

Elucidating the Reaction Mechanism and Deactivation of CO₂-Assisted Propane ODH over VO_x/TiO₂ Catalysts: A Multiple Operando Spectroscopic Study

Leon Schumacher, Kathrin Hofmann, 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)

Abstract

The CO₂-assisted oxidative dehydrogenation (ODH) of propane is of great technical importance and enables the use of CO₂ as a green-house gas in a value adding process. Supported vanadium oxide (VO_x) catalysts are a promising alternative to more active but toxic chromium oxide catalysts. Despite its common use, TiO₂, has not been investigated as support material for VO_x in the CO₂-ODH of propane. In this study, we elucidate the interaction between titania (P25) and vanadia in the reaction mechanism by analyzing the reaction network and investigating the ODH reaction using XRD, multi-wavelength Raman, UV-Vis and DRIFT spectroscopy. Besides direct and indirect ODH reaction pathways, propane dry-reforming (PDR) is identified as a side reaction, which is more prominent on bare titania. The presence of VO_x enhances the stability and selectivity by participating in the redox cycle, activating CO₂ and leading to a higher rate of regeneration. Additionally, VO_x catalyzes the conversion of anatase to rutile, which facilitates CO₂ activation, thereby leading to an incapsulation of vanadium. At higher loadings, reducible VO_x oligomers are present on the surface, facilitating some, but less than on bare P25, PDR. As main deactivation mechanisms of the catalyst system we propose the reduction of the titania lattice and the consumption of vanadium, while carbon formation appears to be less relevant. Our results highlight the importance of analyzing the CO₂-ODH reaction network and applying a multi-spectroscopic approach to obtain a detailed mechanistic understanding of CO₂-assisted propane ODH over supported VO_x catalysts.

1. Introduction

The oxidative dehydrogenation (ODH) of propane is a promising additional process towards propylene production to meet the ever growing demand for this base chemical.^{1,2} This demand cannot be satisfied by traditional production methods like steam cracking or fluid catalytic cracking, resulting in the 'propylene gap'.^{3,4} The ODH of propane adds oxygen to the gas-feed, resulting in several advantages like lower reaction temperatures and therefore energy consumption and less catalyst leaching. However, it is still a challenge to control the oxidation process towards the selective oxidation product and significant amounts of CO_x are formed as a side product.^{1,2,5} To avoid the over-oxidation of propane, CO₂ can be used as a soft-oxidant to increase the selectivity towards propylene. In addition, the heat capacity of CO₂ leads to a more homogenous temperature distribution throughout the reactor and a lower risk of flammability compared to O₂, facilitating a scale-up of the process.^{6,7} From the environmental perspective, the use of the greenhouse gas CO₂ as a soft-oxidant in technical applications would directly assist in the efforts to mitigate the climate change, while creating value-added products in the form of propylene and CO.⁸⁻¹⁰ However, due to the high temperature required for CO₂ activation,^{11,12} a suitable catalyst needs to be employed to obtain sufficient conversions at moderate temperatures without catalyst deactivation (e.g. coking)¹³.

A promising class of catalysts for the CO₂-assisted ODH of propane are supported transition metal oxide catalysts.¹⁴⁻¹⁷ In the past, a research focus was put on chromium oxide (CrO_x) due to its high activity.^{7,18-21} In this context, Mychoreczyk et al.²⁰ described the oxidation state of chromium, as measured via operando UV-Vis spectroscopy, to be of great importance to differentiate between the oxidative and non-oxidative reaction paths, where Cr⁶⁺ species are reduced rapidly to Cr^{2+/3+} species under reaction conditions, which participate in the non-oxidative pathway. However, as chromium oxides are toxic and harmful to the environment, other materials have attracted renewed interest.²² Vanadium oxide (VO_x) is a promising catalyst for CO₂-assisted ODH reactions,²³⁻²⁷ since it is commonly used for oxidation reactions in industrial applications and shows high activity for the ODH of propane using O₂.^{5,28} Besides VO_x, molybdenum oxide (MoO_x) was recently used as the active phase.^{29,30} For the vanadia-based catalysts, a variety of supports such as SiO₂,^{23,27} Al₂O₃,²⁴ and In₂O₃^{25,26} were already studied theoretically and experimentally in the literature. However, the use of CeO₂- and TiO₂-supported vanadia catalysts, which are the most

active support materials in propane ODH using O_2 ,^{31,32} has not been reported in the context of CO_2 -assisted ODH reactions.

An important aspect towards mechanistic understanding is the characterization of the reaction network using CO_2 -assisted propane ODH, as multiple side reactions, like propane dry reforming (PDR),²⁵ carbon formation, cracking, and coke gasing may occur simultaneously.¹³ Furthermore, based on experimental and theoretical work on a WO_x - VO_x / SiO_2 catalyst, Ascoop et al.²³ proposed the occurrence of two pathways for propylene formation, that is a direct pathway via the ODH reaction and an indirect two-step pathway, including direct propane dehydrogenation, resulting in propylene and hydrogen, followed by a reaction of H_2 with CO_2 to CO and water via the reverse water-gas shift (RWGS) reaction. The presence of two simultaneous reaction pathways towards propylene was confirmed experimentally by Rogg et al.²⁷ for VO_x / SiO_2 catalysts, using operando spectroscopy, highlighting the importance of the pre-treatment conditions as partly reduced vanadia chains seem to limit the deep oxidation potential, increasing the propylene selectivity. Regarding the use of active support materials, Jiang et al.^{25,26} have recently described the potential of VO_x / In_2O_3 catalysts, where vanadia was identified to reduce dry-reforming and participate in the redox cycle, resulting in good ODH selectivities. Monomeric VO_x species were proposed as the most active site, due to their strong interaction with indium.²⁶ However, despite these studies, there is a number of open questions related to the mode of operation of VO_x catalysts in CO_2 -assisted propane ODH: What is the role of CO_2 within the reaction network? Is the support actively participating in the reaction? How can the selectivity behavior be explained and possibly controlled? How does the catalyst deactivate?

To answer these questions, we address the mode of operation of different VO_x / TiO_2 catalysts during CO_2 -assisted propane ODH, by combining multiple quasi-in-situ and operando methods in this study. These include multi-wavelength Raman, UV-Vis, and DRIFT spectroscopy, as well as XRD to elucidate the reaction mechanism and to identify the exact role of CO_2 and the support, besides clarifying the vanadia nuclearity-dependence of the observed reactivity behavior. The combination of these methods allows for a dedicated investigation of the active and support phases based on differing selective Raman intensity enhancements and a differentiation between surface, subsurface, and bulk processes due to the different information depth of the applied methods. Furthermore, we address the important aspect of catalyst

deactivation during CO₂-assisted propane ODH by identifying key catalyst deactivation mechanisms relevant to VO_x/TiO₂ catalysts. Our results demonstrate the great potential of combining multiple in situ/operando methods to provide a mechanistic understanding of catalytic reactions with potential industrial applicability. Our approach can readily be transferred to other catalyst materials based on ceria, molybdena or tungstia.

2. Experimental Section

2.1. Catalyst Preparation

Bulk titania and thin-film titania prepared by atomic layer deposition (ALD) was used as support material. Titania P25 (Aeroxide, Sigma-Aldrich, ≥99.5%), consisting of 77% anatase, 16% rutile, and 7% amorphous titania, was used as purchased.³³ The P25 samples were first characterized by nitrogen physisorption and subsequent analysis by the Brunauer-Emmet-Teller (BET) method, yielding a surface area of 73 m²/g and then loaded by wet-impregnation using an aqueous solution containing a 1:2 ratio of ammonium meta vanadate (AMV) and oxalic acid with four different concentrations (1.2, 0.59, 0.25, and 0.05 mol/l), resulting in vanadium surface densities of 2.5, 1.2, 0.5, and 0.1 V/nm², respectively. All samples were loaded below monolayer loading (as confirmed by Raman analysis), thus guaranteeing that only amorphous vanadia was present.³⁴ The loaded samples were dried at 120 °C for 12 h and then calcined at 480 °C for 4 h.

Mesoporous silica SBA-15 was synthesized as described previously,²⁷ and coated with titania using a custom-built ALD set-up, as described previously.²⁸ The theoretical thickness of the thin-film titania corresponds to 10 nm, as determined by ellipsometry for a silicon wafer.³⁵ The sample was calcined in air at 600 °C for 12 h to crystallize the titania. The specific surface area was determined to be 81 m²/g by nitrogen physisorption with subsequent BET analysis. The samples were also loaded by wet-impregnation, employing an aqueous solution with a 1:2 ratio of AMV and oxalic acid with a concentration of 0.67 mol/l, resulting in a vanadium surface density of 1.2 V/nm². The samples were dried and calcined as described above. All samples were prepared

in the same exact way as in our previous VO_x/TiO₂ study on propane ODH using O₂, to guarantee comparability.²⁸

2.2. Catalytic Testing

Catalytic testing was performed in a CCR 1000 reaction cell (Linkam Scientific) equipped with a membrane pump to allow for operation in a fluidized-bed mode, using 60 mg of catalyst for the P25 samples and, due to its much lower density, 25 mg of the ALD-synthesized samples. The samples were first dehydrated in 12.5% O₂/He for 1 h at 550 °C, subsequently cooled to 50 °C, exposed to 12.5% CO₂/12.5% C₃H₈/He with a total flow rate of 40 ml_n/min, and then heated in 45 °C steps up to 550 °C, staying at each temperature for 1 h. The gas-phase composition was analyzed continuously using a gas chromatograph (GC, Agilent Technologies 7890B) equipped with a PoraPlotQ and a Molsieve column as well as a thermal conductivity detector (TCD) and a flame ionization detector (FID) in series. The set-up is connected through a twelve-way valve. One chromatogram is measured every 29 min, resulting in two chromatograms for each temperature, which were averaged. The pressure before and after the GC was monitored to correct the detected areas for pressure fluctuations. The obtained conversions were normalized to the surface area of the catalyst, due to the significantly different sample masses used for P25 and ALD-synthesized catalysts. To analyze the reaction network, the temporal evolution of the reactivity behavior was analyzed at 550 °C. The samples were first dehydrated in 12.5% O₂/He for 1 h, then treated consecutively in 7.5% H₂/Ar, 12.5% CO₂/He, 12.5% CO₂/12.5% C₃H₈/He, and finally regenerated in 12.5% CO₂/He (for 2 h for each gas phase), respectively. The reaction products were analyzed and time-dependent ratios between different products were calculated to determine the relative contributions of the different reaction pathways to the overall product distribution.

2.3. UV-Raman Spectroscopy

UV-Raman spectroscopy was performed at an excitation wavelength of 385 nm generated by a laser system based on a Ti:Sa solid-state laser pumped by a frequency-doubled Nd:YAG laser (Coherent, Indigo). The fundamental wavelength is frequency doubled to 385 nm using a LiB₃O₅ crystal. The light is focused onto the sample, and the scattered light is collected by a confocal mirror setup and focused into a triple-stage

spectrometer (Princeton Instruments, TriVista 555).³⁶ Finally, the Raman contribution is detected by a charge-coupled device (CCD, 2048 × 512 pixels) cooled to −120 °C. The spectral resolution of the spectrometer is 1 cm^{−1}. For Raman experiments, 60 mg of catalyst was placed in a CCR 1000 reactor (Linkam Scientific Instruments) equipped with a CaF₂ window (Korth Kristalle GmbH). A fluidized-bed reactor was employed to avoid laser-induced damage, allowing the use of a laser power of 8 mW at the location of the sample. Data processing included cosmic ray removal and background subtraction. Operando spectra were measured after dehydration for 1 h in 12.5% O₂/He and further pre-treatment in 7.5% H₂/Ar and 12.5% CO₂/He at 550 °C to start from a partially oxidized state. Afterwards, the catalyst was exposed to reactive conditions (12.5% CO₂/12.5% C₃H₈/He) and regenerated under oxidizing conditions (12.5% CO₂/He) with a total flow rate of 40 mL/min for each gas phase. The spectra were further analyzed by a least-squares fitting analysis using Lorentzian functions after normalization to the anatase E_g peak at 630 cm^{−1}. The intensity of the carbon signal was determined by integration over all carbon peaks.

2.4. Vis-Raman Spectroscopy

Visible (Vis) Raman spectroscopy was performed at 514 nm excitation, emitted from an argon ion gas laser (Melles Griot). The light was focused onto the sample, gathered by an optical fiber, and dispersed by a transmission spectrometer (Kaiser Optical, HL5R). The dispersed Raman radiation was subsequently detected by an electronically cooled CCD detector (−40 °C, 1024 × 256 pixels). The spectral resolution was 5 cm^{−1} with a wavelength stability of better than 0.5 cm^{−1}. For Raman experiments, 60 mg of catalyst was filled into a CCR 1000 reactor (Linkam Scientific Instruments) equipped with a quartz window (Linkam Scientific Instruments). A fluidized-bed reactor was employed to avoid laser-induced damage, allowing the use of a laser power of 5 mW at the location of the sample. Data analysis of the Raman spectra included cosmic ray removal and an auto new dark correction. Operando spectra were measured after dehydration in 12.5% O₂/He and further pre-treatment in 7.5% H₂/Ar and 12.5% CO₂/He at 550 °C for 1 h, respectively, to start from a partially oxidized state. Afterwards, the catalyst was exposed to reactive conditions (12.5% CO₂/12.5% C₃H₈/He) for 2 h for time-dependent measurements and regenerated under oxidizing conditions (12.5% CO₂/He) for 1 h with a total flow rate of 40 mL/min for each gas

phase. The spectra were further analyzed by a least-squares fitting analysis using Lorentzian functions after normalization to the anatase E_g peak at 630 cm^{-1} .

