

Original Paper

An isotope-free transient kinetic approach to probe reactivity during the oxidative scission of ketones over $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$

Si-Wen Wang^{*}, Ya-Qin Tang, Ran Zhu, Jesse Q. Bond

Department of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244, USA

ARTICLE INFO

Article history:

Received 12 August 2025

Received in revised form

17 November 2025

Accepted 24 May 2026

Available online 29 May 2026

Edited by Min Li

Keywords:

Ketone oxidation

Transient kinetic analysis

Supported vanadium oxides

Isotope-free methodology

Structure-function relationship

ABSTRACT

Although the oxidative scission mechanism of carbonyl compounds over alumina-supported vanadium oxides has been extensively studied, quantifying surface kinetic parameters under steady-state conditions remains challenging with conventional techniques such as temperature-programmed desorption (TPD). In this work, we establish an isotope-free transient kinetic approach to investigate the oxidative scission of ketones over $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ with surface vanadium loadings ranging from 0.03 to 8 $\text{V}\cdot\text{nm}^{-2}$. Before kinetic measurement, the materials were characterized by Raman and UV-vis spectroscopy. Vanadium species on the inert support were found to exist as isolated tetrahedral VO_4 units at loadings below 0.8 $\text{V}\cdot\text{nm}^{-2}$, polymeric vanadate networks ($\text{V}-\text{O}-\text{V}$) at 0.8–4 $\text{V}\cdot\text{nm}^{-2}$, and crystalline V_2O_5 appearing only above monolayer coverage ($\geq 8 \text{ V}\cdot\text{nm}^{-2}$). Two unlabeled ketones with similar structures were selected as probe reactants, enabling the determination of key kinetic parameters, including the quantity of surface intermediate, mean residence time, surface coverage, and site time yield. The transient profiles revealed two distinct turnover regimes. Specifically, rapid turnover sites were responsible for aldehyde and acid production, and slow turnover was associated with the delayed desorption of unreacted 5-nonanone. Correlating the microkinetic parameter with spectroscopic characterization demonstrated that polymeric vanadate species render the catalyst with the highest oxidative scission activity and site time yields, whereas isolated VO_4 units and V_2O_5 can limit the reactivity. The isotope-free transient approach provides a reliable methodology for quantifying microkinetic parameters under steady-state conditions and offers mechanistic insights into structure-reactivity relationships in $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst.

© 2026 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Selective oxidation reactions of organic molecules contribute a critical portion of modern industrial synthetic chemistry, which transform hydrocarbon feedstocks into value-added chemicals (Yadav et al., 2022). Among various strategies, the direct oxidation of C–H or C–C has proved to be a practical and efficient approach to synthesize complex oxygenates from common and readily accessible starting materials. However, introducing oxygen atoms into unfunctionalized alkanes or alkenes typically requires high energy input due to the strength of C–H or C–C bonds, and the resulting selectivity is often limited (Chatzidimitriou and Bond, 2015). In

contrast, the selective oxidation of oxygenates has gained increasing interest, as these functionalized molecules can often undergo targeted reactions and be operated under milder conditions. Within this class of oxygenate oxidations, the catalytic oxidation of ketones over metal oxides is a promising synthetic route to carboxylic acid, aldehyde, or smaller ketones (Li et al., 2022). To enable these transformations under practical conditions, supported metal oxide catalysts have attracted great attention and been extensively applied in chemical industries due to their robustness and tunable activity (Védérine, 2017). As a supported metal oxide catalyst, the active reducible metal oxides are dispersed onto other inert substances, such as Al_2O_3 , SiO_2 , and TiO_2 , which not only enhance the mechanical strength but also increase the dispersion and accessibility of active sites (Weckhuysen and Keller, 2003). While many studies have focused on product distribution, potential mechanisms, and novel reaction routes in the partial oxidation reactions, a low-cost and in-situ method to quantify the microkinetics of surface-bound

^{*} Corresponding author.

E-mail address: swang2023.syr@outlook.com (S.-W. Wang).

Peer review under the responsibility of China University of Petroleum (Beijing).

intermediates and identify the active sites is still lacking. Therefore, we investigate the oxidative scission of ketones over supported vanadium oxides, combining spectroscopic characterization with transient kinetics to correlate surface speciation with reaction microkinetics.

The excellent selectivity and activity of the supported vanadium oxides have made them attractive candidates for various oxidation reactions, such as the activation of C–H bonds in alkanes as well as the selective oxidation of alcohols or ketones (Broomhead et al., 2022; Burcham and Wachs, 1999; Shan et al., 2022; Wachs and Weckhuysen, 1997). Among these reactions, ketone oxidation is a representative reaction for investigating the performance of supported vanadium oxide catalysts, as it involves well-defined elementary steps that are sensitive to the nature of surface vanadia species. However, correlating the intrinsic reactivity with the complex nature of these sites remains challenging due to variations in their geometric and electronic structures (Carrero et al., 2013). As a function of the surface vanadium density, the deposited vanadium oxides may exist as bulk V_2O_5 crystallites, two-dimensional vanadium oxide polymers, or isolated tetrahedral monomers. These vanadium oxides may render the catalyst distinct reactivity in ketone oxidation, making the precise quantification of catalytically relevant active sites essential for establishing the structure–function relationships.

In previous studies, the quantification of active sites relied on temperature-programmed surface reactions (TPSR) or temperature-programmed desorption (TPD) (Kiani and Wachs, 2024; Tang et al., 2023; Zhu et al., 2019). For example, Zhu et al. (2021) quantified the active site densities through ammonia-TPD and 3-methyl-2-butanone-TPSR. However, it is noteworthy that TPSR quantifies the active sites density on fresh catalysts, resulting in an overestimation of the amount of steady-state active sites. To overcome the limitations of TPSR and TPD in capturing the steady-state surface behavior, transient experiments offer an opportunity to probe catalytic processes and surface-bound intermediates under reaction conditions. In this study, we utilized a transient experiment that is inspired by steady-state isotopic transient kinetic analysis (SSITKA). As a powerful technique to characterize the kinetics of heterogeneous catalytic reactions, SSITKA has been employed in various studies to determine *in situ* kinetic information (Birky et al., 2013; Kammert et al., 2018, 2021; Otroshchenko et al., 2024; Shannon and Goodwin, 1995; Wang et al., 2025). Generally, SSITKA involves a rapid step change between isotopically labeled small molecules while monitoring the transient responses of products. Isotopic labeling is ideal for maintaining the isothermal, isobaric, and compositionally stable conditions during the step change. However, the economy of using isotopes is nonideal for long-time-scale reaction. Studies have shown that it can also be achieved using unlabeled reactants (Kiani and Wachs, 2024). For example, Kammert et al. (2018) reported a transient kinetic analysis using a switch between propionic acid and butyric acid to probe surface processes during the reduction of carboxylic acid. To our best knowledge, very limited research has been conducted using unlabeled reactants to directly investigate the microkinetics of ketone oxidation reactions and further resolve surface intermediate dynamics under steady-state conditions. Unlike previous transient studies that mainly focus on labeled molecules or simple redox reactions, this work introduces an isotope-free transient kinetic analysis method. This work demonstrates a more economical and flexible approach to identify surface intermediates, obtain microkinetic parameters, evaluate the catalytic performance, and elucidate the structure–activity correlations of supported VO_x catalysts without relying on isotopic labeling. Evaluating the corresponding products allows for a direct quantification of intermediates. In addition, surface

coverage, activity distribution on active sites, and other complex kinetic parameters can be further developed. The transient response analysis also allows the identification of rapid and slow turnover regimes, thereby offering new mechanistic insights into the oxidative scission of ketones. Furthermore, by examining various loading vanadium oxide catalysts, it can reveal how the polymerization degree and oxidation state of VO_x species govern the catalytic activity. These aspects collectively represent key innovations beyond existing methodologies.

In this study, we selected two structurally similar, unlabeled probe molecules, which are 4-heptanone and 5-nonanone, to perform transient kinetic analysis while maintaining stable reaction conditions. The oxidative scission of these ketones was conducted over $VO_x/\gamma-Al_2O_3$ catalysts. The catalysts investigated in this study comprise a series with varying vanadium surface densities, all of which were prepared from the same batch as those used in our previous studies, where their structural and textural characteristics have been confirmed. According to established mechanistic knowledge, selective ketone oxidation on vanadium oxide catalysts firstly proceeds via the bond cleavage between the carbonyl carbon and α -carbon, as shown in Fig. 1 (Tsang et al., 2016; Zhang et al., 2013; Zhu et al., 2021). For both linear and symmetric ketones, cleavage on either side of the carbonyl group yields identical primary products. Consequently, the analysis can focus on product distribution without ambiguity from the scission position. In addition, the primary objective of this work is to develop and validate an economical isotope-free steady-state transient kinetic methodology for quantifying surface intermediates and microkinetic parameters, rather than to introduce a new catalyst formulation. The present work addresses the critical challenge of correlating the intrinsic reactivity of $VO_x/\gamma-Al_2O_3$ catalysts with the distribution of surface vanadium oxide species under steady-state conditions. Raman spectroscopy and UV-vis were employed to obtain molecular-level insights into the nature of surface vanadia species and evaluate the degree of surface polymerization. Furthermore, a transient experiment utilizing structurally similar ketones was conducted to quantify the intermediate coverage, residence times, and site time yield (STY) under undisturbed steady-state conditions. By integrating spectroscopic characterization with transient kinetics, this study establishes a direct structure–function relationship between the distribution of active species and the catalytic performance, which offers an applicable approach for investigating heterogeneous oxidation catalysis.

2. Materials and methods

2.1. Reagents

$\gamma-Al_2O_3$ (204 $m^2 \cdot g^{-1}$, Advanced Materials, $\geq 97\%$, particle size: 45–90 μm), oxalic acid (Acros Organic, $\geq 99\%$), and ammonium metavanadate (Sigma-Aldrich, 99.5%) were used to synthesize the

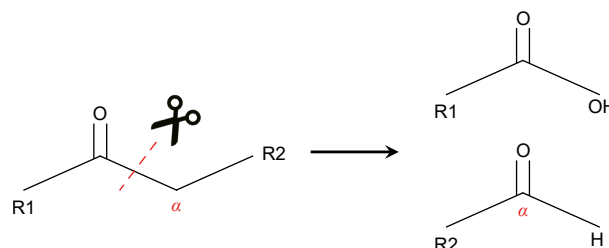


Fig. 1. The C–C cleavage during the selective oxidation of ketones.

catalyst. Vanadium pentoxide (Acros Organic, $\geq 98\%$) was applied as a standard reference in material characterization.

