Supporting Information

Direct Evidence for Active Support Participation in Oxide Catalysis: Multiple *Operando* Spectroscopy of VO_x/Ceria

Patrick Ober†, Simone Rogg†, Christian Hess*

Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany

*Corresponding Author (E-mail: hess@pc.chemie.tu-darmstadt.de)

† Both authors contributed equally

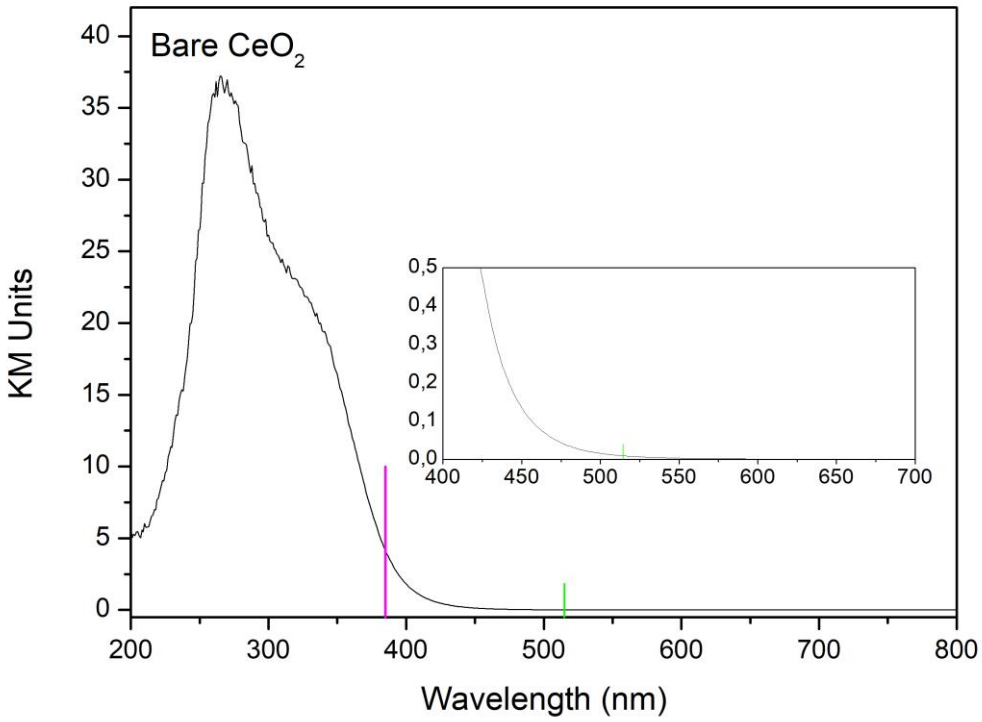

Figure S1. *In situ* DR UV-Vis spectrum of bare ceria catalyst recorded in 8% O_2 / 92% N_2 flow at 100 °C depicting the high self-absorption of ceria below 400 nm. Excitation wavelengths (385 nm, 515 nm) used for the Raman experiments are marked.