2.5. X-Ray Diffraction

Powder X-ray diffraction (XRD) patterns were recorded on a Stadi-P (Stoe & Cie) diffractometer with a Ge(111)-monochromator, Cu $K\alpha_1$ radiation ($\lambda = 1.54060\text{ \AA}$), and a MYTHEN-1K (Dectris) detector, using a flat sample holder in transmission geometry. For quasi in-situ XRD measurements the samples were measured in pristine condition after dehydration in 12.5% O_2/He for 1 h at $550\text{ }^\circ\text{C}$, followed by rapid cooling to room temperature in pure helium in the Linkam reactor and an inert transfer to the diffractometer. For the second set of experiments, the samples were pre-treated consecutively in 12.5% O_2/He , 7.5% H_2/Ar , 12.5% CO_2/He , and 12.5% $CO_2/12.5\%$ C_3H_8/He for 1 h at $550\text{ }^\circ\text{C}$, respectively, followed by rapid cooling to room temperature ($200\text{ }^\circ\text{C/min}$) in pure helium in the Linkam reactor and an inert transfer to the diffractometer.

2.6. Diffuse Reflection UV-Vis Spectroscopy

Diffuse reflectance (DR) UV-Vis spectra were recorded on a Jasco V-770 UV-Vis spectrometer. Dehydrated $BaSO_4$ was used as the white standard and 75 mg of catalyst were placed in the commercially available reaction cell (Praying Mantis High Temperature Reaction Chamber, Harrick Scientific) equipped with transparent quartz glass windows for each experiment. Operando spectra were measured after dehydration in 12.5% O_2/He and further pre-treatment in 7.5% H_2/Ar and 12.5% CO_2/He at $550\text{ }^\circ\text{C}$ for 1 h, respectively, to start from a partially oxidized state. Afterwards, the catalyst was exposed to reactive conditions (12.5% $CO_2/12.5\%$ C_3H_8/He) for 1.5 h for time-dependent measurements and regenerated under oxidizing conditions (12.5% CO_2/He) at $550\text{ }^\circ\text{C}$ for 1 h with a total flow rate of 40 mL/min for each gas phase. The spectra were further analyzed by a least-squares fitting analysis using Gaussian-Lorentzian (70/30) product functions. Product functions were used to account for the large contribution of natural line broadening to the overall line-shape, caused by the short life-time of the electronically excited states (Lorentzian), while also

accounting for the generally better convergence of the fit (Gaussian).³⁷ The band gap energies were determined using Tauc plots.^{38,39}

2.7. Diffuse Reflection Infrared Fourier Transform Spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed using a Vertex 70 spectrometer (Bruker). A liquid nitrogen-cooled mercury cadmium telluride (MCT) detector was used, operating at a resolution of 1 cm⁻¹. Dehydrated potassium bromide was employed as an infrared transparent sample for the background spectrum. For each experiment, 75 mg of catalyst was placed in the commercially available reaction cell (Praying Mantis High Temperature Reaction Chamber, Harrick Scientific) equipped with transparent KBr windows.

For quasi in-situ measurements the samples were treated in 12.5% O₂/He, 7.5% H₂/Ar, 12.5% CO₂/He, 12.5% CO₂/12.5% C₃H₈/He, and finally regenerated in 12.5% CO₂/He for 1 h at 550 °C, respectively. For each gas phase the sample was cooled rapidly to room temperature (200 °C/min) in pure helium in the Linkam reactor for the measurement before heating it back to 550 °C for the next measurement.

Data processing consisted of background removal by subtracting a baseline formed by 12 anchor points and removal of the spectrum recorded in 12.5% O₂/He to subtract the contributions from the pristine catalyst, targeting the surface species formed by the additional gas treatments only. Finally, to quantify the adsorbate peaks in the vanadyl and Ti-OH regions, the spectra were fitted using Lorentzian functions employing the Levenberg-Marquardt algorithm implemented in OriginLab 2022b.

3. Results and Discussion

Reactivity Behavior and Analysis of the Reaction Network

To choose a temperature that is most ideal for the operando spectroscopic investigation of the CO₂-assisted ODH of propane over VO_x/TiO₂, a temperature-dependent analysis of the catalytic activity was performed. Figure 1 summarizes the catalytic performance between 45 and 550 °C, showing the propane conversions (left panel) and selectivities to propylene (right panel).

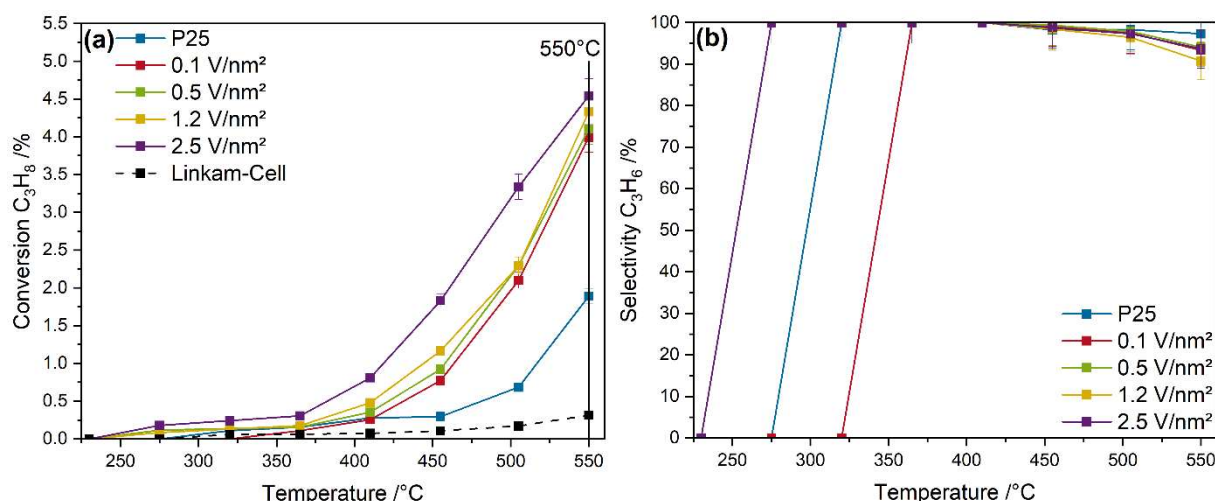


Figure 1: Reactivity behaviour of VO_x/TiO_2 catalysts in CO_2 -assisted propane ODH. Temperature-dependent (a) conversion of propane and (b) selectivity towards propylene of the bare TiO_2 P25 support, the vanadia-loaded samples, and the empty Linkam reactor recorded in a feed of 12.5% $\text{CO}_2/12.5\%$ $\text{C}_3\text{H}_8/\text{He}$ (total flow rate: 40 ml/min). The black line (left panel) highlights the temperature chosen for the mechanistic analysis.

Figure 1a depicts the temperature-dependent conversion of propane, starting at 275 $^\circ\text{C}$ for the three samples with the highest vanadium loading and at 320 $^\circ\text{C}$ for the P25 and P25+0.1 V/nm^2 samples. The conversion increases exponentially with increasing temperature up to 550 $^\circ\text{C}$, where the catalysts reach propane conversions between 2.35 % (bare P25) and 4.54 % (P25+2.5 V/nm^2), showing an increase with increasing vanadium loading. Importantly, the propane conversion strongly increases for the P25+0.1 V/nm^2 sample as compared to bare P25, indicating that the presence of even small amounts of vanadium enhances the catalytic activity. The propane conversion of the empty Linkam reactor (0.31 %) is small compared to that of the VO_x/TiO_2 catalysts. The homogeneous gas-phase reaction occurring in the reactor does not lead to the formation of propane, but rather C_2H_4 , CH_4 , and CO , indicative of mostly cracking or total oxidation reactions. Therefore, the ODH reaction is determined to be exclusively caused by the catalysts. In general, the P25+2.5 V/nm^2 sample is the most active, showing the earliest onset of the reaction, and a significantly higher propane conversion than the other samples, while the other three VO_x/TiO_2 samples, show a somewhat similar conversion behaviour. The conversions are in the same order of magnitude compared to those obtained under similar conditions (vanadia loading, catalyst mass, temperature) in a fixed bed reactor.²⁵ However, due to a lack of literature

data, a direct comparison to other titania catalysts is not possible. The selectivities remain at 100 % for temperatures up to 410 °C, while at higher temperatures, the selectivity drops to an absolute minimum of 91% for the P25+1.2 V/nm² sample at 550 °C, which compares very favourably with other vanadia-based catalysts.^{23–25,27} Therefore, a reaction temperature of 550 °C was chosen for the mechanistic analysis.

To analyse the reaction network in more detail, the catalytic activity of the samples was determined at 550 °C in 12.5% CO₂/12.5% C₃H₈/He, after dehydration at 550 °C in 12.5% O₂/He for 1 h and subsequent pre-treatment in 7.5% H₂/Ar and 12.5% CO₂/He, to establish a partially reduced initial state, that is more representative of the state at which the catalyst is operating during the reaction. Afterwards, the samples are regenerated in 12.5% CO₂/He. The molar product distributions for all gas phases of the P25-based samples are given in the SI (see Figure S1). Figure 2 summarizes the most important kinetic results used to differentiate the different reactions occurring on the catalyst.

Figure 2a depicts the loading-dependent initial conversions of C₃H₈ and CO₂, as well as the initial C₃H₆ selectivity for the bare P25 support and the VO_x/TiO₂ samples, obtained at 550 °C after pre-treatment in O₂, H₂, and CO₂ for 1 h each (see experimental section for details). Starting at 2.35% for P25, the C₃H₈ conversion shows an overall increase with vanadium loading up to 5.65% for P25+2.5 V/nm². In contrast, the CO₂ conversion starts at 2.88% for P25 and then increases to a maximum of 4.25% for P25+2.5 V/nm², staying slightly above the C₃H₈ conversions for low vanadium loadings, indicative of side reactions, such as PDR or cracking, as the dehydrogenation pathways would consume propane and CO₂ at the same rate. In comparison to the propane conversion, after a jump from P25 to P25+0.1 V/nm², the CO₂ conversion increases almost linear with the vanadium loading and exhibits no plateau between 0.1 and 0.5 V/nm². Similar to the conversions, the initial selectivities towards propylene jump from bare P25 to the P25+0.1 V/nm² sample increasing from 82.2% for P25 to 92.9%, and then decrease again to 90% for the P25+2.5 V/nm² sample. Overall, the initial values of propane and CO₂ conversions in combination with the propylene selectivities are at a higher level than those of other VO_x-based catalyst systems,^{23–25,27} and even reach those of some of the supported CrO_x systems.^{18,21,40}

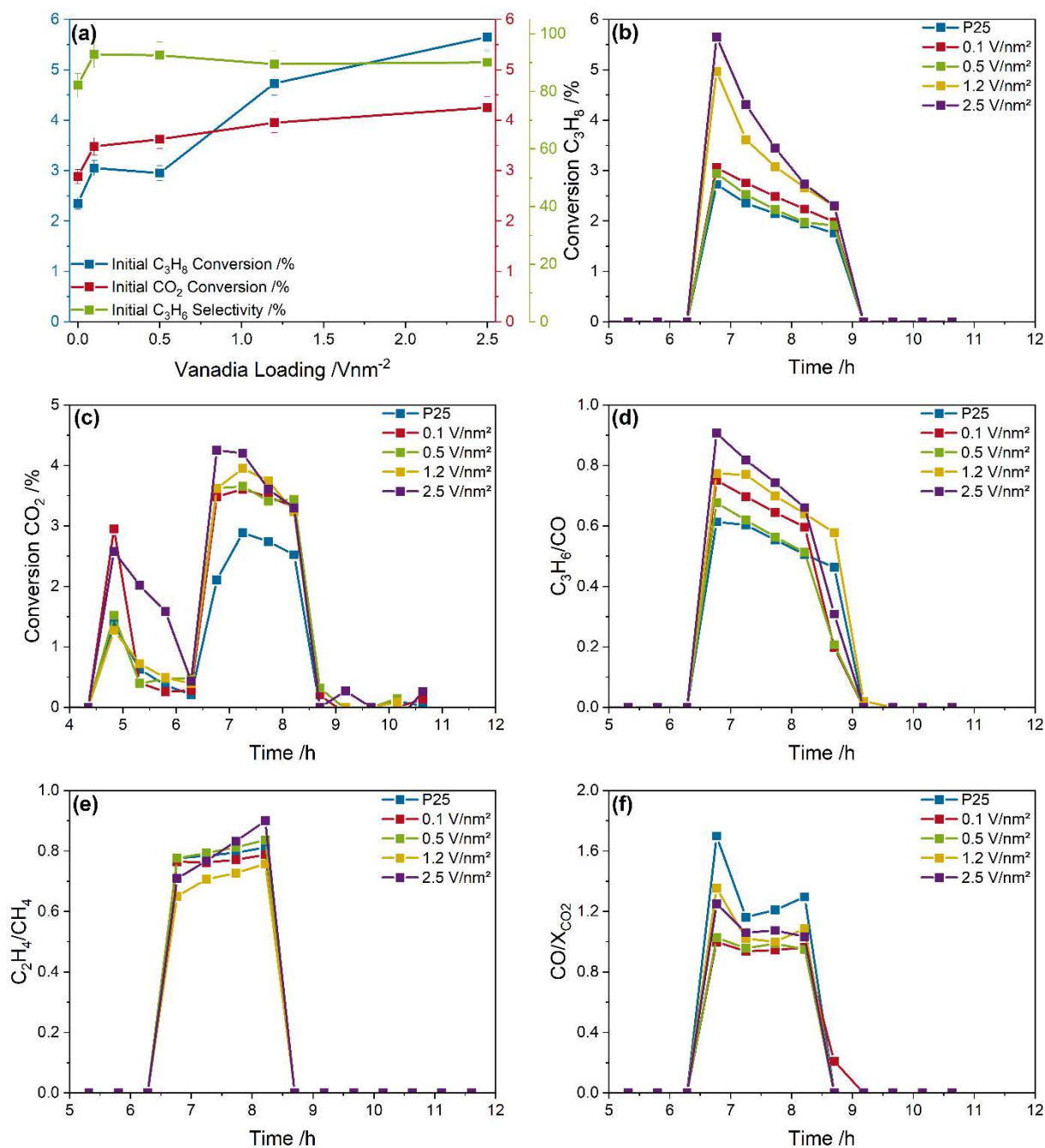


Figure 2: Analysis of the reaction network for bare P25 and vanadia-loaded samples during CO₂-assisted propane ODH: **(a)** Loading-dependent initial conversions of C₃H₈ and CO₂, and C₃H₆ selectivity, time-dependent conversions of **(b)** C₃H₈ and **(c)** CO₂, **(d)** time-dependent C₃H₆/CO ratio, **(e)** time-dependent C₂H₄/H₂ ratio, and **(f)** time-dependent CO/X_{CO2} ratio. Between 0 and 2 h 12.5% O₂/He, between 2 and 4 h 7.5% H₂/Ar, between 4 and 6 h 12.5% CO₂/He, between 6 and 9 h 12.5% CO₂/12.5% C₃H₈/He, and between 9 and 11 h 12.5% CO₂/He were used as gas feed.