5-nonanone (Thermo scientific, 98%) and 4-heptanone (Aldrich, $\geq 98\%$) were selected as probe molecules in both steady-state oxidation reactions and transient experiments. Additional chemicals used for calibration of analytical instruments included propionaldehyde (Acros organics, $\geq 99\%$), butyric acid (Acros organics, $\geq 99\%$), butyraldehyde (Acros organics, $\geq 99\%$), and valeric acid (Acros organics, $\geq 99\%$).

Compressed air was utilized to pre-calcine the catalysts, to remove organic impurities and re-oxidize the vanadium oxides. Helium (Airgas, ultra-high purity) and oxygen (Airgas, ultra-high purity) were individually supplied and manually mixed to serve as carrier gas and oxidant, respectively. In the transient SSITKA experiments, two gas feeds were required to accommodate the switching between two probe reactants. In the 5-nonanone feed line, a pre-mixed He/O₂ (Airgas, 15% O₂, Helium balance) was used to serve as both the oxidant and the carrier gas. In the 4-heptanone feed line, a customized gas mixture, including helium, argon, and ethane (Airgas, 1% Argon, 1% torr ethane, Helium balance) was utilized. In this mixture, helium still served as carrier gas, while ethane and argon acted as the inert tracer to correct gas-phase holdup. To maintain an identical gas-phase oxygen partial pressure in the gas feed, pure O₂ (Airgas, ultra high purity) was diluted with the mixture of He/Ar/ethane at an approximate volumetric ratio of 1:5, thereby providing a consistent aerobic condition.

2.2. Catalyst synthesis

Catalysts were synthesized through the incipient wetness impregnation method (Zhu et al., 2021). The synthesis procedure is schematically shown in Fig. 2. γ -Al₂O₃ was employed as the catalyst support. Prior to impregnation, the support was pre-calcined in compressed air by heating from 293 to 723 K at a ramp rate of 3 K·min⁻¹ and followed by a 4-h hold at 723 K under a 60 sccm air flow to remove surface impurities. The γ -Al₂O₃ was then cooled down to room temperature. Aqueous solutions of ammonium metavanadate (NH₄VO₃) and oxalic acid (C₂O₄H₂) were prepared in a 1:2 M ratio (Feng and Vohs, 2004). The concentration of the vanadium precursor was adjusted to achieve a range of surface vanadium loadings (0.03–8.0 V·nm⁻²), which was calculated according to the following equations (Zhu et al., 2018):

$$V = \frac{N_V \cdot N_A}{m_s \cdot A_s} \quad (1)$$

$$V_M = \frac{N_V}{N_V \cdot MW_V + m_s} \quad (2)$$

here, V is the surface vanadium loading (V·nm⁻²); N_V is the number of moles of vanadium atoms, N_A represents Avogadro's number, m_s is the mass of γ -Al₂O₃, A_s is the surface area of γ -Al₂O₃, V_M is the molar vanadium loading per unit mass of VO_x/γ-Al₂O₃ (μmol V·g⁻¹), and MW_V is the molar mass of vanadium.

After impregnation, the samples were dried overnight at 338K and subsequently calcined under the same conditions as γ -Al₂O₃. This calcination process enables the decomposition of the precursor salts and the formation of vanadium in the +5 oxidation state (Burcham and Wachs, 1999). The solid samples were ground and sieved to obtain fine particles after the calcination.

2.3. Material characterization

2.3.1. Raman spectroscopy

Raman spectroscopy was performed using a confocal Raman microscope consisting of a Raman spectrometer (Renishaw, Invia) combined with a Leica DM2700P microscope. Approximately 50 mg of powdered sample was loaded into a 1/4 borosilicate tube and held by two plugs of quartz wool. Prior to spectral acquisition, the samples were calcined to dehydrate, following the same temperature program described above. A molecular sieve moisture trap was installed in the gas line to remove residual moisture. Then, the sample tube was cooled down to 298 K, pressurized to 2 bar gauge, and sealed by two block valves to prevent hydration during transfer. The sample tube was then transferred to the Raman spectrometer chamber. Spectra were collected at room temperature using 5%–10% laser power and accumulating three scans. Each scan was acquired over 30 s, with a total spectral range of 0–1500 cm⁻¹. Scans were collected at intervals of 5–10 min. No laser-induced sample degradation was observed during measurements.

2.3.2. Diffuse reflectance (DR) UV-vis spectroscopy

Diffuse reflectance (DR) UV-vis spectra were carried out using an Evolution 300 UV-vis spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory and a high temperature chamber (Harrick Scientific). A series of VO_x/γ-Al₂O₃ catalysts (0.03–8.0 V·nm⁻²) was measured. The spectra range was set to 200–800 nm. Approximately 200 mg of the powdered sample was loaded into a 5 mm sample holder and then placed inside the chamber. Prior to data acquisition, samples were calcined in flowing air (100 sccm) at 723 K for 4 h to ensure complete dehydration. Subsequently, the chamber was cooled to 323 K under a flow of

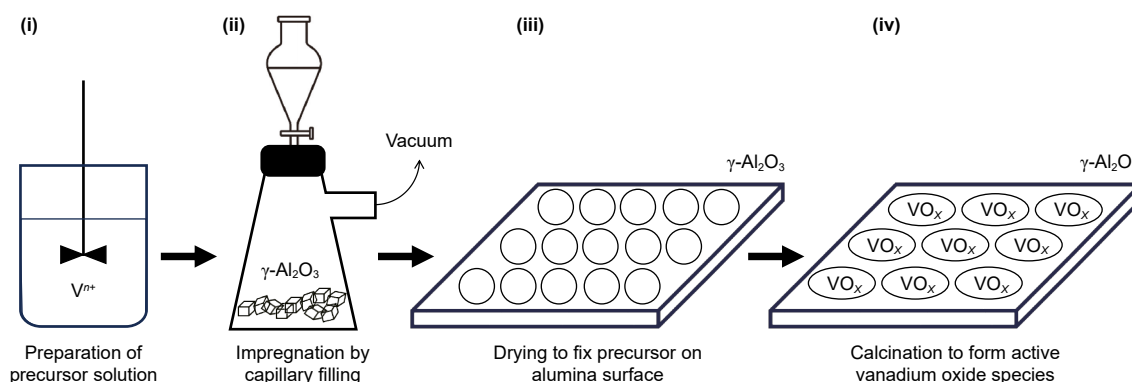


Fig. 2. The scheme of the incipient wetness impregnation method to synthesize the various loading VO_x/γ-Al₂O₃.

helium (100 sccm). A moisture trap was installed to remove the residual water vapor from both helium and air streams (Restek).

Diffuse reflectance data were converted to Kubelka-Munk units using the following transformation equation:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (3)$$

The band edge energy (E_g) for allowed electronic transitions was estimated by extrapolating the linear portion of $[F(R)hv]^2$ versus hv plot in the low-energy range, where hv is the photon energy (Gao and Wachs, 2000).

2.4. The steady state rates of ketone oxidation and conversion measurements

Steady-state oxidative scission reactions of 4-heptanone and 5-nonanone were carried out in an upstream fixed-bed reactor, which was enclosed in a high-temperature furnace. The scheme of the reactor has been shown in our previous study (Zhu et al., 2018). Temperature control, regulation and monitoring were achieved by utilizing a PID temperature controller (Love Controls Series 16A) and a type K thermocouple (Omega). All transfer lines were heat-traced and maintained at 423 K to prevent condensation of chemicals.

For each experiment, 15 mg of $8.0 \text{ V}\cdot\text{nm}^{-2} \text{ VO}_x/\gamma\text{-Al}_2\text{O}_3$ was diluted with quartz powder at a 1:4 ratio to mitigate temperature rising during exothermic reactions. The catalyst bed was positioned at the center of the reactor and secured by two quartz wool plugs. Before the reaction, the $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ was calcined *in situ* under flowing air using the same calcination protocol as described in the catalyst synthesis section. After calcination, the reactor temperature was cooled to the target reaction temperature (433–493 K) before introducing the reaction gas mixture. Subsequently, a mixture of ultra-high-purity helium and oxygen (1:5 volumetric ratio) was introduced by mass flow controllers (Brooks 5850S). Liquid ketones were initially vaporized by the custom-built vaporizer to eliminate solvent effects and then fed by the syringe pump (Cole Parmer series 100) along with the gas stream. The partial pressure of the ketone was adjusted and maintained at 1.07 torr. The feed stream, comprising helium, oxygen, and ketone, was directed either to the packed bed or an empty bypass by a 6-port valve. Initially, the gas mixture was passed through the bypass until the system reached the first steady state. Subsequently, the valve was rapidly switched the 6-port valve to divert the stream through the catalyst bed and initiate the reaction immediately. The system was then continuously operated under reaction conditions until a new steady state was established.

The effluents were analyzed by online gas chromatography (HP 5890 GC). All organic compounds were detected by a flame ionization detector (FID). The detection of carbon oxides was achieved by a thermal conductivity detector (TCD). An HP-INNOWAX column and a Restek ShinCarbon ST Micropacked column were coupled with an FID and an TCD detector, respectively. Accordingly, the molar flow rate of reactants and oxidation products was normalized by catalyst mass. The fractional conversion of ketones to the corresponding aldehyde or acid products j was calculated on a carbon basis, as shown in Eq. (4):

$$X_R = \frac{\sum_{j \neq R} F_j \cdot N_j}{F_R \cdot N_R} \quad (4)$$

here, X_R is the fractional conversion of the ketones, F_j is the mass-normalized flow rate of product j , N_j is the corresponding number of carbon atoms in the molecule of product j , F_R is the feeding

molar flow rate of ketone, and N_R is the number of carbons in the reactant.