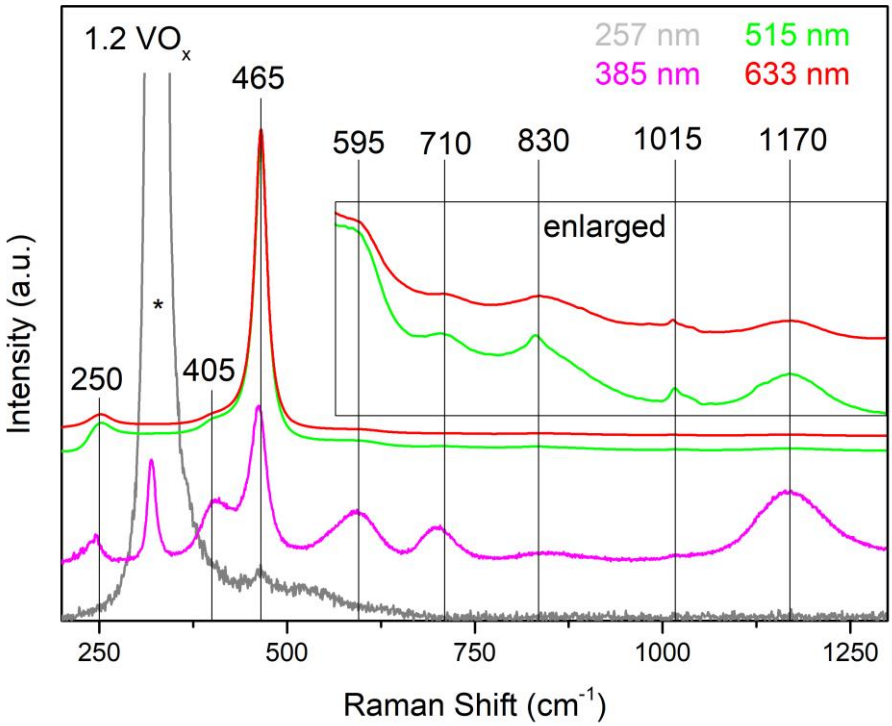

Figure S2. Wavelength-dependent Raman spectra of dehydrated 1.2 VO_x/CeO_2 using 257 nm (grey), 385 nm (magenta), 515 nm (green), and 633 nm (red) excitation. The 257 nm spectra were obtained with the same setup as for 385 nm wavelength excitation by applying 5 mW.[1] The 633 nm spectra were measured using a He-Ne laser for excitation.[2] For 515 and 633 nm excitation, the inset shows an enlarged view of the spectral region between 525 and 1300 cm^{-1}. Spectra are offset for clarity and scaled to allow for the 465 cm^{-1} F_{2g} band to be seen. An artifact due to the cell window is marked (*).

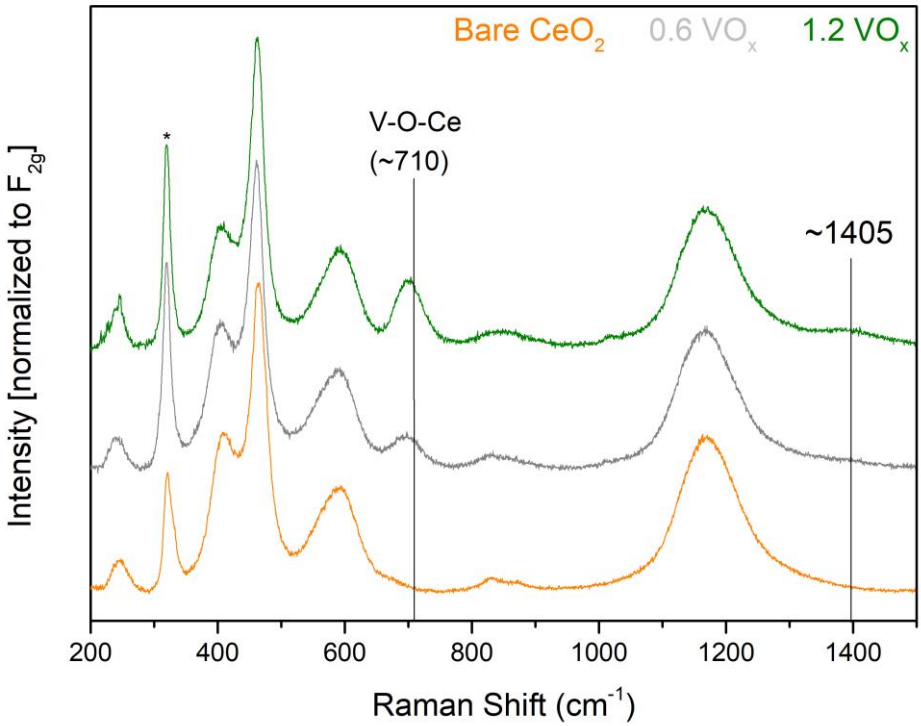

Figure S3. *In situ* UV Raman spectra (385 nm excitation) of bare ceria, 0.6 VO_x/CeO_2, 1.2 VO_x/CeO_2, recorded in 8% O_2 / 92% N_2 flow at 100 °C. Note that the Raman features at around 710 cm^{-1} and 1405 cm^{-1} are only present for the loaded samples and that both increase with vanadia density; hence, they are attributed to the fundamental and overtone of V-O-Ce vibrations.