Figures 2b and c depict the time-dependent conversions of C₃H₈ and CO₂ for the P25-based samples. As shown in Figure 2b, the propane conversion is significantly

higher at the beginning of the reaction, which is most pronounced for the samples loaded with 1.2 and 2.5 V/nm², and then decreases to a similar value of around 2% for all samples after ~3h (P25: 1.75%, P25+2.5 V/nm²: 2.4%). Thus, the decrease in propane conversion is most significant for the samples with the highest loadings. In comparison, the CO₂ conversion stays more constant during the reaction, except for the P25+2.5 V/nm² sample. After the initial 30 minutes, the CO₂ conversion is similar to that of propane for all samples, except for bare P25, indicating the occurrence of more side reactions on the bare support. However, since the propane conversion gradually decreases further and the CO₂ conversion stays more constant, the CO₂ conversion is, at the end of the reaction phase, higher than that of propane. This indicates a deactivation of the catalyst in the course of the ODH reaction, with reoxidation by CO₂ being the rate-limiting step.

For further analysis of the reaction network, the relative amount of different reactions occurring on the catalyst and the importance of the ODH route was studied. To this end, Figures 2d-f show the C₃H₆/CO ratio, as an indicator for the extent of dehydrogenation, the C₂H₄/CH₄ ratio, as an indicator for the amount of cracking, and the CO/X_{CO2} ratio, as an indicator for PDR, respectively. The time-dependent molar product distributions are given in Figure S1. Starting with the C₃H₆/CO ratio, the values decrease over time due to the decreasing propane conversion. The initial values are lowest for bare P25 (0.61) and highest for P25+2.5 V/nm² (0.91), following an increase with increasing vanadium loading. At the end of the reaction phase, values drop to 0.46 for P25 and 0.66 for P25+2.5 V/nm². Generally, more CO than propylene is produced. Since the C₃H₆ to CO ratio should be 1 for the direct (ODH) and indirect (DDH+RWGS) reaction routes, additional reactions are expected to occur. This is supported by the observed CO₂ conversions, which are consistently higher than those of propane. However, the initial ratio is, especially for the P25+2.5 V/nm² sample, close to a value of one, indicating a full dehydrogenation route over the catalyst, in good agreement with other actively supported VO_x systems,^{24–26} which show side reactions in a similar range, but the TiO₂ system seems to be slightly more selective towards propylene.

To gain insight into the side reactions, Figure 2e depicts the C₂H₄ to CH₄ ratio, which is indicative of propane cracking, leading to ethylene and methane. The ratio is close to one with slightly more methane being produced, which is in agreement with the expected product distribution of thermal propane cracking at this temperature.⁴¹ It is important to note that the overall amount of ethylene and methane is comparably

small, especially when considering the fact that one methane and one ethylene molecule are produced from one propane molecule. In fact, the amount of cracking is determined to be <5% of the overall conversion for all samples, based on the molar product distributions (see Figure S1). Furthermore, around ~50% of the detected methane and ethylene (depending on the sample) is produced by the empty reactor, further decreasing the relevance of propane cracking on the catalyst. While the C₂H₄ to CH₄ ratio increases with propane conversion, the overall extent of cracking slightly decreases, which is in good agreement with the ~2% cracking occurring on the catalyst itself, while half of these products are formed by the reactor, which should have a constant product distribution. The slight increase in the C₂H₄ to CH₄ ratio towards the end of the reaction phase is in good agreement with the lower conversion via the ODH reaction, which is exothermic in nature.⁴² As a result, the amount of reaction heat is decreased and the temperature of the system is also slightly decreased (a few degrees), which shifts the cracking products towards ethylene.⁴¹ Overall, due to its weak contribution, propane cracking is considered as less important for the overall reaction network and the behaviour of the catalyst.

Last, Figure 2f shows the ratio between the produced CO and the converted CO₂ (CO₂ based CO selectivity), as an indicator for PDR. For bare P25, within the first 30 minutes, 70% more CO is produced than CO₂ is converted, indicating a high degree of PDR, which then decreases to a stable level of around ~25% more CO. While the ODH/DDH+RWGS should create one CO molecule each, this always converts a CO₂ molecule. Therefore, the excess CO must be produced from propane by PDR. This behaviour might be indicative of highly reducible active sites for the PDR reaction that are quickly consumed, leading to a stable level of CO production. In comparison, the vanadia-loaded samples depict a CO₂ based CO selectivity that is only slightly above one (1.02-1.10), indicating a small contribution of PDR but to a much smaller degree as for bare P25. A similar behaviour was previously observed for supported vanadia systems and explained by the acid-base properties of the system, as the introduction of vanadia as an acidic oxide increases the rate of C-H bond activation in comparison to the more basic support, in this case TiO₂, which activates the C=O bond.²⁵ In principle, such a scenario is consistent with the results observed here for the VO_x/TiO₂ system. Considering the loading dependence the reactivity behaviour of the 0.1 and 0.5 V/nm² samples is characterized mainly by the ODH of propane, whereas the 1.2 and 2.5 V/nm² samples show slightly higher CO/X_{CO2} ratios (~1.1) and also exhibit a

much higher ratio in the first 30 minutes, indicating structural and/or chemical changes on the surface. The observed loading-dependent behaviour may be caused by the different vanadia nuclearity distributions, which has been shown to vary significantly for VO_x/TiO_2 catalysts.²⁸ For example, oligomers, present on the P25+2.5 V/nm² sample, are more reducible and prone to less selective oxidation as compared to monomers and dimers.²⁸

During the reaction, a significant amount of hydrogen is formed (see Figure S1), which increases with the vanadium loading. To explain this behaviour, the following two scenarios are conceivable: First, hydrogen formed by the direct dehydrogenation of propane, might not be fully converted to H_2O in the RWGS, as titania is typically a good RWGS reaction catalyst only in combination with a metal.^{43,44} The second scenario is based on the formation of carbon during the dry reforming process, resulting in a conversion of propane to CO, hydrogen, methane, and carbon coking on the catalyst surface,⁴⁵ might also explain the higher amount of methane than ethylene (see above). In addition, the main product, CO, explains the higher amount of detected CO than converted CO_2 (see Figure 2f). The presence of carbon on the catalyst during the reaction will be discussed in more detail in the operando spectroscopy section. Due to the different possible sources of hydrogen, the H_2/CO ratio is not considered a reliable measure to determine the amount of DDH vs ODH.

Additionally, to compare the results of a bulk TiO_2 to a different TiO_2 -based support material, we exposed vanadia-loaded $\text{TiO}_2/\text{SBA-15}$ (SBA15-T) samples prepared by ALD to the same gas treatments to investigate their catalytic behaviour. The results are given in the SI (see Figures S2 and S3). While the samples show less conversion than the corresponding P25-based samples discussed above, the difference between the vanadia-loaded sample and the bare support regarding C_3H_8 conversion is much less pronounced than for the P25-based samples. An important feature of the ALD-based TiO_2 material is that its propane conversion stays much more stable than that of bulk TiO_2 , which shows a rapid decrease with time on stream. The propane and CO_2 conversions are very similar for both materials, while significantly more CO than propylene is produced, which is supported by the CO_2 -based CO selectivity, which reaches a maximum of 285% for the SBA15-T+1.2 V/nm² sample, indicating a strong contribution of PDR. Bare SBA15-T, on the other hand, rather follows selective dehydrogenation pathways and is more directly comparable to bulk TiO_2 , while maintaining a stable C_3H_8 and CO_2 conversion.

In summary, the VO_x/TiO_2 systems show a good catalytic activity, with overall selectivities above 90% for the vanadia-loaded samples. Typical side reactions like PDR are of relevance on the bare support where significantly more CO is produced than CO_2 is converted, indicating that some propane is consumed to form CO. When vanadia is introduced, the PDR rates are reduced significantly, allowing for an almost exclusive dehydrogenation of propane via either ODH or DDH+RWGS reaction pathways. The presence of free H_2 indicates the occurrence of some PDR that also produces CH_4 and carbon on the catalyst surface, which will be discussed below.

Operando Spectroscopy

To gain insight into the reaction mechanism, multiple operando spectroscopies were employed during the different gas feeds (see experimental section). However, since the propane conversion, especially on the vanadia-loaded samples, does not stay constant and the measurements of different operando/quasi in situ methods occur on different time scales, each method may probe a different state of the catalyst. Therefore, when applying of methods with short acquisition times (Vis-Raman: 30 min, UV-Vis: 5 min) multiple spectra were recorded, to obtain time-dependent insight into the catalyst behaviour, while methods requiring longer acquisition times (UV-Raman: 120 min) were applied in a more integral manner. To further clarify this point, Figure S4 gives a temporal overview of the time of measurement of operando UV-Raman, Vis-Raman, and UV-Vis spectra in comparison to the molar product distributions for P25 and P25+1.2 V/nm².

Starting with UV-Raman spectroscopy, Figure 3 shows spectra of bare P25 and P25+1.2 V/nm² recorded at 385 nm excitation, as well as the results of a quantitative analysis of the observed spectral changes. The UV-Raman spectra for the other vanadia-loaded P25 samples and the ALD-based samples are given in the SI (see Figures S5 and S6). Figure 3a shows the UV-Raman spectra of bare P25 at 550 °C for different gas feeds. During pre-treatment in O_2/He , H_2/Ar , and CO_2/He , the most significant spectral changes are detected for the B_{1g} and A_{1g} phonons of anatase at 398 and 517 cm⁻¹, respectively,⁴⁶ which decrease in intensity in the hydrogen phase and stay constant afterwards. When propane is introduced, a significant amount of carbon appears on the catalyst surface, which cannot be fully removed in the 2 h regenerative CO_2 treatment after the reaction, indicating a slow oxidation of carbon by

CO₂. The P25+1.2 V/nm² sample shows a more pronounced decrease in its anatase phonon intensity, especially the A_{1g} phonon. Additionally, the formation of carbon is observed during reaction conditions, which however is fully regenerated by the CO₂ phase after reaction. The overall amount of deposited carbon during the reaction is smaller than for bare titania, indicating a higher rate of oxidation, which correlates with the increased conversion. The P25 samples loaded with 0.1, 0.5, and 2.5 V/nm² (see Figure S5) show similar structural dynamics to different extents, which is quantified in Figures 3c and d. Notably, no vanadia signals are observed in the UV-Raman spectra, indicating that the high temperature and absorbance of titania inhibits their detection.