2.5. Transient kinetic analysis

Transient kinetic experiments were carried out in a custom-built fixed-bed reactor system equipped for time-resolved product sampling and inert tracer monitoring. 5-nonanone and 4-heptanone were selected as probe molecules due to their structural similarity, enabling a direct comparison of kinetic responses with limited effects on the reaction conditions. All experiments were performed in the vapor phase to avoid solvent effects. A schematic of the reactor system is provided in Fig. 3. The components were quantified by a gas chromatograph (HP 6890 GC), while a residual gas analyzer (RGA) was used to track the inert tracer signal and determine the zero time-on-stream. A 34-port multi-position valve (Valco) enabled sequential sampling of reactor effluent during transients, allowing collection of up to 16 individual time-resolved samples per experiment. The collection of each sample is less than 1 s.

The system included two independent feed gas lines to deliver different ketone reactants: (i) a commercially available helium/15% O_2 mixture, and (ii) a helium/1% ethane/1% argon blended with pure oxygen by mass flow controllers (Valco and Brooks 5850S). The composition of two streams was matched in O_2 partial pressure, thereby avoiding compositional disturbances during switching. All gas containing helium was dried by the molecular sieve (Restek) to remove residual moisture before flowing through the catalyst bed.

The catalyst bed ($\sim 0.1 \text{ g}$, $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$, $0.03\text{--}8 \text{ V}\cdot\text{nm}^{-2}$) was placed between two plugs of quartz wool and held in the center of the tube by quartz chips. Similarly, the catalyst bed was pretreated *in situ* following the same calcination protocol described in previous sections, then cooled to the reaction temperature (493 K) under flowing $\text{He}/15\% \text{ O}_2$. The reactant 5-nonanone was fed into the reactor until a steady-state conversion was reached (typically 20 h). In parallel, the corresponding ketone (4-heptanone) was introduced through the bypass line and held until saturated vapor-phase concentration of 4-heptanone was achieved. A 4-port switching combined with a back-pressure regulator was used to alternate between different ketone feeds. Once both sides stabilized, the rapid switch from 5-nonanone to 4-heptanone was executed, indicating the initiation of the transient period. Effluent samples were collected at defined time points and manually injected into the GC for quantification. Sampling continued until the oxidation of 4-heptanone reached a new steady state and all residual 5-nonanone and the partial oxidation products—butyraldehyde and propionaldehyde were fully desorbed from the catalysts. All transient experiments were repeated at least twice under identical conditions to ensure reproducibility. Minor variations associated with parameter extraction were observed but remained within experimental uncertainty and did not affect the kinetic trends discussed.

To investigate the potential re-adsorption effect, the experiments were individually conducted under the 160–250 sccm gas flow rate. In all cases, the gas-phase holdup was determined by the integration of the transient response of ethane. All transient responses were normalized by the baselines and rescaled from 0 to 1 through Eq. (5) (Efstathiou and Verykios, 1997).

$$F(t) = \frac{y(t) - y_0}{y_{\text{end}} - y_0} \quad (5)$$

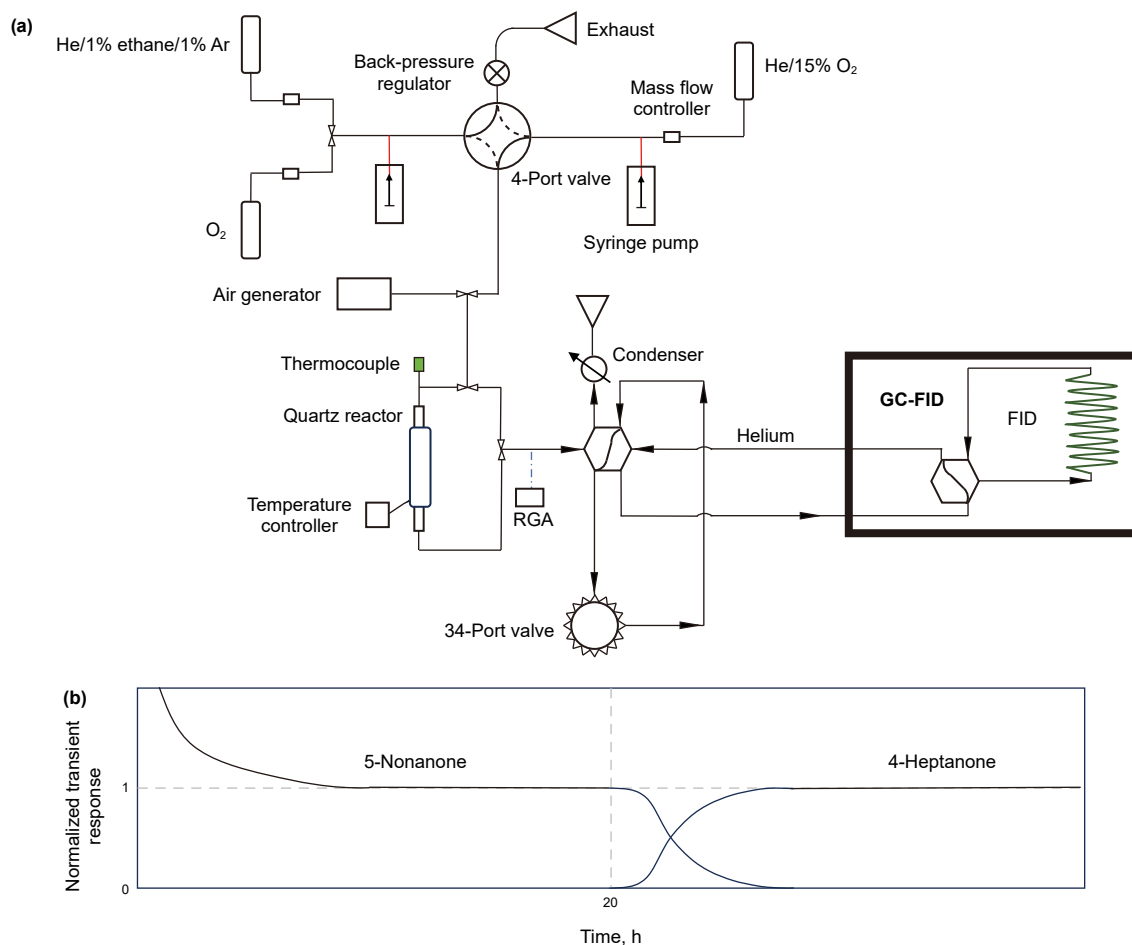


Fig. 3. (a) The scheme of the reactor system used to analyze transient reaction kinetics; (b) The simplified schematic diagram of the switching between 5-nonanone and 4-heptanone.

here, $F(t)$ represents the normalized transient response at time t , and y_0, y_{end} represent the initial and the final signal of intensities, respectively.

The mean surface residence time (τ_i) of each intermediate was determined by integrating the difference between each normalized transient response (F_i) and the inert tracer ethane, as shown in Eq. (6):

$$\tau_i = \int_0^{\infty} (F_i - F_{\text{ethane}}) dt, \quad (i = 5\text{-nonanone, butyraldehyde, valeric acid}) \quad (6)$$

The amount of surface intermediates leading to a specific product was determined by Eq. (7):

$$N_i = \tau_i R_i \quad (7)$$

here, R_i represents the mass-normalized rate of oxidative scission. To simplify interpretation, the rate of oxidative scission was defined by the average formation rate for acetic acid and acetone due to the equimolar formation.

Thereafter, the surface coverage by each species θ_i was estimated by Eq. (8):

$$\theta_i = \frac{N_i}{\text{surface vanadium atoms}} \quad (8)$$

As shown in Eq. (9), the site time yield (STY) is determined:

$$\text{STY} = \frac{R}{m\rho} \quad (9)$$

here R is the oxidative scission rate and ρ is the surface site density.

3. Results and discussions

3.1. Material characterization

Raman spectroscopy was conducted to identify the dispersed vanadium oxides on the catalyst surface, which may include monomeric VO₄, polymeric V–O–V, and bulk V₂O₅. All Raman spectra were normalized by their maximum intensity. The series of spectra, which focus on the spectra window of 600–1200 cm^{−1} are listed in Fig. 4. This window offers critical vibrational signatures reflecting the existence of monomeric, polymeric, and bulk species.

The spectrum of bulk V₂O₅ serves as the standard reference. It exhibits two characteristic bands: a sharp and intense peak at 993 cm^{−1}, attributed to the vanadyl (V=O) stretching vibration, and a prominent band at 693 cm^{−1} corresponding to V–O–V bridging vibrations within the disordered layer structure (Jayachandran et al., 2021). These features are commonly used as benchmarks to identify bulk-like domains in supported vanadium oxides. When examining samples at monolayer coverage

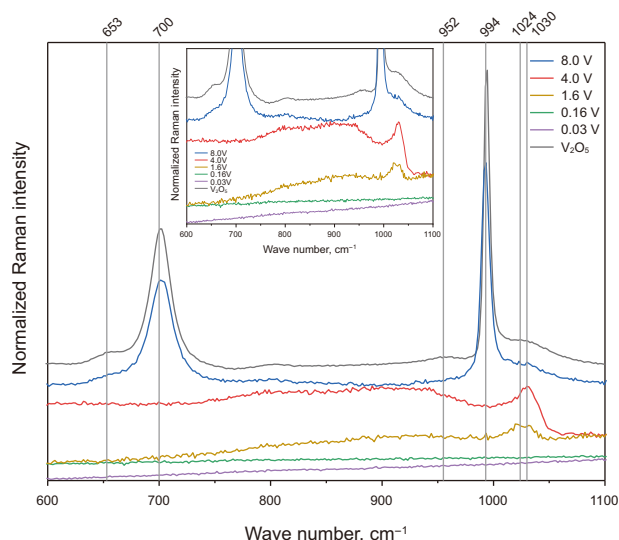


Fig. 4. Raman spectra of various vanadium loading of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$.