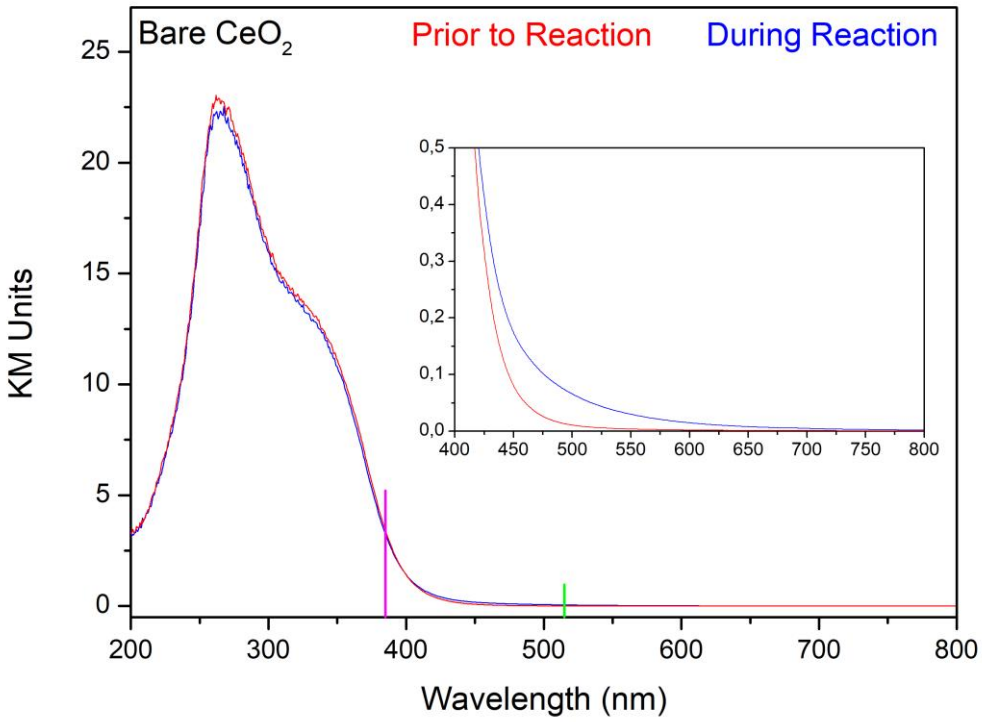

Figure S4. DR UV-Vis spectra of bare ceria prior to (red) and during (blue) ethanol ODH recorded at 100 °C at a total flow rate of 50 mL_n/min. The feed during *in situ* and *operando* conditions consisted of 8% O_2 / 92% N_2 and 1% EtOH / 8% O_2 / 91% N_2, respectively. The excitation wavelengths (385 nm, 515 nm) used for the Raman experiments are marked. The inset gives an enlarged view of the spectra at longer wavelengths