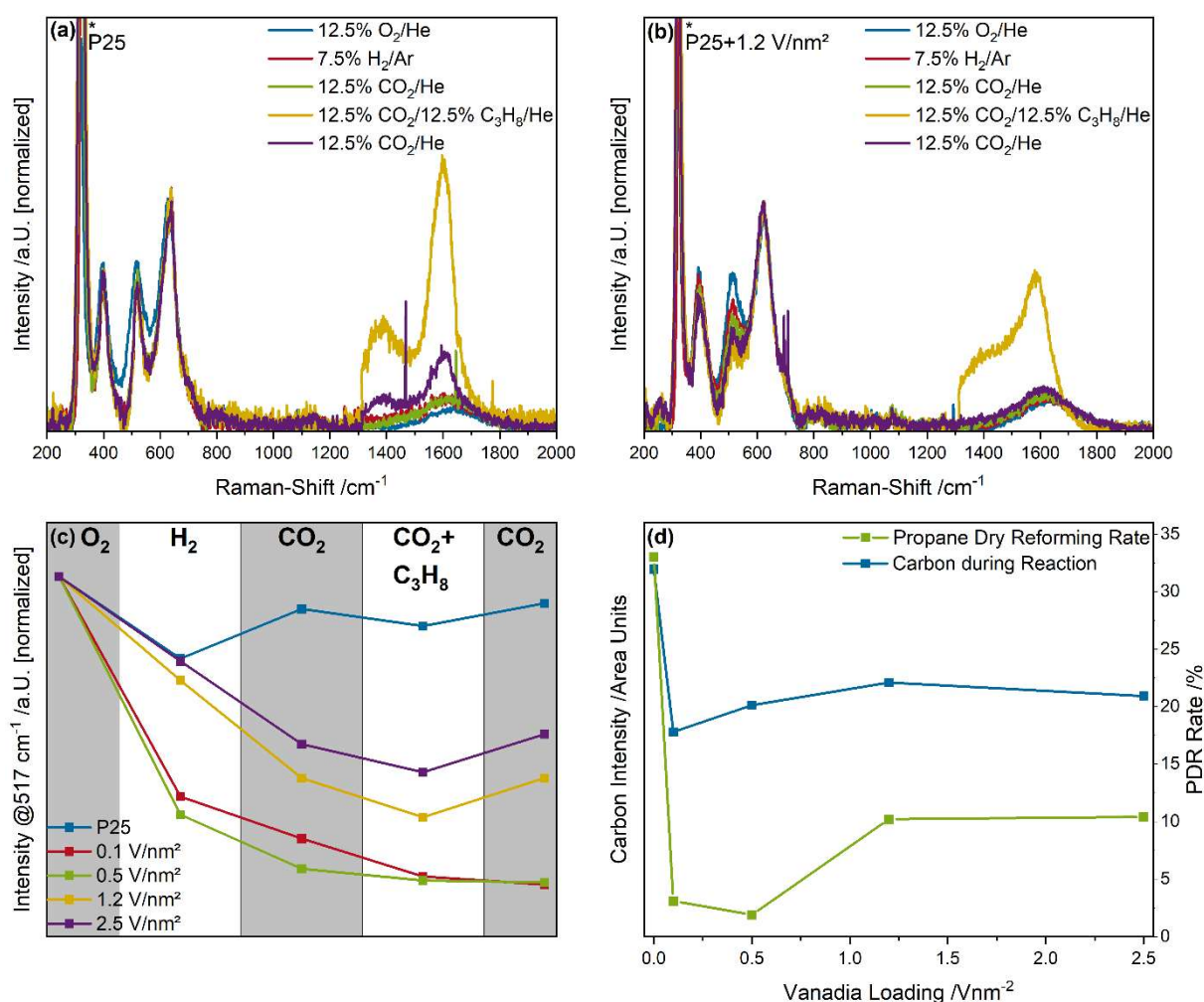


Figure 3: Operando UV-Raman spectra at 385 nm excitation of **(a)** P25 and **(b)** the 1.2 V/nm² sample recorded at 550 °C in different gas feeds. Spectra were normalized to the E_g phonon of anatase at 630 cm⁻¹. The signal marked with an asterisk is caused by the CaF₂ spectroscopic window. The anatase phonon intensity **(c)** and the amount of amorphous carbon detected during reaction conditions **(d)** were quantified and compared to the PDR rate.

The phonon band at 517 cm^{-1} was used as an indicator for the surface reduction of the samples. Its selective decrease at 517 cm^{-1} was observed previously and is caused by two factors.^{47,48} The first factor is the integration of vanadia into the titania lattice as detected during the phase transition from anatase to rutile introducing a doped metal atom that distorts the lattice of titania.⁴⁹ The second is the unilateral disturbance of the local order of the lattice, resulting from a reduction of the lattice with an oxygen gradient towards the surface.⁴⁸ However, no phonons of rutile were observed since their intensity is smaller than those of anatase and the temperature at which the experiments were performed leads to a lower signal to noise ratio.⁴⁶ Furthermore, due to the different absorption behavior, anatase absorbs stronger in the UV region, which leads to different resonance enhancements for anatase and rutile. Due to the strong absorption of titania at 385 nm, a quantification of the anatase phase is only possible at the catalyst surface, while the subsurface and bulk will be discussed later.^{50–52} The phonon intensity of all samples decreases significantly upon reduction of the material via reaction of lattice oxygen with hydrogen to water, which is released from the catalyst surface into the gas phase. The surface of bare P25 is least reduced, while the 0.1 and 0.5 V/nm² sample become much more reduced, leading to an almost complete disappearance of the anatase phonon at 517 cm^{-1} . With increasing vanadium loading, the degree of reduction decreases again. This indicates that vanadia increases the surface reduction at low loadings while increasing the conversion, whereas at higher loadings the reduction may shift from titania to vanadia species present at that loading, thus reducing the titania surface to a smaller extent.

Figure 3d shows the integrated carbon signal during reaction as a function of vanadium loading and its comparison with the observed PDR rate (percentage of CO formed from C₃H₈), indicating that the carbon formation is not necessarily a function of the oxygen mobility in the sample but rather of the PDR activity, which is high in P25, decreases at low vanadia loadings, and increases again at higher loadings. However, a combination of both mechanisms seems most likely, as the samples loaded with 0.1 and 0.5 V/nm² show no PDR and still form a significant amount of carbon on the surface. Therefore, besides PSD, the reduction of the catalyst might lead to an increased amount of carbon. The vanadia-loaded samples show less carbon deposition than bare P25, which can be explained by a higher rate of surface reoxidation using CO₂, facilitated by the presence of vanadia.

Notably, for the P25+2.5 V/nm² sample (see Figure S5), the V-O-V and V=O peaks are visible during the initial oxidative phase, but disappear for the other gas feeds, only regenerating slightly at 920 cm⁻¹ for the regenerative CO₂ phase, indicating V-O-V participation.⁵³ The peak at 860 cm⁻¹, representing the V-O-Ti signal is also present (as for the P25+1.2 V/nm² sample), but does not change upon switching between the different gas feeds.⁵⁴ Therefore, the results indicate that similar vanadia species as during the propane ODH using O₂ are participating in the reaction.²⁸ A detailed analysis of the vanadyl region will be performed on the basis of the DRIFTS data (see below).

The UV-Raman spectra of the ALD-based samples (see Figure S6) also show carbon formation on the surface but no changes of the titania phonons. The vanadyl peak is clearly visible for the SBA15-T+1.2 V/nm² sample during initial oxidative conditions and under CO₂ exposure, indicating vanadyl reduction and reoxidation.

To further understand the reduction of titania, Figure 4 shows the anatase E_g shift determined from Vis-Raman spectra (see Figures S7 and S8), as an indicator of titania subsurface reduction.^{55,56} The Vis-Raman spectra of the ALD-based samples are given in Figure S9.

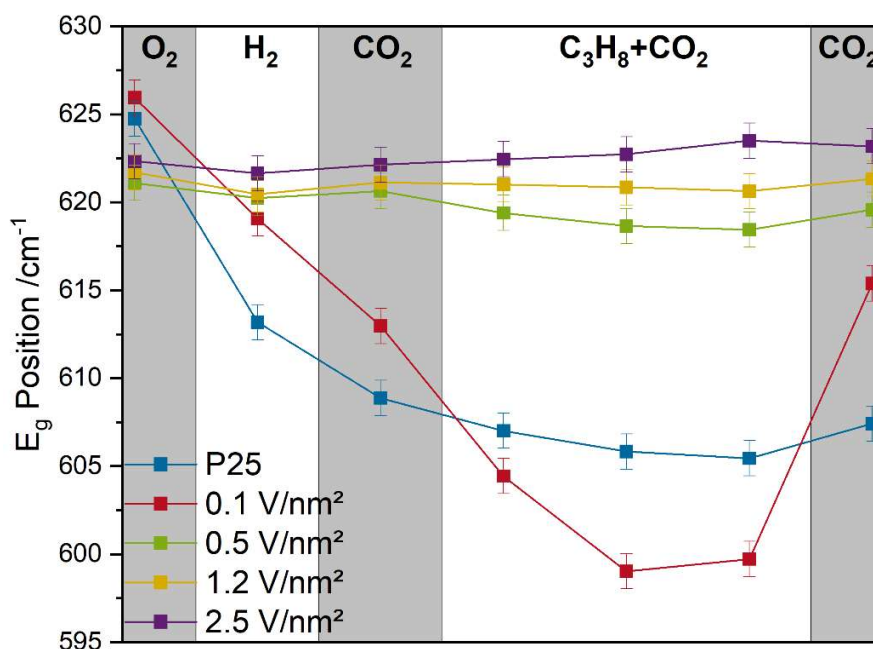


Figure 4: Position of the anatase E_g phonon determined from operando Vis-Raman spectra (at 514 nm excitation) recorded during exposure to 12.5% O₂/He, 7.5% H₂/Ar, 12.5% CO₂/He, 12.5% CO₂/12.5% C₃H₈, and 12.5% CO₂/He. The corresponding Raman spectra are shown in Figures S7 and S8.

The E_g position of bare P25 strongly red-shifts when switching from the 12.5% O_2/He to the 7.5% H_2/Ar feeds, red-shifts only slightly further in the following CO_2 -containing feeds, and finally blue-shifts again in the last regenerative 12.5% CO_2/He phase. In comparison, the P25+0.1 V/nm^2 sample red-shifts less in the pre-treatment phases, but red-shifts even more under reaction conditions, indicating strong subsurface reduction of titania. It is then regenerated more significantly than bare P25 in the last CO_2/He phase, indicating a stronger activation of CO_2 on the vanadia-loaded catalyst, which is likely caused by the dispersed vanadia species present on the sample.²⁸ At vanadia loadings higher than 0.1 V/nm^2 , no shift of the E_g position is observed. In agreement with the UV-Raman results, the P25 and 0.1 V/nm^2 sample show a similar behavior, pointing to a reduction of the surface and subsurface, while the P25+0.5 V/nm^2 sample shows the strongest surface reduction, but exhibits no subsurface reduction. For the 1.2 and 2.5 V/nm^2 samples no subsurface reduction is detected, while the surface reduction is less pronounced than that for the 0.5 V/nm^2 sample. This indicates that part of the redox cycle shifts from titania to surface-located vanadia and/or that CO_2 is much more easily activated over the VO_x/TiO_2 samples, which increases the rate of regeneration of titania by gas phase CO_2 , necessitating less oxygen diffusion within the support.

To obtain a more integral picture of the titania reduction, and to identify a potential phase-transformation of titania to the rutile phase, which is difficult to observe in the Raman spectra, quasi in situ XRD of P25 and the 1.2 V/nm^2 sample was applied (see Figure 5). Figure 5a shows the quasi in situ XRD patterns of bare P25 recorded after pre-treatment in 12.5% O_2/He and after pretreatment and exposure to reactive conditions, i.e. 12.5% $CO_2/12.5\% C_3H_8/He$ at 550 °C, followed by rapid cooling and inert transfer into the XRD sample holder. It can be seen that the amount of rutile in bare P25 stays unchanged, while the amount of anatase significantly decreases, which is in agreement with the Raman spectra (see Figure 3a) and indicates that the reduction of bare titania extends to the bulk, in order to regenerate the surface for the reaction.⁵⁷ This continuously reduces the titania to a point where the reaction slows down due to a depletion of available surface oxygen sites, which is reflected in the decreasing propane conversion (see Figure 2).

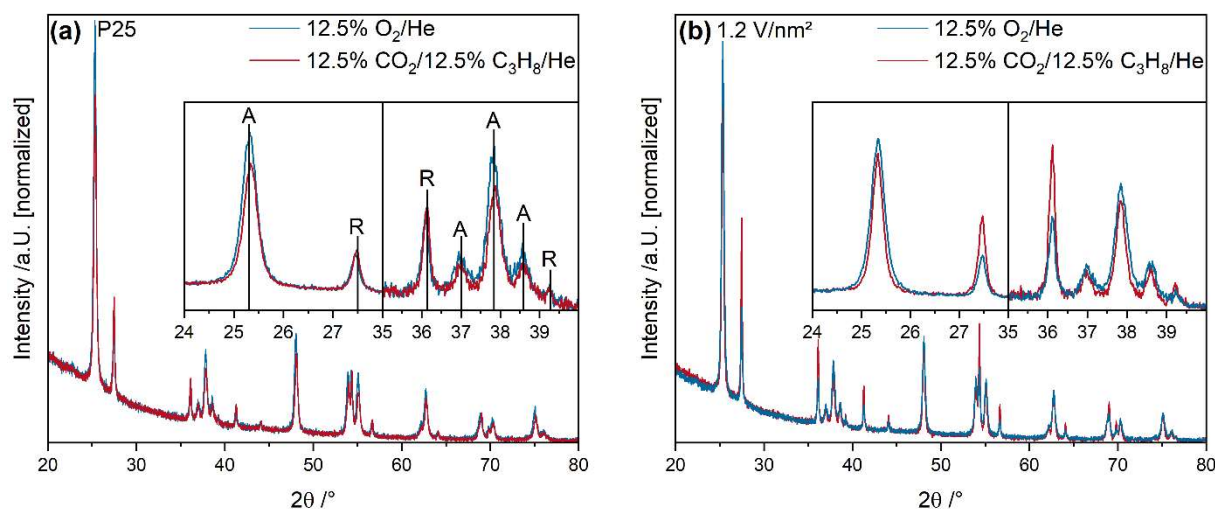


Figure 5: Quasi in-situ XRD patterns for **(a)** P25 and **(b)** the 1.2 V/nm² sample recorded after treatment in 12.5% O₂/He and after pretreatment and exposure to reactive conditions, i.e. 12.5% CO₂/12.5% C₃H₈/He at 550 °C, followed by rapid cooling to room temperature in He. The diffraction patterns were normalized and the inset shows selected regions in an enlarged view. The detected reflexes are assigned to the anatase (A) and rutile (R) phase of TiO₂.

In comparison, Figure 5b shows the quasi in situ XRD patterns of the 1.2 V/nm² sample after the same pre-treatments as for bare P25. It shows a small decrease in the anatase intensity, while the rutile intensity simultaneously increases. This indicates that anatase is not reduced as in case of bare titania, but that a phase transition towards a higher rutile content occurs. This was not observed using Raman spectroscopy, due to the small rutile intensity. As shown previously, rutile activates CO₂ more easily than anatase, thus facilitating catalyst reoxidation.^{58,59} As absent for bare P25, this transformation is proposed to be catalyzed by the presence of vanadia, which can also be encapsulated in the titania when it is present as V⁴⁺, which is likely during the strongly reducing reaction conditions at 550 °C.⁴⁹ Such a transformation in the presence of V⁴⁺ species also correlates well with the increased conversions and the less pronounced reduction of titania, as rutile might regenerate the catalyst more quickly due to its easier CO₂ activation in addition to the surface vanadia species which might be able to participate in the redox cycle, increasing the overall amount of surface oxygen sites present for the reaction. On the other hand, the increased presence of rutile might also be responsible for the higher contribution of PDR occurring at higher loadings, which will be discussed in more detail in the DRIFTS section.

