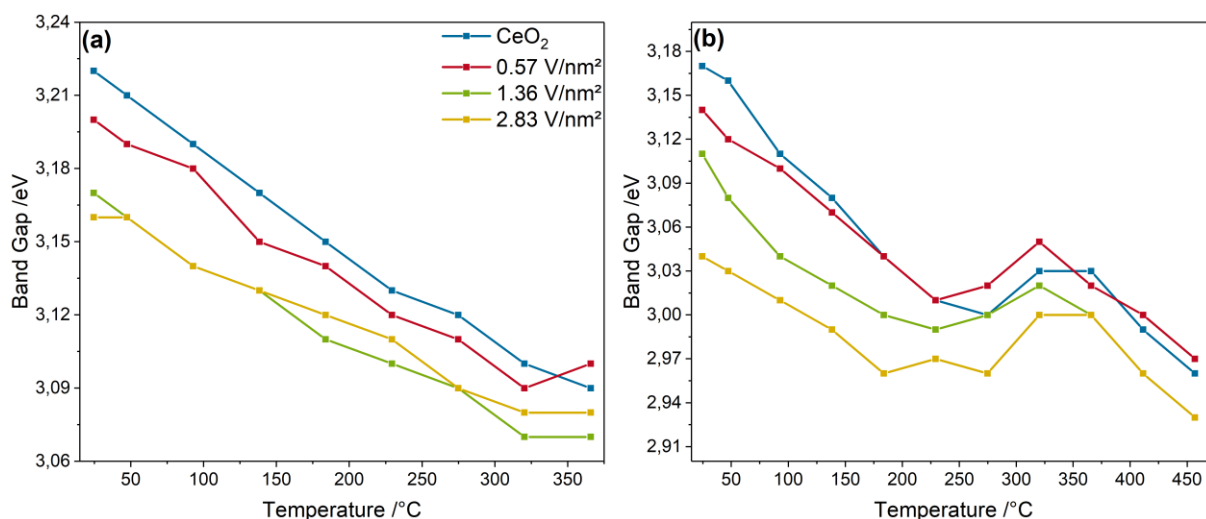


Figure S8: Band gap shifts determined in (a) helium and (b) 7.5% H₂/Ar for bare ceria and vanadia-loaded samples between 25 °C and 366 °C (a) and between 25 °C and 457 °C (b). For the corresponding UV-Vis spectra refer to Figures S5 and S6.