($8.0 \text{ V}\cdot\text{nm}^{-2}$ $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$), the band centered at 700 cm^{-1} and an intense peak at 995 cm^{-1} can also be observed, indicating the presence of vanadyl groups. However, the relatively lower intensity compared to bulk V_2O_5 indicates that the surface of the catalyst does not possess as many bulk particles as bulk V_2O_5 . In addition, a key feature for polymeric structure is the band near $1024\text{--}1030 \text{ cm}^{-1}$, which is assigned to the short $\text{V}=\text{O}$ bonds located in edge-sharing polyvanadate units (Wachs, 2013). This feature becomes prominent in the spectra of $4.0 \text{ V}\cdot\text{nm}^{-2}$ and $1.6 \text{ V}\cdot\text{nm}^{-2}$ $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$, suggesting the appearance of a polymeric structure. In the meantime, the disappearance of features at 995 and 700 cm^{-1} implies a structural transition from crystalline domains to polymeric networks. In contrast, no distinct Raman bands are observed at the lowest loadings (0.16 and $0.03 \text{ V}\cdot\text{nm}^{-2}$). The two most plausible reasons are: (i) the low vanadium surface density, which reduces the scattering cross section, and (ii) strong background fluorescence from the support, which may cover the weak signal originating from the VO_x . Although the surface is supposed to be covered by monomeric VO_4 , the above factors hinder the detection of its characteristic features. In conclusion, supported vanadium oxides exist as a two-dimensional phase below monolayer coverage, while the formation of a complete VO_x monolayer leads to the emergence of crystalline V_2O_5 nanoparticles, as illustrated in Fig. 5.

To further provide insight into the structural analysis, diffuse reflectance UV-vis spectroscopy (UV-vis) was conducted across a series of supported vanadium catalysts with loading ranging from 0.03 to $8.0 \text{ V}\cdot\text{nm}^{-2}$. The results are shown in Fig. 6, and the calculated edge energies are summarized in Table 1. The diffuse reflectance UV-vis spectra are presented in Kubelka-Munk units, $F(R)$, to reflect the absorption behavior of supported vanadium oxide species. For the investigation of supported vanadium oxides by UV-vis, absorption from $\gamma\text{-Al}_2\text{O}_3$ is negligible compared to the vanadium cations (Gao and Wachs, 2000). Therefore, the edge energy (E_g) obtained from UV-vis directly reflects the electronic transitions associated with vanadium oxides. Therefore, by analyzing the variation in E_g , information on local structures and polymerization state of VO_x on $\gamma\text{-Al}_2\text{O}_3$ can be obtained.

It can be observed that E_g decreases from 3.67 eV at the lowest vanadium loading sample ($0.03 \text{ V}\cdot\text{nm}^{-2}$) to 2.29 eV at the highest loading sample ($8.0 \text{ V}\cdot\text{nm}^{-2}$). Such variations of edge energies indicate a change in the electronic environment of the local

vanadium structure. The high energy absorption at low vanadium loading sample suggests that the highly dispersed monomers VO_4 dominate the surface, which requires higher energy for electronic transitions due to their more localized electronic environments (Yoshida et al., 2004). In contrast, increasing vanadium concentration promotes the formation of oligomeric species or nanoparticles on the support surface, resulting in a lower energy absorption. In summary, there is a transformation from isolated monomer to more polymerized vanadate species and eventually to bulk V_2O_5 along with the increasing loading. The calculated values of E_g are in agreement with the literature (Gao and Wachs, 2000). Among low vanadium loading samples, E_g values are observed above 3.5 eV , which are typically attributed to highly distorted isolated VO_4 units or ligand effects. The band gap in the range of $2.8\text{--}3.2 \text{ eV}$ is observed in the catalysts that include polymeric VO_x . Moreover, the $8.0 \text{ V}\cdot\text{nm}^{-2}$ sample and the vanadium pentoxide exhibit the $E_g \leq 2.3 \text{ eV}$, indicating the existence of bulk V_2O_5 .

To further investigate the extent of polymerization on the surface, the average number of bridging oxygen atoms per vanadium atom (CVB) was calculated by Eq. (10) (Gao and Wachs, 2000).

$$\text{CVB} = (14.03 - 3.95 E_g) (\pm 0.34) \quad (10)$$

The values of average CVB indicate the degree of polymerization of the vanadium oxide species on the support. Consequently, corresponding vanadium oxide structures can be assigned as summarized in Table 1. In summary, the UV-vis results are consistent with the trend of Raman spectra. At and above monolayer coverage ($8 \text{ V}\cdot\text{nm}^{-2}$), the catalyst surface is highly polymerized as well as partially covered by crystalline V_2O_5 . As the loading decreases to 4 and $1.6 \text{ V}\cdot\text{nm}^{-2}$, bulk V_2O_5 features diminish. Meanwhile, polymeric V-O-V networks become dominant, and potentially accompanied by a small fraction of isolated monomer VO_4 . When the vanadium loading drops below $1 \text{ V}\cdot\text{nm}^{-2}$, the surface is covered by monomeric vanadia species. Moreover, it is worth mentioning that all ketone oxidation reactions were conducted under aerobic conditions over various vanadium loading catalysts. The coordination structure of supported VO_x species remains stable under aerobic conditions due to the Eley-Rideal mechanism. The details have been provided in our group's previous paper (Zhu et al., 2021).

3.2. Steady-state oxidative scission of ketones

Since maintaining stable concentrations of reactants and products as well as flow rates is critical during the rapid switching process, the steady-state measurement was necessary to ensure the comparable steady-state kinetics of probe molecules (Shannon and Goodwin, 1995). In this study, two structurally analogous ketones, 4-heptanone and 5-nonanone, were selected due to their similar carbon chain structures, minimal steric hindrance, and identical carbonyl functional groups. It is important to clarify that the oxidative scission of linear ketones over $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ under the present aerobic conditions follows an Eley-Rideal (ER) mechanism rather than a Mars-van Krevelen redox cycle, which has been reported by Zhu et al. (2021). In this framework, gaseous molecular oxygen participates directly from the gas phase in reactions with adsorbed ketone-derived intermediates, without invoking lattice oxygen removal or cyclic $\text{V}^{5+}/\text{V}^{4+}$ redox transitions. Therefore, the steady-state and transient kinetics discussed below should be interpreted within an ER mechanism. When interacting with molecular oxygen, the reactions proceeded through selective C–C bond cleavage adjacent to the carbonyl group. This transformation yields nearly equimolar aldehyde-acid product pairs, as

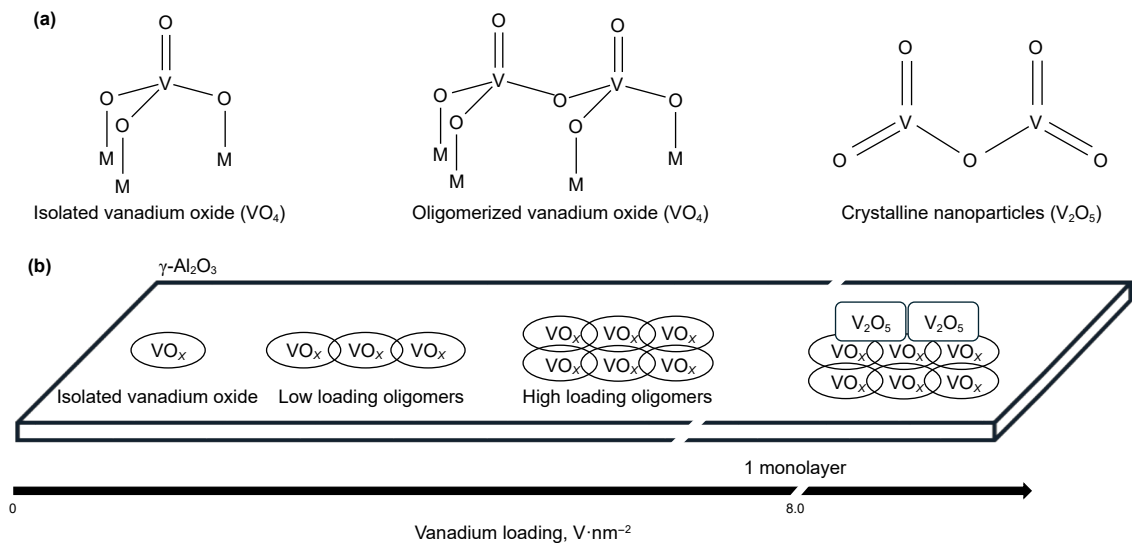


Fig. 5. Structural of dehydrated surface vanadium oxides on γ -Al₂O₃. (a) The potential types of vanadium oxides after depositing on the support. (b) The structure evolution of supported vanadium oxide species as a function of surface vanadium loading.

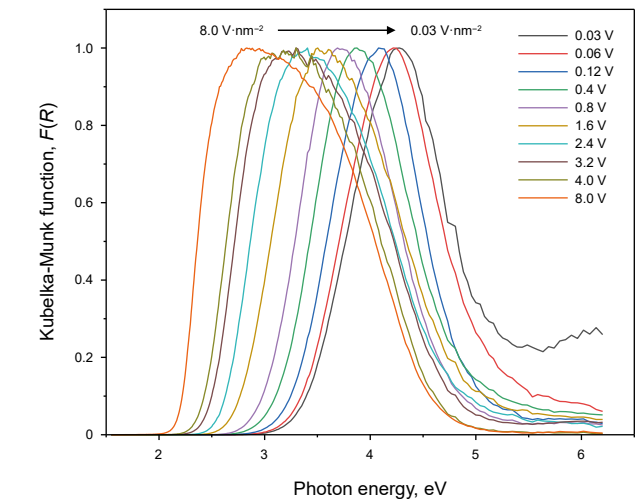


Fig. 6. UV-vis spectra over various loading vanadium oxide catalyst.

reported in a previous investigation of ketone oxidation (Chatzidimitriou and Bond, 2015; Zhu et al., 2019). A schematic representation of the proposed oxidative scission mechanism of 4-heptanone and 5-nonanone is shown in Fig. 7 to illustrate this process. The high-coverage catalyst (8.0 V·nm⁻² VO_x/γ-Al₂O₃) was

employed to achieve a more stable and measurable steady-state conversion. To ensure kinetic relevance and minimize mass transfer limitations, all steady-state reactions were maintained under differential conditions by keeping the conversion of ketones below 10% (Ountaksinkul et al., 2022).