To obtain an integral picture of the reduction of all samples, including the reduction of vanadia, operando UV-Vis spectra were recorded and the structural

changes observed were quantified. To gain insight into the temporal evolution of the catalysts, three spectra were recorded during the reaction and during the last regenerative phase. The results for P25 and the 1.2 V/nm² sample are depicted in Figure 6, whereas the UV-Vis spectra of the remaining samples are given in Figure S10 and those of the ALD-based samples in Figure S11.

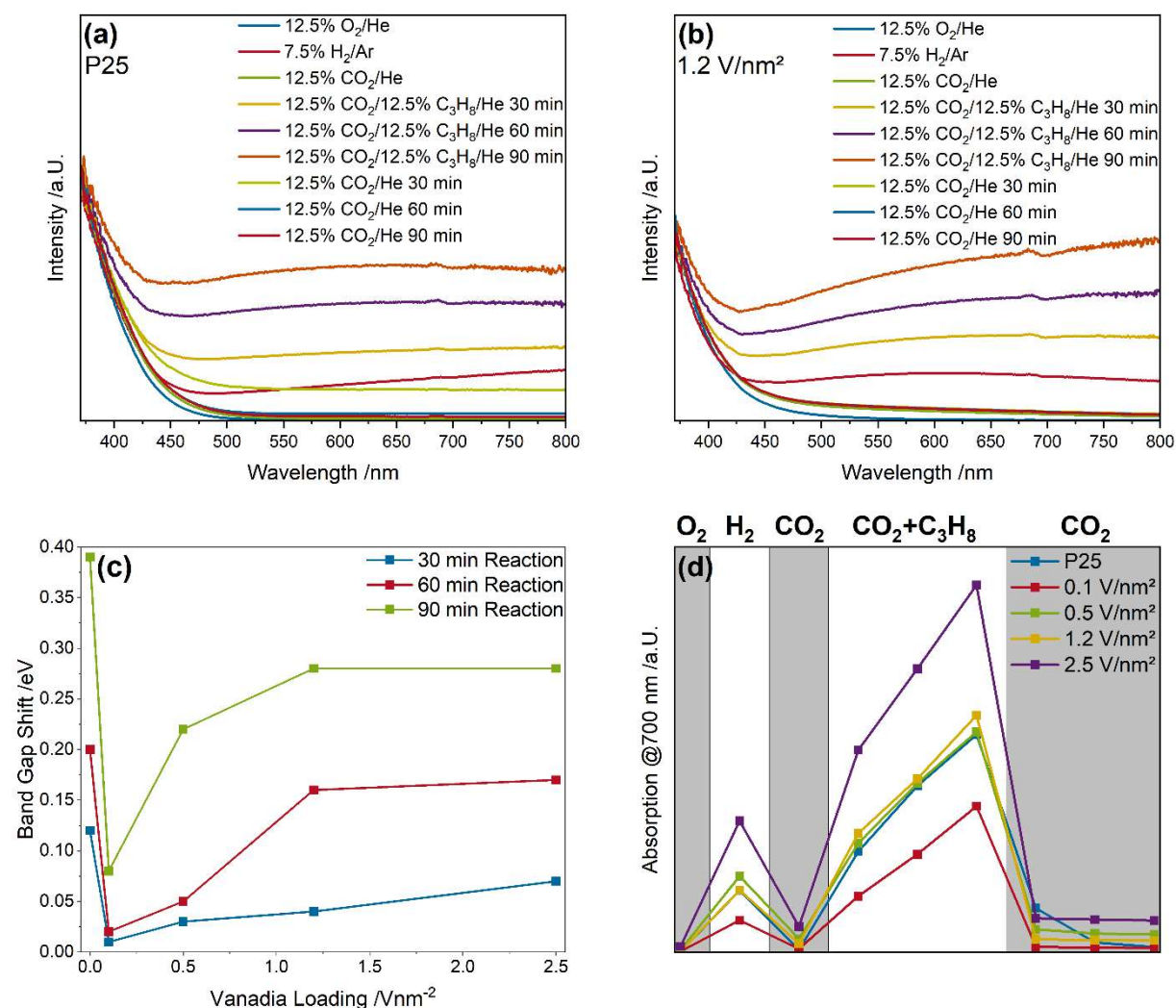


Figure 6: Operando UV-Vis spectra for (a) P25 and (b) the 1.2 V/nm² sample recorded at 550 °C in different gas feeds (see experimental section). Based on the UV-Vis spectra, (c) the band gap energy shift and (d) the absorption at 700 nm (indicative of the degree of reduction) were quantified. The spectra of the other P25-based samples are shown in Figure S10.

Figure 6a shows the operando UV-Vis spectra of bare P25. Two spectral changes can be observed, a shift in the band gap energy and an increase in the absorption between 500 and 800 nm. The red-shift in the band gap energy is associated with the reduction

of titania and the subsequent creation of states within the band gap, lowering its energy,⁶⁰ while the increase in absorption between 500 and 800 nm originates from charge transfer between reduced and oxidized states of titania (Ti^{3+} to Ti^{4+}).^{61,62} The observed red-shift in the band gap and the absorption increase between 500-800 nm correlate well with the reducibility of the corresponding gas phase. In comparison, the 1.2 V/nm² sample shows the same kind of spectral changes, but with the vanadia causing an additional contribution in the region between 500 and 800 nm, due to the possibility of vanadia d-d transitions.⁶³

Figures 6c and 6d summarize the results of the quantifications of the band gap shifts and the absorption increase between 500 and 800 nm for all samples. Starting with the band gap energies for the P25 sample a continuous red-shift of the band gap energy between 30 and 90 minutes of reaction is observed, with a shift of around 0.4 eV in total, indicating a strong reduction of titania that cannot be explained by a phase transition that increases the amount of rutile, as bare P25 only reduces the anatase phase (see Figure 5). In comparison, the 0.1 and 0.5 V/nm² sample show almost no red-shift during the first 60 minutes, but a significant red-shift after 90 minutes, indicating a much slower reduction of titania, in good agreement with the results from UV- and Vis-Raman spectroscopy. The phase transition from anatase to rutile, catalyzed by V^{4+} , might red-shift the band gap energy, as rutile has a lower band gap energy than anatase.^{64,65} This seems to be especially true for the 0.5, 1.2, and 2.5 V/nm² samples, showing a significant shift in their band gap energy, despite their lack of subsurface reduction, which is likely caused by the more extensive transformation of anatase to rutile, as more vanadia is present on the catalyst to catalyze the transformation.

The above findings are confirmed by the quantification of the absorption between 500 and 800 nm (see Figure 6d). During reaction conditions, P25 shows a continuously increasing absorption indicative of titania reduction due to $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$ transitions, in agreement with the band gap energy shift and previous results. The introduction of small amounts of vanadium (0.1 V/nm²) leads to a smaller increase in absorption, that indicates significantly less titania reduction, particularly when considering the contribution of vanadia d-d transitions. This behavior is in agreement with the band gap energy shift and shows that this sample is not as strongly reduced as bare titania, as a result of increased regeneration via CO_2 . At higher loadings (0.5 and 1.2 V/nm²) the absorption behavior resembles that of bare P25, likely caused by

the increased amount of vanadia participating in d-d transitions. The latter contribution further increases for the 2.5 V/nm² sample. Overall, the intensity of d-d transitions correlates well with the observed conversions, indicating the participation of vanadia in the reaction mechanism.

To obtain a more detailed understanding of surface adsorbates and the contribution of different vanadia species, quasi in situ DRIFTS was performed, following the procedure as in case of the XRD measurements (see Figure 5). Figure 7a depicts the DRIFT spectra of P25+1.2 V/nm², while Figure 7b shows the difference spectra for all five samples. Figures 7c and d summarize the quantification results of the V=O and Ti-OH regions, respectively. The DRIFT spectra of the remaining P25-based samples and the ALD-based samples are given in the Si (see Figures S12 and S13). As can be seen in Figure 7a, the DRIFT spectra of the 1.2 V/nm² sample show differences in the V=O and Ti-OH region, that are clearly visible in the difference spectra between oxidative (12.5% O₂/He) and reactive (12.5% CO₂/12.5% C₃H₈/He) conditions (see Figure 7b). Here, in agreement with the previous spectroscopic data on the TiO₂ reducibility, P25 and the P25+0.1 V/nm² sample show a strong intensity decrease of the feature at ~925 cm⁻¹, originating from the Ti-O vibration of Ti-OH species, which indicates strong surface reduction compared to oxidative conditions. The samples with higher vanadia loadings do not show these differences, but rather a pronounced decrease in the vanadyl region (see left inset). In the carbonate region almost no changes are observed, indicative of the absence of surface adsorbates (based on DRIFTS), while different Ti-OH species participate in the reaction for all samples (see right inset). The intensity changes in the vanadyl and Ti-OH region are summarized in Figure 7c and d, respectively.

As can be seen in Figure 7c, the 0.1 V/nm² sample shows only one highly symmetric V=O contribution that was previously attributed to a monomeric species.²⁸ For the samples loaded with 0.5 and 1.2 V/nm², an asymmetric vanadyl feature with an additional contribution at higher wavenumbers is observed, which was previously assigned to dimeric species.^{28,66–68} For the P25+2.5 V/nm² sample, additional peaks at higher wavenumbers are observed that can be attributed to trimeric and oligomeric species, which is in agreement with the increased vanadia d-d absorption (see Figure 6).^{28,66–68} The contribution of monomers drops with increasing vanadium loading in favor of a significantly increased contribution of dimers, while all species show an increased contribution for the highest loading. As the quantification is performed on the

basis of difference spectra, it is assumed that all of these species are either reduced or participating in the reaction mechanism leading to the ODH or PDR reaction. The participation of monomeric vanadia can be observed both in the increase in CO₂ and propane conversion (see Figure 2). Furthermore, it reduces the deep reduction of titania (see Figure 6) compared to P25, while being heavily reduced itself due to the low amount of VO_x. In comparison, no deep reduction of titania is observed for the 0.5 V/nm² sample, and the reduction of titania is even further reduced at higher loadings.

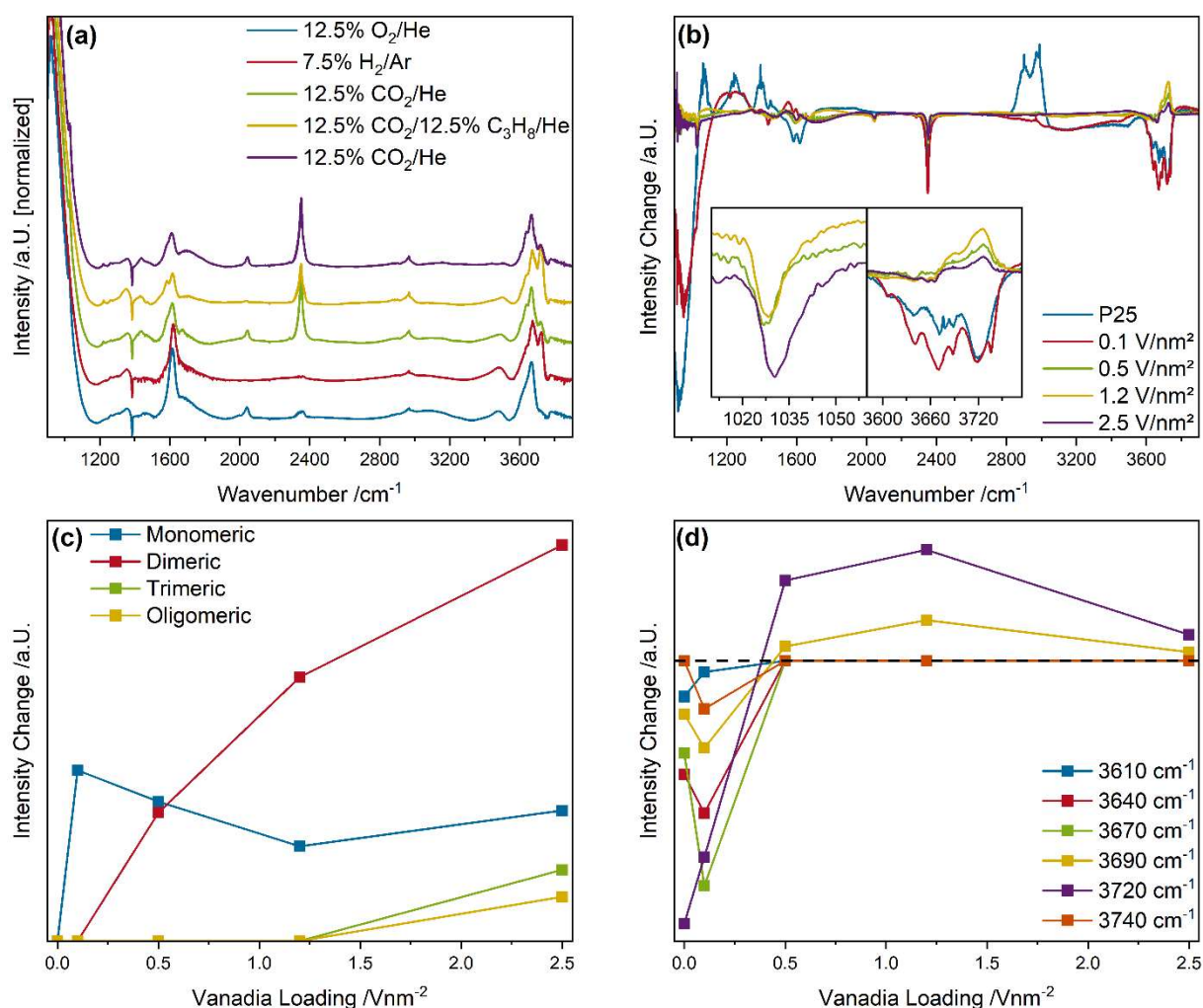


Figure 7: (a) Quasi in-situ DRIFT spectra of the 1.2 V/nm² sample recorded after treatment in different gas feeds (see experimental section) at 550 °C and subsequent rapid cooling to room temperature in He. Spectra were normalized and offset for clarity. (b) Difference between the spectra recorded in 12.5% CO₂/12.5% C₃H₈/He and 12.5% CO₂/He for P25 and vanadia-loaded samples. The insets highlight the intensity changes in the V=O region (0.5, 1.2, and 2.5 V/nm²) and in the Ti-OH region (all samples). Loading-dependent quantification of (c) the intensities of different nuclearities in the V=O region and (d) the different contributions to the Ti-OH region. The horizontal dashed line indicates no change in intensity. The quasi in-situ DRIFT spectra of the other P25-based samples are shown in Figure S12.