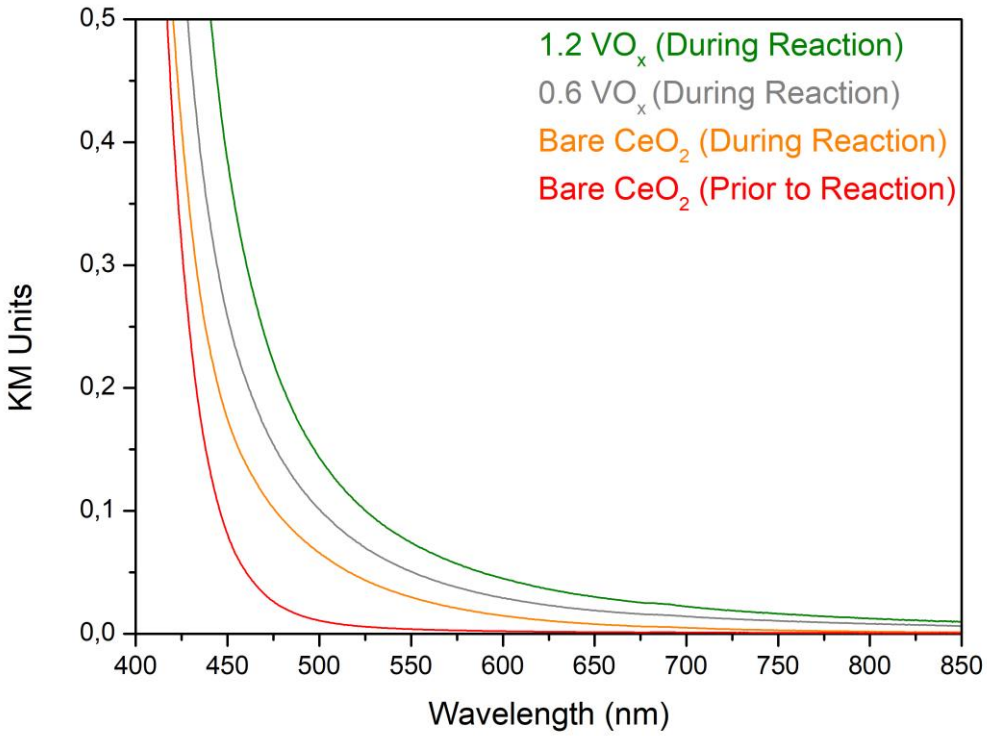

Figure S5. Enlarged DR UV-Vis spectra of pure ceria, 0.6 VO_x/CeO_2, and 1.2 VO_x/CeO_2 under reaction conditions (1% EtOH / 8% O_2 / 91% N_2), in comparison to the spectrum of bare ceria prior to reaction after initial dehydration. The broad band extending over the shown region increases with vanadium loading.

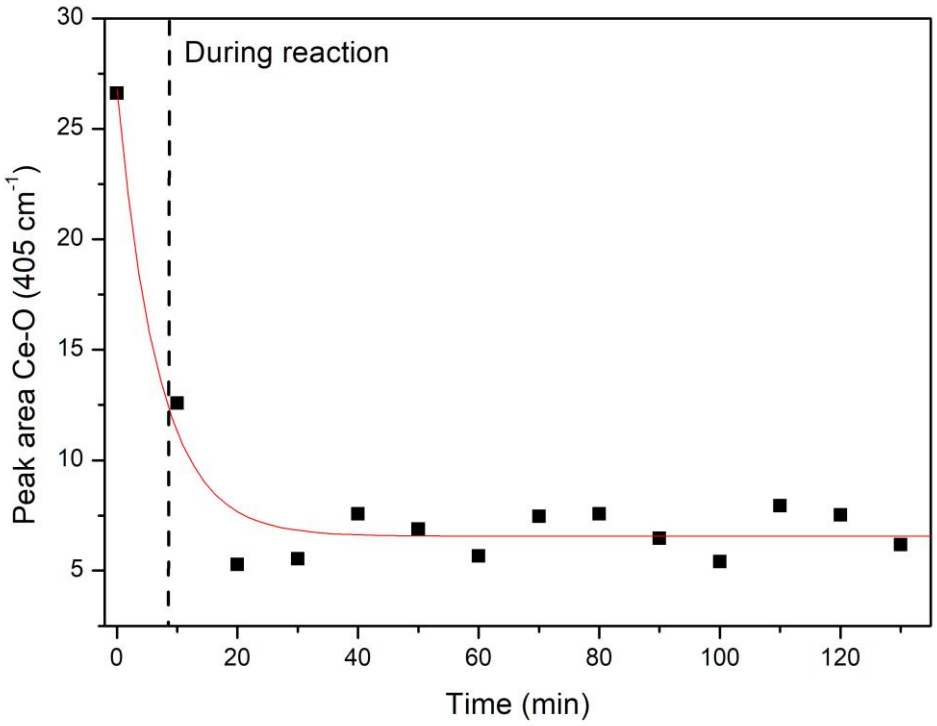

Figure S6. Temporal evolution of the Raman signal at 405 cm^{-1} of 0.6 VO_x/CeO_2 upon switching from oxidative to reactive conditions at 100 °C at a total flow rate of 50 mL_n /min. The feed consisted initially of 8% O_2 / 92% N_2, and then of 1% EtOH / 8% O_2 / 91% N_2. The Raman spectra were recorded at 385 nm excitation. The red line is a guide to the eye.