The catalyst bed was deactivated by 1.07 torr 5-nonanone at 453 K to evaluate catalyst reactivity, as shown in Fig. 8. Upon exposure to the catalyst, rapid formation of BOH and VCOOH was observed, with initial rates of 14.62 and 13.16 μmol·g⁻¹·min⁻¹, respectively. The near-equimolar product distribution is consistent with the proposed selective oxidation pathway of ketones over supported vanadium oxides. In addition, the simplified distribution of products enables straightforward mechanistic interpretation and quantification of oxidative scission products. Subsequently, a pronounced decrease in activity occurred within the first 5 h of reaction, and then the first steady state was reached by approximately 18 h. Due to the reactions being performed under aerobic conditions, the coke effect can be avoided. The temporary loss of activity is attributed to the coverage of the active site by reactants and intermediates. At steady state, primary product formation rates of BOH and VCOOH decreased to 2.16 and 2.33 μmol·g⁻¹·min⁻¹, respectively. No carbon oxides, including CO and CO₂, were detected, suggesting the full oxidation to aldehyde and acid products without combustion. The slight discrepancy between the formation rates of BOH and VCOOH is attributed to the secondary oxidation of aldehyde fragments. Butyraldehyde

Table 1
Surface structures of various loading VO_x/γ-Al₂O₃.

Vanadium loading, V·nm ⁻²	Edge energy, eV	Average CVB number	Assigned structure
0.03	3.67	0	Isolated VO ₄
0.06	3.61	0	Isolated VO ₄
0.12	3.47	0	Isolated VO ₄
0.4	3.34	0.83	Isolated VO ₄ (d)
0.8	3.21	1.35	Polymeric VO _x
1.6	2.97	2.32	Polymeric VO _x
2.4	2.78	3.01	Polymeric VO _x
3.2	2.63	3.65	Polymeric VO _x
4.0	2.56	3.93	Polymeric VO _x
8.0	2.29	4.99	Bulk V ₂ O ₅ (dominant)
Bulk V ₂ O ₅	2.33	4.83	Bulk V ₂ O ₅

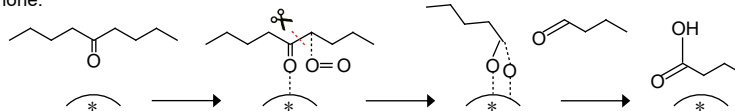
Scheme A: Steady-state of 5-nonanone

- 1) $5N + * \rightleftharpoons 5N^*$
- 2) $O_2(g) + 5N^* \rightleftharpoons I1^*$
- 3) $I1^* \rightleftharpoons BOH + I2^*$
- 4) $I2^* \rightleftharpoons VCOOH + *$

Scheme B: Transient kinetic analysis

- 1) $O_2(g) + 5N^* \rightleftharpoons I1^*$
- 2) $I1^* \rightleftharpoons BOH + I2^*$
- 3) $I2^* \rightleftharpoons VCOOH + *$
- 1) $4H + * \rightleftharpoons 4H^*$
- 2) $O_2(g) + 4H^* \rightleftharpoons I3^*$
- 3) $I3^* \rightleftharpoons POH + I4^*$
- 4) $I4^* \rightleftharpoons BCOOH + *$

The oxidative scission of 5-nonanone:



The oxidative scission of 4-heptanone:

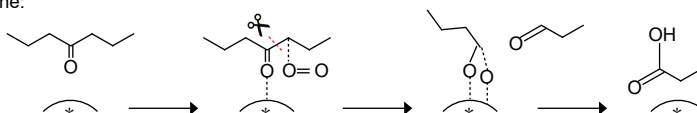
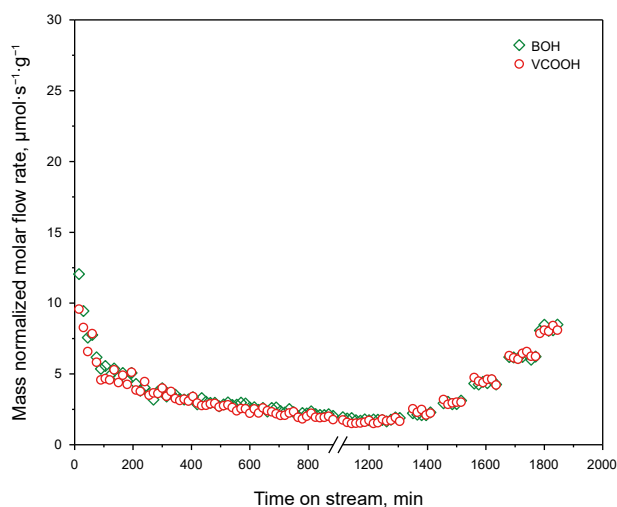


Fig. 7. The elementary steps of the oxidative scission of 5-nonanone and 4-heptanone at steady-state.

Fig. 8. Time on stream plot showing the deactivation and steady-state profile of 5N over 8.0 $VO_x/\gamma-Al_2O_3$ at various temperatures (453–493 K). Reference condition: $P_{5N} = 1.07$ torr, $P_{O_2} = 120$ torr, helium balanced, $T = 453$ K.

underwent further oxidation to produce propionaldehyde (POH) and butyric acid (BCOOH) due to the observation of trace amounts of POH and BCOOH ($\sim 0.09 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$). However, such side reactions were not the focus of this study. Therefore, the side reactions will not be taken into consideration in the later discussion.

Although the conversion of 5-nonanone was 0.97% at 453 K, the detection and quantitative accuracy of the analysis are extremely limited in subsequent transient studies. To improve both chromatographic resolution and kinetic resolution while maintaining low-conversion conditions, the reaction temperature was

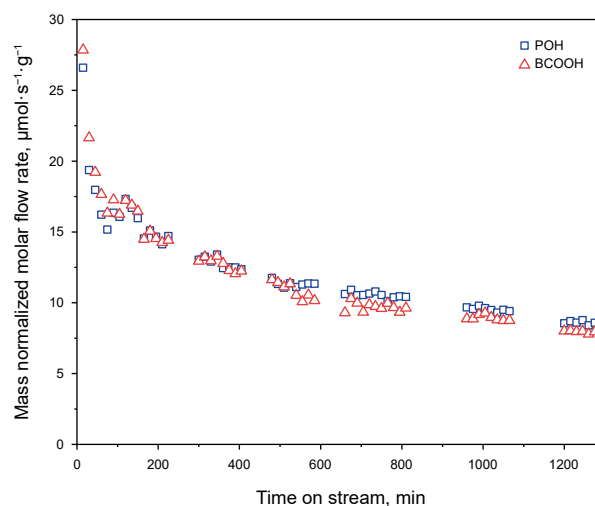
Table 2

Steady state rate and conversion of the oxidative scission of 5N at each temperature.

Temperature, K	Steady state rate, $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$			Conversion, %
	5N	BOH	VCOOH	
453	288.80	2.16	2.33	0.97
463	272.11	2.96	3.00	1.28
473	275.53	4.36	4.52	1.92
483	273.20	6.19	6.29	2.69
493	260.89	8.23	8.17	3.53

incrementally raised from 453 to 493 K in 10 K intervals, and the reaction reached steady state at each temperature step. As shown in Table 2, the conversion increased from 0.97% to 3.53% along with the rising temperature. The steady-state rates of BOH and VCOOH reached 8.23 and 8.17 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ at 493 K, respectively. This demonstrates enhanced catalyst reactivity at elevated temperature, as expected for thermally activated oxidative scission reactions. According to these results, all subsequent transient experiments were conducted at 493 K with 1.07 torr 5-nonanone.

After the evaluation of 5-nonanone, the oxidative scission of 4-heptanone was independently examined over the same catalyst bed under the identical reaction conditions to confirm the mechanistic consistency between the two ketones. The results are present in Fig. 9. The oxidation of 4-heptanone yielded product formation rates of 22.61 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ for POH and 23.02 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ for BCOOH. After approximately 20 h of deactivation, the system reached steady state with rates of 8.3 and 7.96 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, respectively, corresponding to the carbon conversion of 4.3%. The rate difference between 5N and 4H is less than 0.1%. The near-equimolar aldehyde-acid product pair and comparable kinetic values support the operation of a similar reaction pathway for both ketones. The consistency validates the

Fig. 9. Time on stream plot showing the deactivation and steady-state profile of 4H over 8.0 $VO_x/\gamma-Al_2O_3$ at 493 K. Reference condition: $P_{4H} = 1.07$ torr, $P_{O_2} = 120$ torr, He balanced, $T = 493$ K.

feasibility of the substitution of 5-nonanone with 4-heptanone in transient kinetic studies.

3.3. Transient kinetic analysis

Steady-state kinetic measurements enabled the identification of optimal conditions for probing surface intermediates during transient kinetic experiments. The transient kinetic experiment followed SSITKA methodology, which allows the examination of key kinetic parameters, including mean surface residence times (τ), the number of active intermediates (N_i), and surface coverages. These kinetic parameters are of great significance to further determine the microkinetic modeling. In this study, isotope-free steady state transient kinetic analysis was performed over $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts ($0.03\text{--}8.0\text{ V}\cdot\text{nm}^{-2}$), respectively. During the oxidation of 5-nonanone, trace side products (POH and BCOOH) were detected, which are identified as the primary scission products from 4-heptanone. To simplify the transient analysis, the switching was performed from 5-nonanone to 4-heptanone to prevent the secondary contributions from new probe molecules. Namely, the observed desorbed species were solely originating from the scission of 5-nonanone. This strategy eliminates ambiguity in the quantification of intermediates and strengthens the mechanistic interpretation of the transient data. A schematic diagram of reactions during the transient switch is shown in Fig. 10. Before the switch, the catalyst surface was predominantly covered by 5-nonanone-related intermediates, such as chemisorbed 5-nonanone and the precursors of BOH and VCOOH. Once the supply of 5-nonanone was switched to 4-heptanone, the incoming 4-heptanone rapidly established the new cycle of adsorption and activation. The pre-existing oxygenated species, derived from 5-nonanone, continued to evolve through the intrinsic transformation and desorption steps until they were completely consumed. It is noteworthy that the introduction of 4-heptanone only initiates a parallel catalytic cycle instead of creating a new reaction pathway because both ketones follow the same oxidative scission mechanism (Eley-Rideal mechanism) and engage the same classes of active sites. Importantly, the present method is

designed for quantitative kinetic analysis under steady-state operation and short transient perturbations conducted within a total experimental time-on-stream ($\leq 48\text{ h}$). As a result, it is not intended to replace dedicated long-term ($>48\text{ h}$) deactivation studies. Accordingly, catalyst stability beyond the time-on-stream window used here is outside the scope of this work.