At these loadings, an increasing amount of dimeric and oligomeric species is present and the PDR rate increases again (see Figure 3), which seems to indicate that dimeric and oligomeric species are more active in the PDR rate. For the 2.5 V/nm² sample, this is likely caused by the presence of highly reducible linear V-O-V bonds of oligomeric vanadia,^{28,67,68} that may be prone to the PDR reaction but also further increase the amount of converted propane and CO₂ compared to the 1.2 V/nm² sample, despite the similar PDR rate. These highly reducible vanadia bonds might also be responsible for the initial jumps in the CO₂ and C₃H₈ conversions as well as the PDR rate (see Figure 2), which in the course of the reaction decrease towards a lower level, indicating that these bonds might not be regenerated after the initial reaction. In total, the sum of monomeric and dimeric species correlates well with the observed increase in conversion (see Figure 2), indicating their participation in propane conversion.

Figure 7d summarizes the loading-dependent quantification of the Ti-OH related intensity changes. Bare P25 and the P25+0.1 V/nm² sample show a strong decrease in the intensity of all Ti-OH signals present, as the surface of the catalyst is heavily reduced and most Ti-OH bonds are consumed during reactive conditions. This is emphasized by the DRIFT spectra for the reactive and last regenerative gas phase (see Figure S12). Therefore, the decrease of Ti-OH species for these samples is not related to the reaction mechanism, but rather to catalyst deactivation. In comparison, the samples with higher vanadium loadings show an increase in the intensity of Ti-OH species located at 3690 and 3720 cm⁻¹, which are assigned to bridged and isolated Ti-OH species, respectively.^{69–72} Bridged Ti-OH species have previously been associated with hydrogen storage during ODH reaction, thus acting as observer species, while isolated Ti-OH species were reported to be actively involved in the hydrogen transfer from propane to the catalyst.²⁸ Notably, no intensity change at the position associated with V-OH species is detected, indicating either a very fast or no involvement in the reaction mechanism. The intensity changes of both Ti-OH species correlate with the conversion for the 0.5 and 1.2 V/nm² samples. However, for the 2.5 V/nm² sample, only smaller changes are observed, which might be explained by the presence of different vanadia nuclearities, that is oligomers, changing the reaction mechanism and increasing the PDR rate.

Finally, to further elucidate the main route of deactivation for the catalysts, a long-term catalytic experiment during reaction conditions with different CO₂

concentrations was performed (see Figure 8). This was motivated by the fact that the samples with higher vanadium loadings, which are not as heavily reduced as bare P25, still show a decrease in propane conversion while staying constant in their CO₂ consumption, indicating that they might be reduced very slowly. For these experiments, the 0.5 V/nm² sample was chosen, as it shows less reduction than the lower loadings without the PDR influence of the higher loadings. The results are normalized to the initial propane conversion to emphasize the decrease observed over time (see Figure 8).

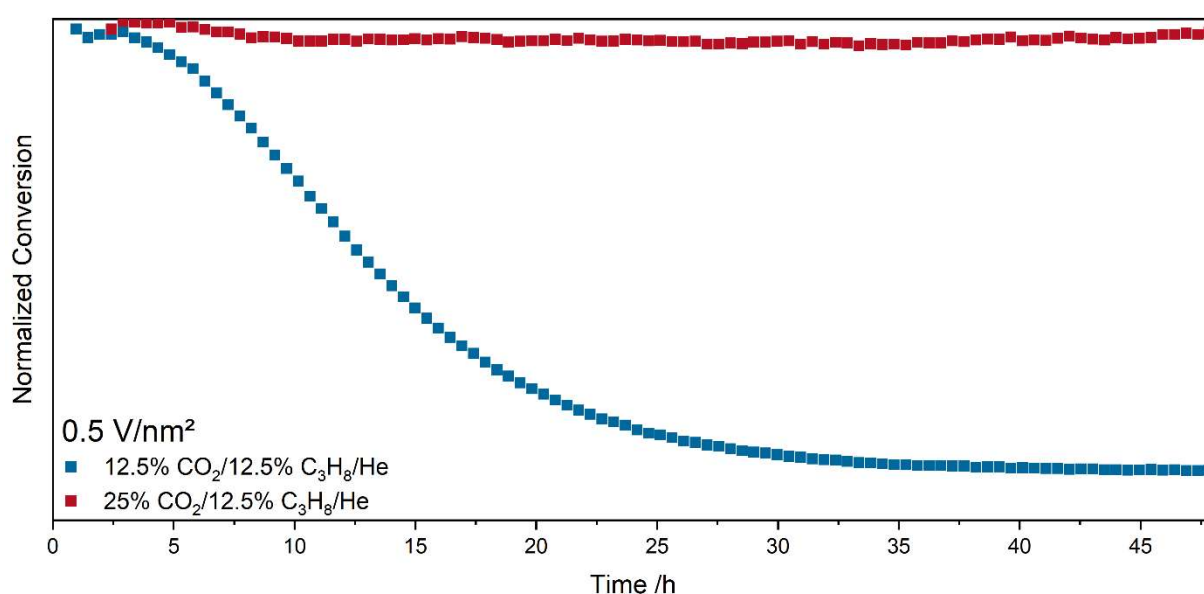


Figure 8: Long-term analysis of the propane conversion of the 0.5 V/nm² sample with CO₂/C₃H₈ gas-phase ratios of 1:1 (blue) and 2:1 (red) at 550 °C. The initial conversions were normalized for better comparability.

For a 1:1 ratio of CO₂ and C₃H₈, the conversion ratio stays constant for the first 3 h before decreasing continuously to 10% of the initial conversion. In contrast, when increasing the CO₂/C₃H₈ ratio to 2:1, the conversion stays constant over the full duration of the run (48 h). This behaviour indicates that, first, catalyst deactivation also occurs for the higher loadings but at a lower rate, which is outside the range of our spectroscopic experiments, and second, that an increase in CO₂ conversion can stop the catalyst deactivation. Three main deactivation routes were observed in our spectroscopic experiments, that is, carbon deposition on the surface, deep reduction of the catalyst, and V⁴⁺ integration into titania. The first two might be impeded by the

increased amount of CO₂ due to either an increased rate of regeneration or increased reaction of deposited carbon with CO₂ towards CO. The integration of vanadia into titania seems to be an important path, at least for the 1.2 and 2.5 V/nm² samples, since the decrease in propane conversion accelerates towards these loadings and might be due to the inability of CO₂ to reoxidize V⁴⁺ states, which can then only migrate into the titania lattice.²⁷ However, the conversion behaviour might also be caused by the reduction of different vanadia species as discussed above (see Figure 7). In addition, bare titania and the 0.1 and 0.5 V/nm² sample also show a decrease in propane conversion where the most likely deactivation mechanism appears to be the deep reduction of the catalyst, since the ALD-based samples show no dynamics in the titania phonons or their band gap (see Figures S6, S9, and S11) and had a constant conversion during the catalytic test. However, these samples show significant amounts of carbon during reaction conditions (see Figure S6), which may indicate that carbon deposition is a less important deactivation mechanism. In addition, due to the different titania structure, titania does not seem to transform from anatase to rutile and to incorporate vanadia, as vanadyl dynamics can be observed for these samples (see Figure S6). Overall, the deactivation due to deep reduction seems to be the main deactivation route for the studied VO_x/TiO₂ catalysts, which can be impeded by an increase in the gas concentration of CO₂ leading to an increased rate of regeneration.

Mechanistic Discussion

The reaction mechanism of the CO₂-assisted propane ODH over VO_x/TiO₂ can be categorized according to the vanadium loading, that is, (near)zero loading (0 and 0.1 V/nm²), medium loading (0.5 and 1.2 V/nm²), and high loading (2.5 V/nm²). As first step, hydrogen transfer is proposed to precede from propane to the titania surface for all samples (see Figure 7), followed by formation of water and an oxygen vacancy in the titania lattice. This is regenerated by oxygen diffusion from the subsurface/bulk for bare P25 and the 0.1 V/nm² sample, leading to a deep reduction of the catalyst, which especially favors the PDR reaction as already observed for the bare support of the VO_x/In₂O₃ system. No adsorbed intermediates are observed for any of the samples, indicating that the reaction occurs with a very high selectivity towards propylene. The deep reduction of titania seems to be the main deactivation mechanism due to a reduced rate of regeneration (see Figure 8). Since there is no selectivity difference

between the samples except for the observed PDR rate, only the identified structures responsible for the ODH rate are discussed.

The vanadia-loaded samples are proposed to undergo a similar hydrogen transfer but are heavily reduced themselves (see Figures 3, 6, and 7), indicating their participation in the reaction mechanism by delivering oxygen to drive the reaction. In addition, the rate of surface reoxidation by gas-phase activation of CO₂ is significantly increased due to the presence of vanadia, which is confirmed by the increased CO₂ conversion with increasing vanadium loading, despite the reduced PDR rate (see Figure 2). This is further supported by the conversion behavior, which increases linearly with the vanadium loading, emphasizing its importance for the conversion. The presence of vanadia may facilitate the CO₂ activation in two ways: First, the reduced vanadyl peak can activate CO₂ itself, regenerating the catalyst, and second, vanadia reduced to oxidation state V⁴⁺ can catalyze the transformation of anatase into rutile (see Figure 5), which is much more active towards CO₂ and might thereby regenerate titania much faster. This is emphasized by the point that the titania reduction decreases with increasing vanadium loading. In fact, for the 2.5 V/nm² sample, even the surface of the catalyst is barely reduced. The integration of V⁴⁺ into the lattice is further supported by the fact, that for the samples with a notable formation of rutile during reaction conditions, no vanadia-related signals are observed (see Figure 3), while for the ALD-based samples, structural dynamics is clearly visible for the vanadyl peak but not within the titania lattice due to the highly amorphous nature of the film.

Regarding the nuclearity dependence of the reactivity behavior, the increase in conversion correlates well with the sum of monomeric and dimeric vanadia species (see Figure 7), as previously observed for the reaction with O₂, indicating its importance as the oxygen site for the reaction. Therefore, a transfer of hydrogen from the titania lattice to vanadia is likely, followed by its integration into the lattice or a fast reduction to water due to the elevated temperatures. This is indicated by the clear reduction of vanadia (see Figures 6 and 7) while no V-OH species are present (see Figure 7d). The higher nuclearities, especially the linear V-O-V bonds of oligomeric vanadia species seem to favor the PDR significantly and react quickly at the beginning of the reaction (see Figures 2 and 7). The 0.5 V/nm² sample shows almost no PDR, but a selectivity of close to 100% with a very small contribution from cracking. This sample contains no vanadia species with higher nuclearity and is not deeply reduced,

with the ability to form rutile during the reaction. These properties seem to be most important for pushing the selectivity towards the ODH reaction.

4. Conclusion

In this study, we addressed the CO₂-assisted ODH of propane over VO_x/TiO₂ catalysts and elucidated important structural features relevant to the catalytic performance and the catalyst deactivation, by using multiple in situ/operando methods. To unravel the role of the catalyst properties, we varied the vanadium loadings (0-2.5 V/nm²) and used two types of titania supports, i.e. bulk P25 and ALD-prepared thin film titania on silica.

The catalytic performance of the catalysts depends strongly on the vanadium loading. Bare P25 shows a lower conversion, with a significant contribution of PDR. With increasing vanadium loading, the conversion of propane and CO₂ increases, but over time, the propane conversion decreases again, while the CO₂ conversion stays constant. The PDR rate decreases to zero for the 0.1 and 0.5 V/nm² sample, but increases again for the 1.2 and 2.5 V/nm² sample, while staying significantly lower than that of bare P25. Besides dehydrogenation and PDR, no significant side reactions were observed, except for some cracking, which is mostly caused by the reactor.

As a result of the mechanistic analysis, three main reaction paths were identified. Titania lattice oxygen is an important oxygen site for the reaction, which is heavily reduced in bare P25 during reaction conditions, leading to a deep reduction of titania. As a result, the catalyst gradually deactivates, leading to a significant increase in PDR as the main side reaction. The introduction of vanadia leads to a better activation of CO₂, enabling faster catalyst regeneration, which may occur via two routes. First, hydrogen can be transferred from the titania lattice to vanadia, where it forms water and reduces the vanadia species, leaving an oxygen vacancy. Since vanadium activates CO₂ better than titania, it can be regenerated more easily by gas phase CO₂, which impedes titania deep reduction and increases the overall reaction rate, while also decreasing the PDR route. Second, one hydrogen can be transferred from titania to vanadia, reducing it to V⁴⁺, which can then catalyze the anatase to rutile transformation, whereby vanadium is integrated into the titania bulk. The higher activation rate of CO₂ over rutile compared to anatase enables the titania to be less reduced and to achieve a higher reoxidation rate.