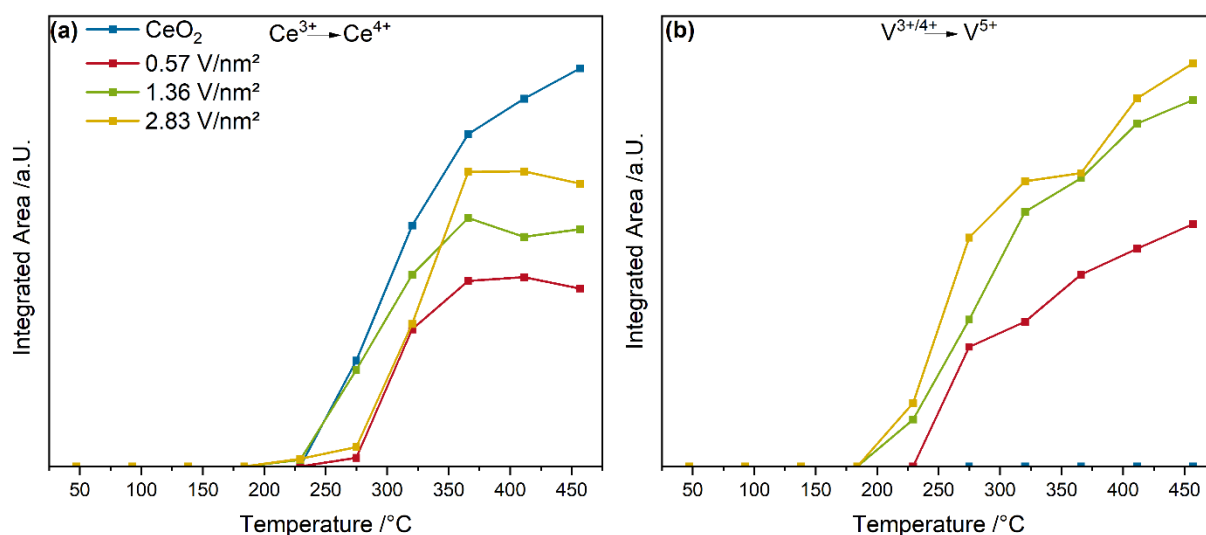


Figure S9: Integrated areas for (a) Ce³⁺ → Ce⁴⁺ transitions at 633 nm and (b) V^{3+/4+} → V⁵⁺ d-d transitions at 775 nm determined by a peak fit analysis for UV-Vis spectra of bare ceria and vanadia-loaded samples. The samples were treated in 7.5 % H₂/Ar between 25 °C and 457 °C. For the UV-Vis spectra and details on the peak fit analysis refer to Figures S5, S6, and S7, as well as the experimental section.

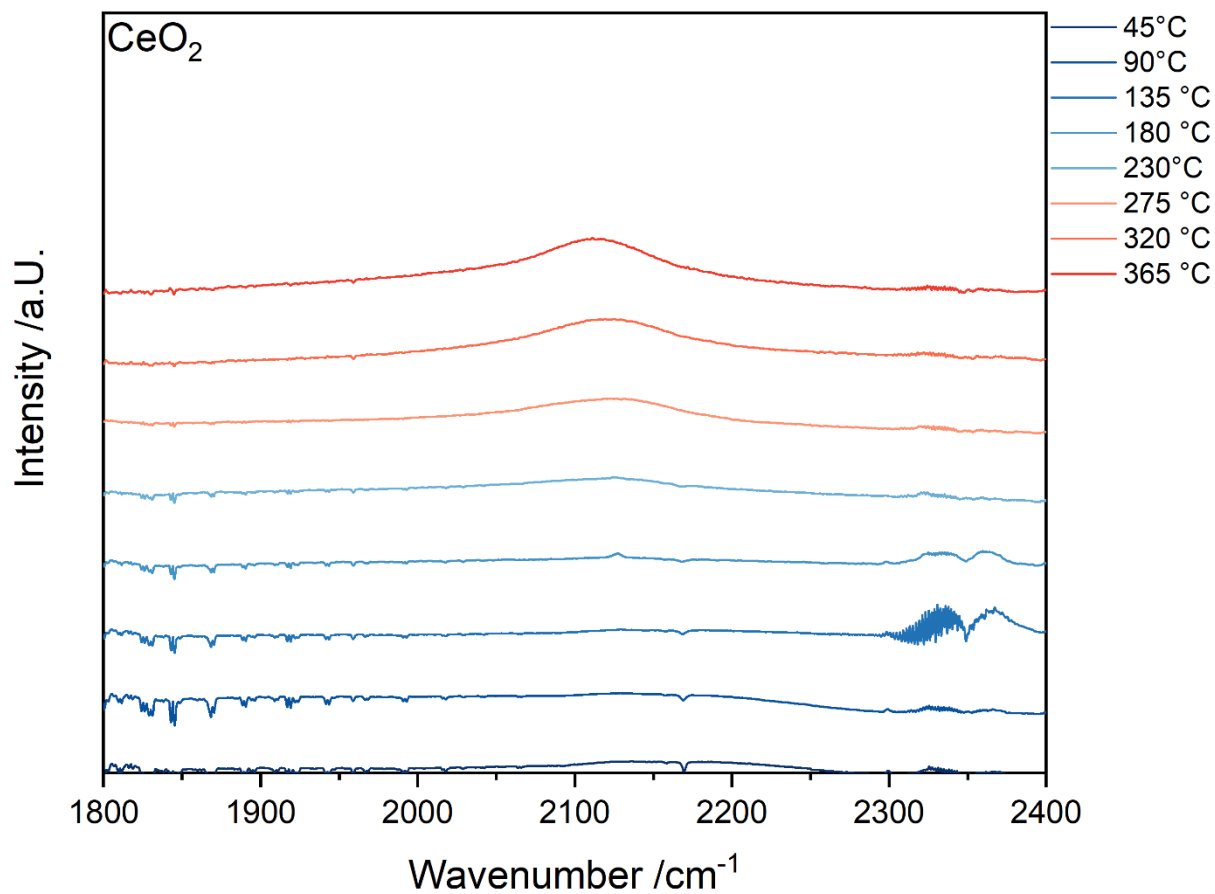


Figure S10: Temperature-dependent in-situ DRIFT spectra of ceria in 7.5% H_2/Ar recorded between 45 and 365 °C.