3.3.1. Validation of transient response

Before analyzing the transient response, it was necessary to validate the measurement accuracy by correcting potential artifacts. Two primary sources of potential error need to be taken into consideration, which are gas-phase holdup and re-adsorption on the catalyst surface.

Gas-phase holdup arises from weak adsorption of gas molecules on the reactor wall or the catalyst, which may extend the apparent residence times (Shannon and Goodwin, 1995). With the correction of gas-phase hold up, interactions between gas molecules and the reactor system can be considered negligible (Kammert et al., 2018). To this end, 1% ethane was co-fed with 5-nonanone as an inert tracer due to its non-adsorptive and non-reactive nature on the supported vanadium catalysts and negligible interaction with the reactor system. When the feeding was terminated, a rapid decay of ethane was observed, as shown in the inset of Fig. 11. The residence time of ethane reflects the contribution from gas-phase holdup. And the value remained consistent across all experiments as 0.08 min, which aligns with the values of Argon measured by residual gas analyzer (RGA). This value was applied to correct for gas-phase holdup in all subsequent kinetic analysis.

In addition to gas-phase holdup, chromatographic effects arising from reversible adsorption of the species lead to a significant tail (Ledesma et al., 2014). Birky et al. (2013) proposed a mathematical correction method that extrapolated residence time versus inverse flow rate ($1/F$). However, its application to our system produced nonphysical negative results across all experiments, rendering it unsuitable for this study. Shannon and Goodwin (1995) reported that the magnitude of re-adsorption effects decreased at higher flow rates due to reduced residence

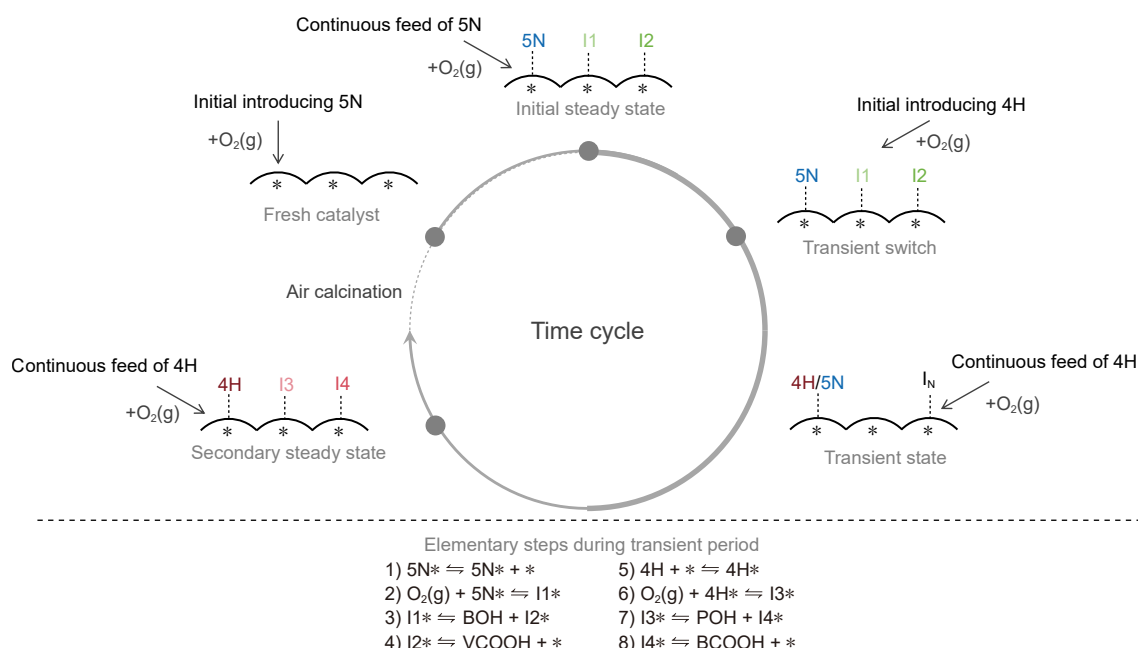


Fig. 10. The elementary steps of transient switching between 5-nonanone and 4-heptanone.

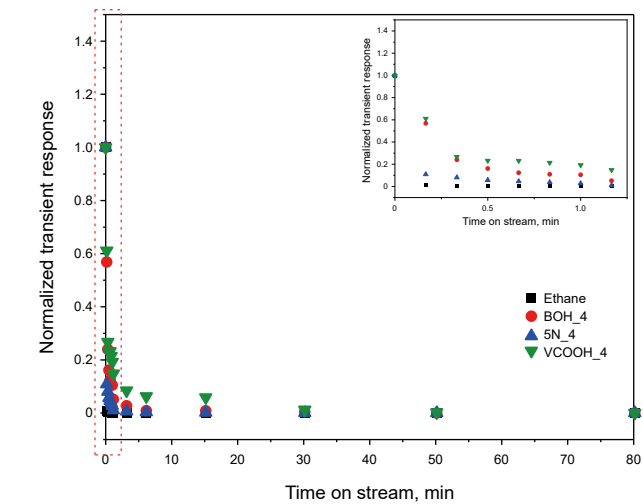


Fig. 11. 5N and products normalized transient response as a function of time over 4.0 VO_x/γ-Al₂O₃. *T* = 493 K, *P*_{5N} = 1.07 torr, *P*_{O₂} = 120 torr, 250 sccm.

times in the reactor. They also suggested that increasing the space flow rate and the length of the catalyst bed can significantly affect the transient profile until the carrier gas flow rate reaches 250 sccm. Therefore, the flow rate was set to 250 sccm, which effectively minimized the re-adsorption effect and removed residual 5-nonanone. All kinetic parameters reported in the next discussion were determined under these optimized conditions to guarantee accuracy and reproducibility.

3.3.2. Transient kinetic analysis

Since 4-heptanone was introduced after 5-nonanone reached steady state, the subsequent observed decay profiles during the transient period reflected exclusively the behavior of intermediates derived from 5-nonanone. To maintain clarity and avoid signal convolution, the discussion in this section focuses solely on the transient responses associated with the oxidation of 5-nonanone. Fig. 11 displays the normalized transient decay profiles of ethane, butyraldehyde, valeric acid, and 5-nonanone, obtained from the transient experiments on 4.0 VO_x/γ-Al₂O₃. Representative results for other vanadium loadings are provided in supplementary information, which are listed as Figs. S1–S4.

Typically, all the transient responses exhibit three distinct phases: a rapid decay, a slow decay, and a persistent background.

Such behavior is consistent across all examined catalysts. The first two phases are hereafter named as Pool A and Pool B, respectively. The identification of two distinct kinetic regimes further highlights the heterogeneity of surface reaction pathways and provides microkinetic insight into the surface behavior of reaction intermediates. Therefore, to further provide insight into the nature of Pool A and Pool B, a bi-exponential model was applied and found to be consistent with the curve of transient responses (Shou and Davis, 2013). The bi-exponential model is listed in Eq. (11) below.

$$F(t) = X_A \exp(- (t - t_0) \cdot T_A) + X_B \exp(- (t - t_0) \cdot T_B) + X_{BKG}$$
 (11)

Here, *X*_A and *X*_B represent the fractional coverage of species associated with rapid and slow turnover, while *X*_{BKG} accounts for the residual background signal. *T*_A and *T*_B are the reciprocal of the system holdup time for each pool. The parameters of curve fits are listed in Table 3, and the fitted curves are shown in Fig. 12. In addition, a plot includes fitted curves and experimental curves is listed in Fig. S5 as an example. For all fitted profiles, the coefficient of determination (*R*²) exceeded 0.98 and residuals showed no systematic deviation, supporting the adequacy of the bi-exponential model for distinguishing Pool A and Pool B. The bi-exponential model fitted curves allow the integration of each normalized transient response and further quantify key kinetic parameters, which are calculated with Eqs. (6)–(9). The calculated parameters are summarized in Table 4 and further utilized to provide insight into the microkinetic and transient behavior of reactive intermediates as discussed below.

It was found that the transient profile of 5-nonanone features a sharp decay completed within the initial 20 s (Pool A), which closely resembles the ethane tracer profile. It indicates a fast removal or consumption of 5-nonanone. It is highly possible to attribute to the desorption of weakly adsorbed 5-nonanone species due to the broken equilibrium. As shown in Table 3, the *X*_A of 5-nonanone (≤15%) showed that only a minor portion of 5-nonanone was correlated with fast turnover. In contrast, the slowly decaying Pool B represents a slow release of strongly binding 5-nonanone. When the feed of reactant was terminated, these chemisorbed species may undergo a delayed desorption due to a slow displacement by 4-heptanone. A substantial fractional coverage of slow turnover 5-nonanone species was found as greater than 85%.

For BOH and VCOOH, they exhibit a similar two-phase desorption behavior, with Pool A majorly arising from the rapid

Table 3
Fractional contribution of different sites on various loading of VO_x/γ-Al₂O₃ during the transient switch from 5N to 4H.