The nuclearity-dependence of the reaction shows that both monomeric and dimeric species increase the reaction rate and decrease the PDR route, while being actively reduced. However, higher nuclearities (e.g. oligomers in the 2.5 V/nm² sample) contain highly reducible oxygen atoms, that increase the contribution of the PDR route. Therefore, a selectivity maximum for the ODH route and therefore for propylene is achieved at a medium vanadium loading between 0.1 and 1.2 V/nm², where almost 100 % propylene selectivity is achieved.

The main deactivation route is the catalyst's deep reduction, which depletes the active oxygen sites, leading to a continuous decrease in propane conversion, while the CO₂ conversion stays constant. Further deactivation mechanisms include the depletion of vanadia surface species, due to their integration into the newly formed rutile phase, and the formation of carbon. However, the ALD-based samples exhibit strong carbon deposition, while no significant titania lattice reduction is observed and the conversion stays constant, indicating carbon deposition to be of lower importance. Catalyst deactivation can be avoided by increasing the CO₂ gas-phase concentration.

Our results highlight the potential of combining multiple operando and in situ approaches to investigate the reaction mechanism of CO₂ activation during propane ODH, which is a highly relevant reaction with the potential of technical application. The VO_x/TiO₂ catalysts showed a highly promising performance that is more selective than that of most other oxide-based systems and comparable to CrO_x catalysts. For the first time, the reaction mechanism including the complex interplay between surface vanadia and multi-phase TiO₂ was elucidated. With this knowledge the catalyst performance can be improved. Our approach is readily transferable to other systems that are still missing from the literature, e.g. VO_x/CeO₂, to understand the important support contribution to the performance of vanadia-based catalysts in CO₂ activation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supporting Information

The supporting information contains additional information about the reactivity behavior and additional results from operando spectroscopic analysis.

Acknowledgements

The authors acknowledge Till Wissel for performing nitrogen-adsorption experiments and BET analysis. This work was supported by the Deutsche Forschungsgemeinschaft (DFG, HE 4515/11-1).

References

- (1) Amghizar, I.; Vandewalle, L. A.; van Geem, K. M.; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, 3 (2), 171–178. DOI: 10.1016/j.eng.2017.02.006.
- (2) Cavani, F.; Ballarini, N.; Cericola, A. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal. Today* **2007**, 127 (1-4), 113–131. DOI: 10.1016/j.cattod.2007.05.009.
- (3) Lavrenov, A. V.; Saifulina, L. F.; Buluchevskii, E. A.; Bogdanets, E. N. Propylene production technology: Today and tomorrow. *Catal. Ind.* **2015**, 7 (3), 175–187. DOI: 10.1134/S2070050415030083.
- (4) Phung, T. K.; Le Pham, T. M.; Vu, K. B.; Busca, G. (Bio)Propylene production processes: A critical review. *J. Environ. Chem. Eng.* **2021**, 9 (4), 105673. DOI: 10.1016/j.jece.2021.105673.
- (5) Carrero, C. A.; Schloegl, R.; Wachs, I. E.; Schomaecker, R. Critical Literature Review of the Kinetics for the Oxidative Dehydrogenation of Propane over Well-Defined Supported Vanadium Oxide Catalysts. *ACS Catal.* **2014**, 4 (10), 3357–3380. DOI: 10.1021/cs5003417.
- (6) Carter, J. H.; Bere, T.; Pitchers, J. R.; Hewes, D. G.; Vandegehuchte, B. D.; Kiely, C. J.; Taylor, S. H.; Hutchings, G. J. Direct and oxidative dehydrogenation of propane: from catalyst design to industrial application. *Green Chem.* **2021**, 23 (24), 9747–9799. DOI: 10.1039/D1GC03700E.
- (7) Baek, J.; Yun, H. J.; Yun, D.; Choi, Y.; Yi, J. Preparation of Highly Dispersed Chromium Oxide Catalysts Supported on Mesoporous Silica for the Oxidative Dehydrogenation of Propane Using CO₂: Insight into the Nature of Catalytically Active Chromium Sites. *ACS Catal.* **2012**, 2 (9), 1893–1903. DOI: 10.1021/cs300198u.
- (8) Kätelhön, A.; Meys, R.; Deutz, S.; Suh, S.; Bardow, A. Climate change mitigation potential of carbon capture and utilization in the chemical industry. *Proc. Natl. Acad. Sci. USA* **2019**, 116 (23), 11187–11194. DOI: 10.1073/pnas.1821029116. Published Online: May. 13, 2019.
- (9) Baena-Moreno, F. M.; Rodríguez-Galán, M.; Vega, F.; Alonso-Fariñas, B.; Vilches Arenas, L. F.; Navarrete, B. Carbon capture and utilization technologies: a literature

review and recent advances. *Energ. Source A: Recovery, Util. Environ. Effects* **2019**, 41 (12), 1403–1433. DOI: 10.1080/15567036.2018.1548518.

(10) Al-Mamoori, A.; Krishnamurthy, A.; Rownaghi, A. A.; Rezaei, F. Carbon Capture and Utilization Update. *Energy Technol.* **2017**, 5 (6), 834–849. DOI: 10.1002/ente.201600747.

(11) Álvarez, A.; Borges, M.; Corral-Pérez, J. J.; Olcina, J. G.; Hu, L.; Cornu, D.; Huang, R.; Stoian, D.; Urakawa, A. CO₂ Activation over Catalytic Surfaces. *Chem. Phys. Chem.* **2017**, 18 (22), 3135–3141. DOI: 10.1002/cphc.201700782. Published Online: Oct. 5, 2017.

(12) Jacquemin, M.; Beuls, A.; Ruiz, P. Catalytic production of methane from CO₂ and H₂ at low temperature: Insight on the reaction mechanism. *Catal. Today* **2010**, 157 (1–4), 462–466. DOI: 10.1016/j.cattod.2010.06.016.

(13) Lei, T.-q.; Cheng, Y.-h.; Miao, C.-x.; Hua, W.-m.; Yue, Y.-h.; Gao, Z. Silica-doped TiO₂ as support of gallium oxide for dehydrogenation of ethane with CO₂. *Fuel Process. Technol.* **2018**, 177, 246–254. DOI: 10.1016/j.fuproc.2018.04.037.

(14) Atanga, M. A.; Rezaei, F.; Jawad, A.; Fitch, M.; Rownaghi, A. A. Oxidative dehydrogenation of propane to propylene with carbon dioxide. *Appl. Catal. B: Environ.* **2018**, 220, 429–445. DOI: 10.1016/j.apcatb.2017.08.052.

(15) Gambo, Y.; Adamu, S.; Tanimu, G.; Abdullahi, I. M.; Lucky, R. A.; Ba-Shammakh, M. S.; Hossain, M. M. CO₂-mediated oxidative dehydrogenation of light alkanes to olefins: Advances and perspectives in catalyst design and process improvement. *Appl. Catal. A: Gen.* **2021**, 623, 118273. DOI: 10.1016/j.apcata.2021.118273.

(16) Jiang, X.; Sharma, L.; Fung, V.; Park, S. J.; Jones, C. W.; Sumpter, B. G.; Baltrusaitis, J.; Wu, Z. Oxidative Dehydrogenation of Propane to Propylene with Soft Oxidants via Heterogeneous Catalysis. *ACS Catal.* **2021**, 11 (4), 2182–2234. DOI: 10.1021/acscatal.0c03999.

(17) Rigamonti, M. G.; Shah, M.; Gambu, T. G.; Saeys, M.; Dusselier, M. Reshaping the Role of CO₂ in Propane Dehydrogenation: From Waste Gas to Platform Chemical. *ACS Catal.* **2022**, 12 (15), 9339–9358. DOI: 10.1021/acscatal.2c01374.

(18) Botavina, M. A.; Martra, G.; Agafonov, Y.A.; Gaidai, N. A.; Nekrasov, N. V.; Trushin, D. V.; Coluccia, S.; Lapidus, A. L. Oxidative dehydrogenation of C₃–C₄

paraffins in the presence of CO₂ over CrO_x/SiO₂ catalysts. *Appl. Catal. A: Gen.* **2008**, 347 (2), 126–132. DOI: 10.1016/j.apcata.2008.05.037.

(19) Gashoul Daresibi, F.; Khodadadi, A. A.; Mortazavi, Y.; Huotari, S.; Ritala, M. Highly dispersed atomic layer deposited CrO_x on SiO₂ catalyst with enhanced yield of propylene for CO₂-mediated oxidative dehydrogenation of propane. *Mol. Catal.* **2022**, 526 (80–), 112396. DOI: 10.1016/j.mcat.2022.112396.

(20) Michorczyk, P.; Pietrzyk, P.; Ogonowski, J. Preparation and characterization of SBA-1-supported chromium oxide catalysts for CO₂ assisted dehydrogenation of propane. *Microporous Mesoporous Mater.* **2012**, 161, 56–66. DOI: 10.1016/j.micromeso.2012.05.011.

(21) Wang, H.; Nguyen, T. D.; Tsilomelekis, G. Propane oxidative dehydrogenation using CO₂ over CrO_x/Fe–CeO₂ catalysts. *Catal. Sci. Technol.* **2023**, 13 (8), 2360–2369. DOI: 10.1039/D2CY01563C.

(22) Wang, Z.-Y.; He, Z.-H.; Li, L.-Y.; Yang, S.-Y.; He, M.-X.; Sun, Y.-C.; Wang, K.; Chen, J.-G.; Liu, Z.-T. Research progress of CO₂ oxidative dehydrogenation of propane to propylene over Cr-free metal catalysts. *Rare Met.* **2022**, 41 (7), 2129–2152. DOI: 10.1007/s12598-021-01959-y. Published Online: Mar. 11, 2022.

(23) Ascoop, I.; Galvita, V. V.; Alexopoulos, K.; Reyniers, M.-F.; van der Voort, P.; Bliznuk, V.; Marin, G. B. The role of CO₂ in the dehydrogenation of propane over WO_x–VO_x/SiO₂. *J. Catal.* **2016**, 335, 1–10. DOI: 10.1016/j.jcat.2015.12.015.

(24) Balogun, M. L.; Adamu, S.; Ba-Shammakh, M. S.; Hossain, M. M. Promotional effects of CO₂ on the oxidative dehydrogenation of propane over mesoporous VO_x/γAl₂O₃ catalysts. *J. Ind. Eng. Chem.* **2021**, 96 (20), 82–97. DOI: 10.1016/j.jiec.2020.12.022.

(25) Jiang, X.; Lis, B. M.; Purdy, S. C.; Paladugu, S.; Fung, V.; Quan, W.; Bao, Z.; Yang, W.; He, Y.; Sumpter, B. G.; Page, K.; Wachs, I. E.; Wu, Z. CO₂-Assisted Oxidative Dehydrogenation of Propane over VO_x/In₂O₃ Catalysts: Interplay between Redox Property and Acid–Base Interactions. *ACS Catal.* **2022**, 12 (18), 11239–11252. DOI: 10.1021/acscatal.2c02099.

(26) Jiang, X.; Lis, B. M.; Wu, Y.; Wachs, I. E.; Wu, Z. Effect of the Molecular Structure of Surface Vanadia on Activity and Regenerability of VO_x/In₂O₃ Catalysts for CO₂-

Assisted Oxidative Dehydrogenation of Propane. *J. Phys. Chem. C* **2023**, 127 (13), 6311–6320. DOI: 10.1021/acs.jpcc.3c00183.

(27) Rogg, S.; Hess, C. CO₂ as a soft oxidant for propane oxidative dehydrogenation: A mechanistic study using operando UV Raman spectroscopy. *J. CO₂ Utiliz.* **2021**, 50 (9), 101604. DOI: 10.1016/j.jcou.2021.101604.

(28) Schumacher, L.; Pfeiffer, J.; Shen, J.; Gutmann, T.; Breitzke, H.; Buntkowsky, G.; Hofmann, K.; Hess, C. Collaborative Mechanistic Effects between Vanadia and Titania during the Oxidative Dehydrogenation of Propane Investigated by Operando and Transient Spectroscopies. *ACS Catal.* **2023**, 8139–8160. DOI: 10.1021/acscatal.3c01404.

(29) Balogun, M. L.; Adamu, S.; Bakare, I. A.; Ba-Shammakh, M. S.; Hossain, M. M. CO₂ Assisted Oxidative Dehydrogenation of Propane to Propylene over Fluidizable MoO₃/La₂O₃-γAl₂O₃ Catalysts. *J. CO₂ Utiliz.* **2020**, 42, 101329. DOI: 10.1016/j.jcou.2020.101329.

(30) Balogun, M. L.; Gambo, Y.; Adamu, S.; Ba-Shammakh, M. S.; Hossain, M. M. Kinetic modeling of oxidative dehydrogenation of propane with CO₂ over MoO_x/La₂O₃-Al₂O₃ in a fluidized bed. *AIChE J.* **2023**, 69 (3). DOI: 10.1002/aic.17903.

(31) Beck, B.; Harth, M.; Hamilton, N. G.; Carrero, C.; Uhlich, J. J.; Trunschke, A.; Shaikhutdinov, S.; Schubert, H.; Freund, H.-J.; Schlögl, R.; Sauer, J.; Schomäcker, R. Partial oxidation of ethanol on vanadia catalysts on supporting oxides with different redox properties compared to propane. *J. Catal.* **2012**, 296, 120–131. DOI: 10.1016/j.jcat.2012.09.008.