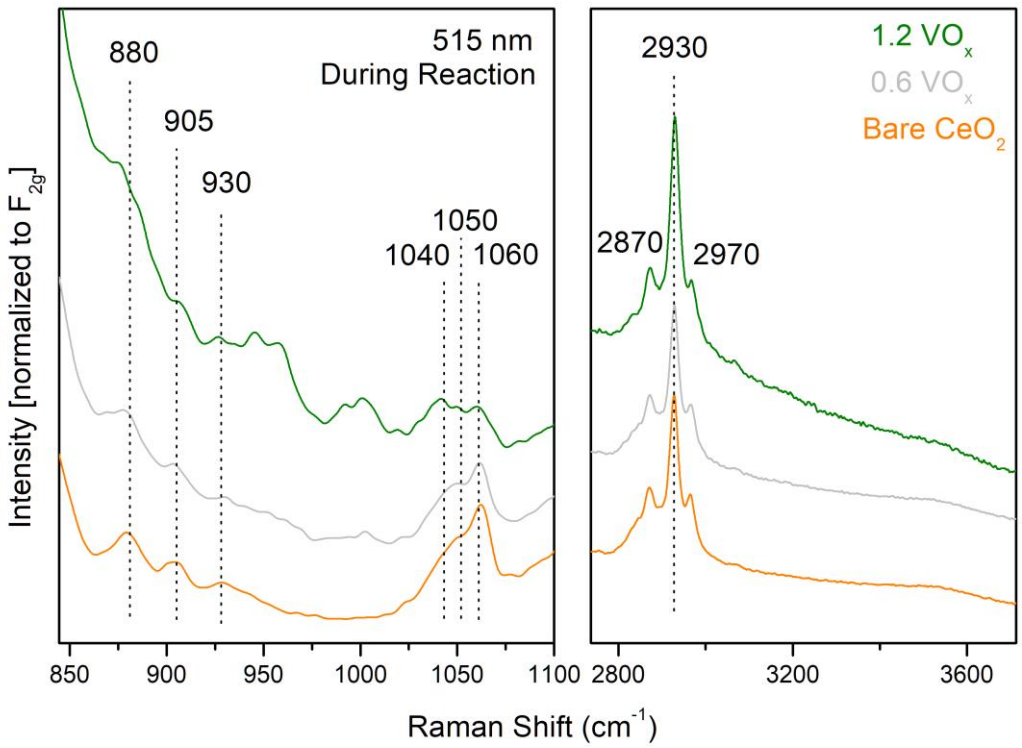

Figure S7. *Operando* Raman spectra (515 nm excitation) of bare ceria, 0.6 VO_x/CeO_2, 1.2 VO_x/CeO_2 recorded at 100 °C at a total flow rate of 50 mL_n /min. The feed during *operando* conditions consisted of 1% EtOH / 8% O_2 / 91% N_2. Spectra were normalized to the F_{2g} band and offset for clarity. Note that the ethoxy-related Raman features at around 880, 905, 930 cm^{-1} (C-C vibrations) and 1040, 1050, 1060 cm^{-1} (C-O vibrations) decrease with vanadia density; hence, they are attributed to different ethoxy species at the ceria surface.

Table S1. F_{2g} band position (515 nm excitation) of bare ceria, 0.6 VO_x/CeO_2, and 1.2 VO_x/CeO_2 recorded at 100 °C at a total flow rate of 50 mL_n /min, when switching between oxidative and reactive conditions.

Gas phase	CeO_2	1.2 VO_x/CeO_2	0.6 VO_x/CeO_2
8% O_2 / 92% N_2	464.0	464.1	464.1
1% EtOH / 8% O_2 / 91% N_2	463.0	462.8	462.8
8% O_2 / 92% N_2	463.6	463.3	463.6
8% O_2 / 92% N_2 (400°C, 1 h)	464.0	464.0	464.0

References

(1) Waleska, P.; Rupp, S.; Hess, C. Operando Multiwavelength and Time-Resolved Raman Spectroscopy. *J. Phys. Chem. C* **2018**, *122*, 3386–3400.

(2) Hess, C. Direct Correlation of the Dispersion and Structure in Vanadium Oxide Supported on Silica SBA-15. *J. Catal.* **2007**, *248*, 120–123.