Vanadium loading, V·nm ⁻²	Molecule	Pool A		Pool B		Background
		<i>X</i> _A	<i>T</i> _A , min	<i>X</i> _B	<i>T</i> _B , min	<i>X</i> _{BKG}
8	5N	0.02	0.35	0.982	201.20	0.00
	BOH	0.77	3.70	0.20	350.57	0.03
	VCOOH	0.73	1677.12	0.24	0.79	0.04
4	5N	0.15	1.79	0.85	201.20	0.00
	BOH	0.90	3.15	0.11	201.20	0.00
	VCOOH	1.02	3.17	0.00	0.000	0.05
1.6	5N	0.08	1.83	0.92	201.20	0.00
	BOH	1.04	2.50	0.00	201.20	0.00
	VCOOH	1.03	1.46	0.00	201.20	0.00
0.16	5N	0.02	0.64	0.98	201.20	0.00
	BOH	1.18	2.41	0.00	201.20	0.00
	VCOOH	1.22	2.13	0.00	201.20	0.00
0.03	5N	0.04	0.53	0.96	201.20	0.00
	BOH	1.11	2.27	0.00	350.97	0.02
	VCOOH	0.03	0.02	1.65	1.72	0.00

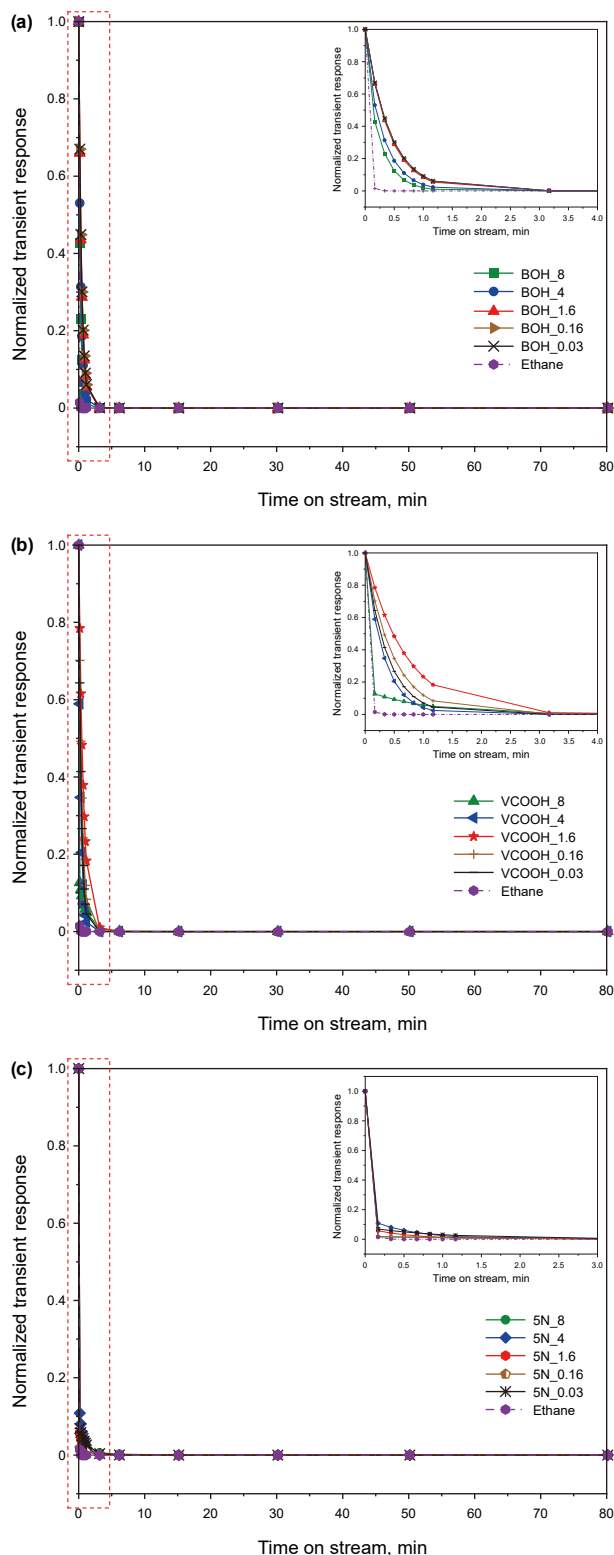


Fig. 12. The exponential fit transient response. (a) Responses of BOH; (b) responses of VCOOH; (c) responses of 5N. Reference condition: $P_{5N} = 1.07$ torr; $P_{O_2} = 120$ torr; $T = 493$ K; gas flow rate = 250 sccm.

conversion of pre-existing intermediates. It was found that a significantly higher fractional coverage of Pool A species than Pool B, as shown in Table 3. Therefore, it demonstrated that under previous steady-state conditions, the surface had already

accumulated a significant population of 'ready-to-turnover' intermediates that can quickly form aldehydes and carboxylic acids once the supply of reactants is removed. In contrast, Pool B for BOH and VCOOH reflects the slower transformations of intermediates, which only occupied a smaller portion compared to Pool A. As discussed above, the formation of aldehyde and carboxylic acid involve multiple steps, including the insertion of oxygen into the ketone, C–C bond cleavage, rearrangement, and subsequent desorption, resulting in the sluggish conversion in Pool B. In summary, these trends reinforce the interpretation that Pool A captures rapid product formation from pre-existing intermediates, while Pool B reflects slower desorption of transformation processes that persist after the removal of the reactant.

The identification of Pool B is based on exclusion criteria derived from the characteristic features of the transient response rather than on explicit separation of transport contributions. Transport-related effects such as axial bed diffusion or reversible re-adsorption typically manifest as systematic distortions in transient profiles, including pronounced tail broadening or fluctuating response. However, the sharp decaying responses of 5N and its products were observed under extremely high space flow rate, indicating the minimal effect of bed diffusion or re-adsorption. When considered together with the tracer-corrected transient methodology and the Eley-Rideal reaction mechanism, these characteristics support interpretation of Pool B as a kinetically meaningful surface process associated with strongly bound reactant-derived species or slowly transforming intermediates, rather than as a primary consequence of bed diffusion or re-adsorption.

The distinct contributions of rapid and slow turnover reflect the different surface dynamics of reactants and products. We therefore correlated the calculated kinetic parameters with surface vanadium oxide structure to gain further insight into structure-function relationships. The comparison of mean surface residence times of each species over various loading of $VO_x/\gamma-Al_2O_3$ is shown in Fig. S6. The consistently short residence time for 5-nonanone indicates that most of the adsorbed reactant was rapidly converted into reaction intermediates rather than remaining in the unreacted form to desorb. Additionally, the surface residence times of BOH and VCOOH were found to be nearly identical, with VCOOH exhibiting a slightly longer duration. The difference is likely due to mechanistic factors as aldehyde products are generated through the simple C(=O)C bond, and the formation of carboxylic acid products involves additional surface transformations. The trend is consistent with the analysis of different pool contributions.

Regarding the reaction rate, while a decrease in surface vanadium density leads to a reduction in oxidative scission activity, the reaction rate does not decrease proportionally. Specifically, the observed trend in reaction rate is $8 \text{ V} \cdot \text{nm}^{-2} \approx 4 \text{ V} \cdot \text{nm}^{-2} > 1.6 \text{ V} \cdot \text{nm}^{-2} > 0.16 \text{ V} \cdot \text{nm}^{-2} \approx 0.03 \text{ V} \cdot \text{nm}^{-2}$, indicating that catalytic activity is not solely governed by total vanadium concentration, even though vanadium species are commonly considered as the active centers. As reported by Burcham and Wachs (1999), redox-active V–O–M bridging sites are primary centers of oxidation reaction on the metal oxide supported vanadium oxides, rather than the terminal V=O groups. Therefore, the catalytic activity is supposed to be strongly influenced by the polymerization state of surface vanadia. The hypothesis is further supported by spectroscopic characterizations and kinetic analysis. As discussed previously, UV-vis and Raman analysis have revealed that the dominant surface species of the supported vanadium catalyst shift from polymeric oligomeric vanadate ($>0.8 \text{ V} \cdot \text{nm}^{-2}$) to isolated monomeric VO_4 ($<0.4 \text{ V} \cdot \text{nm}^{-2}$). Among these catalysts, the $8.0 \text{ V} \cdot \text{nm}^{-2}$ exhibits the highest site time yield (STY), indicating the highest reactivity. However, the

Table 4

Kinetic parameters derived from transient kinetic analysis of the aerobic oxidative scission of 1 torr 5-nonanone at 493 K.

Vanadium loading		Molecule	Tau ^a	Ni ^b	Site density ^c	Oxidative scission rates	STY1 ^d	STY2 ^e	θ
V·nm ⁻²	μmol·g ⁻¹		min	μmol·g ⁻¹	μmol·g ⁻¹	μmol·g ⁻¹ ·min ⁻¹			
8	2174	5N	0.06	6.29	6.90	6.58	0.95	0.00	0.003
		BOH	0.17	1.12					
		VCOOH	0.03	0.20					
4	1206	5N	0.08	9.08	10.63	6.52	0.61	0.01	0.009
		BOH	0.24	2.11					
		VCOOH	0.26	1.11					
1.6	516	5N	0.04	4.82	6.92	4.13	0.60	0.01	0.013
		BOH	0.36	1.72					
		VCOOH	0.69	2.40					
0.16	54	5N	0.04	2.88	3.25	1.14	0.35	0.021	0.061
		BOH	0.38	0.78					
		VCOOH	0.44	0.10					
0.03	10	5N	0.09	2.35	2.73	1.10	0.40	0.11	0.273
		BOH	0.38	0.50					
		VCOOH	0.33	0.29					

^a Calculated by exponential fit curve and only using data switching from 5N to 4H.^b Calculated by the sum of all carbon species.^c Calculated by the average of the steady-state rate of butyraldehyde and valeric acid.^d Calculated based on site density obtained from the transient study.^e Calculated based on the surface vanadium atom quantity.

comparable reaction rates obtained from 8.0 to 4.0 V·nm⁻² imply that increasing vanadium surface density does not significantly enhance reaction kinetics. Although 8.0 V·nm⁻² VO_x/γ-Al₂O₃ exhibits the highest degree of polymerization, the existing bulk V₂O₅ on 8.0 V·nm⁻² VO_x/γ-Al₂O₃ may hinder it from reaching a higher reactivity. Additionally, at the lowest coverages, where monomers predominate, activity declines significantly, indicating the limited ability of isolated VO₄ units to facilitate scission reactions. These results underscore the importance of polymeric vanadate species in achieving high catalytic performance.

4. Conclusion

This study provided a comprehensive microkinetic examination of the oxidative scission of ketones over 0.03 to 8 V·nm⁻² VO_x/γ-Al₂O₃ and established a transient method between two structurally similar and unlabeled probe molecules. The transient method incorporated tracer correction and flow optimization to minimize artifacts, which enable reliable quantification of rapid (Pool A) and slow (Pool B) desorption regimes. The quantification of Pool A and Pool B found that rapid turnover predominantly contributed to scission products (BOH and VCOOH), and unreacted 5-nonanone was mainly associated with slow turnover. Residence time analysis revealed a mechanistic difference between the aldehyde and acid form. Carboxylic acid as a scission product requires additional surface transformations, which is consistent with the previously derived ketone oxidation mechanism. Correlating kinetic parameters with the spectroscopic characterizations indicated that polymeric vanadate species are responsible for better catalytic performance, referring to a higher reaction rate and STY. These findings provide microkinetic and structural insights for optimizing supported vanadium oxide catalysts, which emphasize the promotion of appropriate vanadium loading to form polymeric species and enhance the catalytic performance.