(32) Dinse, A.; Frank, B.; Hess, C.; Habel, D.; Schomäcker, R. Oxidative dehydrogenation of propane over low-loaded vanadia catalysts: Impact of the support material on kinetics and selectivity. *J. Mol. Catal. A: Chem.* **2008**, 289 (1-2), 28–37. DOI: 10.1016/j.molcata.2008.04.007.

(33) Jiang, X.; Manawan, M.; Feng, T.; Qian, R.; Zhao, T.; Zhou, G.; Kong, F.; Wang, Q.; Dai, S.; Pan, J. H. Anatase and rutile in evonik aerioxide P25: Heterojunctioned or individual nanoparticles? *Catal. Today* **2018**, 300, 12–17. DOI: 10.1016/j.cattod.2017.06.010.

- (34) Christodoulakis, A.; Machli, M.; Lemonidou, A. A.; Boghosian, S. Molecular structure and reactivity of vanadia-based catalysts for propane oxidative dehydrogenation studied by in situ Raman spectroscopy and catalytic activity measurements. *J. Catal.* **2004**, 222 (2), 293–306. DOI: 10.1016/j.jcat.2003.10.007.
- (35) Spende, A.; Sobel, N.; Lukas, M.; Zierold, R.; Riedl, J. C.; Gura, L.; Schubert, I.; Moreno, J. M. M.; Nielsch, K.; Stühn, B.; Hess, C.; Trautmann, C.; Toimil-Molares, M. E. TiO₂, SiO₂, and Al₂O₃ coated nanopores and nanotubes produced by ALD in etched ion-track membranes for transport measurements. *Nanotechnol.* **2015**, 26 (33), 335301. DOI: 10.1088/0957-4484/26/33/335301. Published Online: Jul. 30, 2015.
- (36) Waleska, P. S.; Hess, C. Oligomerization of Supported Vanadia: Structural Insight Using Surface-Science Models with Chemical Complexity. *J. Phys. Chem. C* **2016**, 120 (33), 18510–18519. DOI: 10.1021/acs.jpcc.6b01672.
- (37) Antonov, L.; Nedeltcheva, D. Resolution of overlapping UV–Vis absorption bands and quantitative analysis. *Chem. Soc. Rev.* **2000**, 29 (3), 217–227. DOI: 10.1039/A900007K.
- (38) Dolgonos, A.; Mason, T. O.; Poeppelmeier, K. R. Direct optical band gap measurement in polycrystalline semiconductors: A critical look at the Tauc method. *J. Solid State Chem.* **2016**, 240 (11), 43–48. DOI: 10.1016/j.jssc.2016.05.010.
- (39) Filtschew, A.; Hofmann, K.; Hess, C. Ceria and Its Defect Structure: New Insights from a Combined Spectroscopic Approach. *J. Phys. Chem. C* **2016**, 120 (12), 6694–6703. DOI: 10.1021/acs.jpcc.6b00959.
- (40) Bugrova, T. A.; Dutov, V. V.; Svetlichnyi, V. A.; Cortés Corberán, V.; Mamontov, G. V. Oxidative dehydrogenation of ethane with CO₂ over CrO_x catalysts supported on Al₂O₃, ZrO₂, CeO₂ and Ce_xZr_{1-x}O₂. *Catal. Today* **2019**, 333, 71–80. DOI: 10.1016/j.cattod.2018.04.047.
- (41) Buekens, A. G.; Froment, G. F. Thermal Cracking of Propane. Kinetics and Product Distributions. *Ind. Eng. Chem. Proc. Des. Dev.* **1968**, 7 (3), 435–447. DOI: 10.1021/i260027a022.
- (42) Gomez, E.; Kattel, S.; Yan, B.; Yao, S.; Liu, P.; Chen, J. G. Combining CO₂ reduction with propane oxidative dehydrogenation over bimetallic catalysts. *Nat.*

Commun. **2018**, 9 (1), 1398. DOI: 10.1038/s41467-018-03793-w. Published Online: Apr. 11, 2018.

(43) Chen, L.; Allec, S. I.; Nguyen, M.-T.; Kovarik, L.; Hoffman, A. S.; Hong, J.; Meira, D.; Shi, H.; Bare, S. R.; Glezakou, V.-A.; Rousseau, R.; Szanyi, J. Dynamic Evolution of Palladium Single Atoms on Anatase Titania Support Determines the Reverse Water-Gas Shift Activity. *J. Am. Chem. Soc.* **2023**, 145 (19), 10847–10860. DOI: 10.1021/jacs.3c02326. Published Online: May. 5, 2023.

(44) Doherty, F.; Goldsmith, B. R. Rhodium Single-Atom Catalysts on Titania for Reverse Water Gas Shift Reaction Explored by First Principles Mechanistic Analysis and Compared to Nanoclusters. *ChemCatChem* **2021**, 13 (13), 3155–3164. DOI: 10.1002/cctc.202100292.

(45) Siahvashi, A.; Adesina, A. A. Hydrogen production via propane dry reforming: Carbon deposition and reaction-deactivation study. *Int. J. Hydrog. Energ.* **2018**, 43 (36), 17195–17204. DOI: 10.1016/j.ijhydene.2018.07.118.

(46) Balachandran, U.; Eror, N. G. Raman spectra of titanium dioxide. *J. Solid State Chem.* **1982**, 42 (3), 276–282. DOI: 10.1016/0022-4596(82)90006-8.

(47) Zhang, J.; Chen, X.; Shen, Y.; Li, Y.; Hu, Z.; Chu, J. Synthesis, surface morphology, and photoluminescence properties of anatase iron-doped titanium dioxide nano-crystalline films. *Phys. Chem. Chem. Phys.* **2011**, 13 (28), 13096–13105. DOI: 10.1039/c0cp02924f. Published Online: Jun. 21, 2011.

(48) Ishioka, K.; Petek, H. Raman generation of coherent phonons of anatase and rutile TiO₂ photoexcited at fundamental absorption edges. *Phys. Rev. B* **2012**, 86 (20). DOI: 10.1103/PhysRevB.86.205201.

(49) Martínez-Huerta, M. V.; Fierro, J.L.G.; Bañares, M. A. Monitoring the states of vanadium oxide during the transformation of TiO₂ anatase-to-rutile under reactive environments: H₂ reduction and oxidative dehydrogenation of ethane. *Catal. Commun.* **2009**, 11 (1), 15–19. DOI: 10.1016/j.catcom.2009.08.002.

(50) Glassford, K. M.; Chelikowsky, JR. Optical properties of titanium dioxide in the rutile structure. *Phys. Rev. B Condens. Matter* **1992**, 45 (7), 3874–3877. DOI: 10.1103/physrevb.45.3874.

- (51) Daude, N.; Gout, C.; Jouanin, C. Electronic band structure of titanium dioxide. *Phys. Rev. B* **1977**, *15* (6), 3229–3235. DOI: 10.1103/PhysRevB.15.3229.
- (52) Tang, H.; Berger, H.; Schmid, P. E.; Lévy, F. Optical properties of anatase (TiO₂). *Solid State Commun.* **1994**, *92* (3), 267–271. DOI: 10.1016/0038-1098(94)90889-3.
- (53) Burcham, L. J. In situ IR, Raman, and UV-Vis DRS spectroscopy of supported vanadium oxide catalysts during methanol oxidation. *Top. Catal.* **2000**, *11/12* (1/4), 85–100. DOI: 10.1023/A:1027275225668.
- (54) Kryukova, G. N.; Zenkovets, G. A.; Mestl, G.; Schlögl, R. Structural study of titanium doped vanadia and vanadium doped titania catalysts. *React. Kin. Catal. Lett.* **2003**, *80* (1), 161–169. DOI: 10.1023/A:1026000829726.
- (55) Lejon, C.; Österlund, L. Influence of phonon confinement, surface stress, and zirconium doping on the Raman vibrational properties of anatase TiO₂ nanoparticles. *J. Raman Spectrosc.* **2011**, *42* (11), 2026–2035. DOI: 10.1002/jrs.2956.
- (56) Hearne, G. R.; Zhao, J.; Dawe, A. M.; Pischedda, V.; Maaza, M.; Nieuwoudt, M. K.; Kibasomba, P.; Nemraoui, O.; Comins, J. D.; Witcomb, M. J. Effect of grain size on structural transitions in anatase TiO₂: A Raman spectroscopy study at high pressure. *Phys. Rev. B* **2004**, *70* (13), 717. DOI: 10.1103/PhysRevB.70.134102.
- (57) Tobaldi, D. M.; Pullar, R. C.; Seabra, M. P.; Labrincha, J. A. Fully quantitative X-ray characterisation of Evonik Aeroxide TiO₂ P25®. *Mater. Lett.* **2014**, *122*, 345–347. DOI: 10.1016/j.matlet.2014.02.055.
- (58) Liu, L.; Zhao, H.; Andino, J. M.; Li, Y. Photocatalytic CO₂ Reduction with H₂O on TiO₂ Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry. *ACS Catal.* **2012**, *2* (8), 1817–1828. DOI: 10.1021/cs300273q.
- (59) Kovačič, Ž.; Likozar, B.; Huš, M. Electronic properties of rutile and anatase TiO₂ and their effect on CO₂ adsorption: A comparison of first principle approaches. *Fuel* **2022**, *328* (19), 125322. DOI: 10.1016/j.fuel.2022.125322.
- (60) Amore Bonapasta, A.; Filippone, F.; Mattioli, G.; Alippi, P. Oxygen vacancies and OH species in rutile and anatase TiO₂ polymorphs. *Catal. Today* **2009**, *144* (1-2), 177–182. DOI: 10.1016/j.cattod.2009.01.047.

- (61) Kuriechen, S. K.; Murugesan, S.; Paul Raj, S. Mineralization of Azo Dye Using Combined Photo-Fenton and Photocatalytic Processes under Visible Light. *J. Catal.* **2013**, *2013* (4), 1–6. DOI: 10.1155/2013/104019.
- (62) Yang, J.; Bai, H.; Tan, X.; Lian, J. IR and XPS investigation of visible-light photocatalysis—Nitrogen–carbon-doped TiO₂ film. *Appl. Surf. Sci.* **2006**, *253* (4), 1988–1994. DOI: 10.1016/j.apsusc.2006.03.078.
- (63) Lamoureux, B.; Singh, V. R.; Jovic, V.; Kuyyalil, J.; Su, T.-Y.; Smith, K. E. Structural and electronic properties of thermally evaporated V₂O₅ epitaxial thin films. *Thin Solid Films* **2016**, *615*, 409–414. DOI: 10.1016/j.tsf.2016.07.062.
- (64) Choudhury, B.; Choudhury, A. Oxygen defect dependent variation of band gap, Urbach energy and luminescence property of anatase, anatase–rutile mixed phase and of rutile phases of TiO₂ nanoparticles. *Phys. E* **2014**, *56*, 364–371. DOI: 10.1016/j.physe.2013.10.014.
- (65) Landmann, M.; Rauls, E.; Schmidt, W. G. The electronic structure and optical response of rutile, anatase and brookite TiO₂. *J. Phys. Condens. Matter.* **2012**, *24* (19), 195503. DOI: 10.1088/0953-8984/24/19/195503. Published Online: Apr. 19, 2012.
- (66) Lian, Z.; Deng, H.; Xin, S.; Shan, W.; Wang, Q.; Xu, J.; He, H. Significant promotion effect of the rutile phase on V₂O₅/TiO₂ catalysts for NH₃-SCR. *Chem. Commun.* **2021**, *57* (3), 355–358. DOI: 10.1039/d0cc05938b.
- (67) Jaegers, N. R.; Lai, J.-K.; He, Y.; Walter, E.; Dixon, D. A.; Vasiliu, M.; Chen, Y.; Wang, C.; Hu, M. Y.; Mueller, K. T.; Wachs, I. E.; Wang, Y.; Hu, J. Z. Mechanism by which Tungsten Oxide Promotes the Activity of Supported V₂O₅/TiO₂ Catalysts for NO_x Abatement: Structural Effects Revealed by ⁵¹V MAS NMR Spectroscopy. *Angew. Chem. Int. Ed.* **2019**, *58* (36), 12609–12616. DOI: 10.1002/anie.201904503. Published Online: Aug. 1, 2019.
- (68) Hu, J. Z.; Xu, S.; Li, W.-Z.; Hu, M. Y.; Deng, X.; Dixon, D. A.; Vasiliu, M.; Craciun, R.; Wang, Y.; Bao, X.; Peden, C. H. F. Investigation of the Structure and Active Sites of TiO₂ Nanorod Supported VO_x Catalysts by High-Field and Fast-Spinning ⁵¹V MAS NMR. *ACS Catal.* **2015**, *5* (7), 3945–3952. DOI: 10.1021/acscatal.5b00286.

(69) Primet, M.; Pichat, P.; Mathieu, M. V. Infrared study of the surface of titanium dioxides. I. Hydroxyl groups. *J. Phys. Chem.* **1971**, *75* (9), 1216–1220. DOI: 10.1021/j100679a007.

(70) Tanaka, K.; White, J. M. Characterization of species adsorbed on oxidized and reduced anatase. *J. Phys. Chem.* **1982**, *86* (24), 4708–4714. DOI: 10.1021/j100221a014.

(71) Hadjiivanov, K. I.; Klissurski, D. G. Surface chemistry of titania (anatase) and titania-supported catalysts. *Chem. Soc. Rev.* **1996**, *25* (1), 61. DOI: 10.1039/cs9962500061.

(72) Mathieu, M. V.; Primet, M.; Pichat, P. Infrared study of the surface of titanium dioxides. II. Acidic and basic properties. *J. Phys. Chem.* **1971**, *75* (9), 1221–1226. DOI: 10.1021/j100679a008.