5. Proposed future direction

The oxidative scission of ketones over VO_x catalysts represents a highly complex reaction network involving chemisorption, redox, and acid-base interaction on various vanadium

species. This study has developed a novel approach of utilizing unlabeled probe molecules to obtain microkinetic parameters and determine structure-activity correlations in ketone oxidative scission reactions, which provides a solid foundation for future research.

A major next step will involve density functional theory (DFT) calculations to provide atomic-level insight into the elementary steps underlying the experimentally observed transient behavior. From a computational perspective, these studies can be conducted using either periodic slab models or cluster models representative of isolated VO₄ units, polymeric VO_x domains, and V₂O₅-like motifs supported on γ-Al₂O₃. Plane-wave DFT packages (e.g., VASP or Quantum ESPRESSO) employing the projector-augmented-wave (PAW) method and GGA functionals such as PBE, with dispersion corrections when appropriate, can be employed (Kammert et al., 2021; Penschke et al., 2013). Theoretical analysis will focus on evaluating adsorption energies of ketones and key surface intermediates, as well as activation barriers associated with C–C bond scission and subsequent oxygen insertion steps. By directly comparing computed energetics with experimentally derived residence times, surface coverages, and site time yields from the isotope-free transient kinetic approach, a quantitative microkinetic framework can be established to link transient kinetic signatures with specific elementary surface processes.

CRediT authorship contribution statement

Si-Wen Wang: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Ya-Qin Tang:** Writing – review & editing, Visualization, Validation, Formal analysis, Data curation. **Ran Zhu:** Writing – review & editing, Project administration, Methodology, Conceptualization. **Jesse Q. Bond:** Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

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.

Acknowledgments

This work was supported by funding from the National Science Foundation, United States (Award 1454346) and conducted independently of any ongoing research projects in the authors' current institution.

Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petsci.2026.05.040>.

References

- Birky, T.W., Kozlowski, J.T., Davis, R.J., 2013. Isotopic transient analysis of the ethanol coupling reaction over magnesia. *J. Catal.* 298, 130–137. <https://doi.org/10.1016/j.jcat.2012.11.014>.
- Broomhead, W.T., Tian, W., Herrera, J.E., Chin, Y.H.C., 2022. Kinetic coupling of redox and acid chemistry in methanol partial oxidation on vanadium oxide catalysts. *ACS Catal.* 12 (19), 11801–11820. <https://doi.org/10.1021/acscatal.2c01852>.
- Burcham, L.J., Wachs, I.E., 1999. The origin of the support effect in supported metal oxide catalysts: *in situ* infrared and kinetic studies during methanol oxidation. *Catal. Today* 49 (4), 467–484. [https://doi.org/10.1016/S0920-5861\(98\)00442-8](https://doi.org/10.1016/S0920-5861(98)00442-8).
- Carrero, C.A., Keturakis, C.J., Orrego, A., Schomäcker, R., Wachs, I.E., 2013. Anomalous reactivity of supported V_2O_5 nanoparticles for propane oxidative dehydrogenation: influence of the vanadium oxide precursor. *Dalton Trans.* 42 (35), 12644–12653. <https://doi.org/10.1039/C3DT50611H> Chatzidimitriou.
- Chatzidimitriou, A., Bond, J.Q., 2015. Oxidation of levulinic acid for the production of maleic anhydride: breathing new life into biochemicals. *Green Chem.* 17 (8), 4367–4376. <https://doi.org/10.1039/C5GC01000D>.
- Efstathiou, A.M., Verykios, X.E., 1997. Transient methods in heterogeneous catalysis: experimental features and application to study mechanistic aspects of the CH_4/O_2 (OCM), NH_3/O_2 and NO/He reactions. *Appl. Catal. Gen.* 151 (1), 109–166. [https://doi.org/10.1016/S0926-860X\(96\)00262-1](https://doi.org/10.1016/S0926-860X(96)00262-1).
- Feng, T., Vohs, J.M., 2004. A TPD study of the partial oxidation of methanol to formaldehyde on CeO_2 -supported vanadium oxide. *J. Catal.* 221 (2), 619–629. <https://doi.org/10.1016/j.jcat.2003.10.002>.
- Gao, X., Wachs, I.E., 2000. Investigation of surface structures of supported vanadium oxide catalysts by UV–vis–NIR diffuse reflectance spectroscopy. *J. Phys. Chem. B* 104 (6), 1261–1268. <https://doi.org/10.1021/jp992867t>.
- Jayachandran, M., Rose, A., Maiyalagan, T., Poongodi, N., Vijayakumar, T., 2021. Effect of various aqueous electrolytes on the electrochemical performance of V_2O_5 spindle-like nanostructures as electrode material for supercapacitor application. *J. Mater. Sci. Mater. Electron.* 32 (5), 6623–6635. <https://doi.org/10.1007/s10854-021-05378-8>.
- Kammert, J.D., Xie, J., Godfrey, I.J., Unocic, R.R., Stavitski, E., Attenkofer, K., et al., 2018. Reduction of propionic acid over a Pd-Promoted ReO_x/SiO_2 catalyst probed by X-ray absorption spectroscopy and transient kinetic analysis. *ACS Sustain. Chem. Eng.* 6 (9), 12353–12366. <https://doi.org/10.1021/acscuschemeng.8b02820>.
- Kammert, J.D., Chemburkar, A., Miyake, N., Neurock, M., Davis, R.J., 2021. Reaction kinetics and mechanism for the catalytic reduction of propionic acid over supported ReO_x promoted by Pd. *ACS Catal.* 11 (3), 1435–1455. <https://doi.org/10.1021/acscatal.0c04328>.
- Kiani, D., Wachs, I.E., 2024. Practical considerations for understanding surface reaction mechanisms involved in heterogeneous catalysis. *ACS Catal.* 14 (22), 16770–16784. <https://doi.org/10.1021/acscatal.4c05188>.
- Ledesma, C., Yang, J., Chen, D., Holmen, A., 2014. Recent approaches in mechanistic and kinetic studies of catalytic reactions using SSITKA technique. *ACS Catal.* 4 (12), 4527–4547. <https://doi.org/10.1021/cs501264f>.
- Li, J., Huang, C.Y., Li, C.J., 2022. Deoxygenative functionalizations of aldehydes, ketones and carboxylic acids. *Angew. Chem.* 134 (10), e202112770. <https://doi.org/10.1002/ange.202112770>.
- Otroshchenko, T., Kondratenko, V.A., Zanina, A., Zhang, Q., Kondratenko, E.V., 2024. Progress through temporal analysis of products and steady-state isotopic transient kinetic analysis to elucidate oxidation, CO_2 hydrogenation and lower olefins production reactions. *ChemCatChem* 16 (16), e202400081. <https://doi.org/10.1002/cctc.202400081>.
- Ountaksinkul, K., Sripinun, S., Bumphenkiattikul, P., Vongachariya, A., Praserttham, P., Assabumrungrat, S., 2022. A review of packed bed reactor and gradient-less recycle reactor for determination of intrinsic reaction kinetics. *Eng. J.* 26 (12), 17–42. <https://doi.org/10.4186/ej.2022.26.12.17>.
- Penschke, C., Paier, J., Sauer, J., 2013. Oligomeric vanadium oxide species supported on the CeO_2 (111) surface: structure and reactivity studied by density functional theory. *J. Phys. Chem. C* 117 (10), 5274–5285. <https://doi.org/10.1021/jp400520j>.
- Shan, Y.L., Sun, H.L., Zhao, S.L., Tang, P.L., Zhao, W.T., Ding, J.W., et al., 2022. Effects of support and CO_2 on the performances of vanadium oxide-based catalysts in propane dehydrogenation. *ACS Catal.* 12 (10), 5736–5749. <https://doi.org/10.1021/acscatal.2c00878>.
- Shannon, S.L., Goodwin, Jr, J.G., 1995. Characterization of catalytic surfaces by isotopic-transient kinetics during steady-state reaction. *Chem. Rev.* 95 (3), 677–695. <https://doi.org/10.1021/cr00035a011>.
- Shou, H., Davis, R.J., 2013. Multi-product steady-state isotopic transient kinetic analysis of CO hydrogenation over supported molybdenum carbide. *J. Catal.* 306, 91–99. <https://doi.org/10.1016/j.jcat.2013.06.009>.
- Tang, S., Feng, Z., Han, Z., Sha, F., Tang, C., Zhang, Y., et al., 2023. Mononuclear Re sites on ln_2O_3 catalyst for highly efficient CO_2 hydrogenation to methanol. *J. Catal.* 417, 462–472. <https://doi.org/10.1016/j.jcat.2022.12.026>.
- Tsang, A.S.K., Kapat, A., Schoenebeck, F., 2016. Factors that control C–C cleavage versus C–H bond hydroxylation in copper-catalyzed oxidations of ketones with O_2 . *J. Am. Chem. Soc.* 138 (2), 518–526. <https://doi.org/10.1021/jacs.5b08347>.
- Védrine, J.C., 2017. Heterogeneous catalysis on metal oxides. *Catalysts* 7 (11), 341. <https://doi.org/10.3390/catal7110341>.
- Wachs, I.E., 2013. Catalysis science of supported vanadium oxide catalysts. *Dalton Trans.* 42 (33), 11762–11769. <https://doi.org/10.1039/C3DT50692D>.
- Wachs, I.E., Weckhuysen, B.M., 1997. Structure and reactivity of surface vanadium oxide species on oxide supports. *Appl. Catal. Gen.* 157 (1–2), 67–90. [https://doi.org/10.1016/S0926-860X\(97\)00021-5](https://doi.org/10.1016/S0926-860X(97)00021-5).
- Wang, S., Lou, X., Liu, B., 2025. Probing heterolytic H_2 dissociation on heterogeneous catalysts: a brief review of experimental strategies. *Processes* 13 (5), 1465. <https://doi.org/10.3390/pr13051465>.
- Weckhuysen, B.M., Keller, D.E., 2003. Chemistry, spectroscopy and the role of supported vanadium oxides in heterogeneous catalysis. *Catal. Today* 78 (1–4), 25–46. [https://doi.org/10.1016/S0920-5861\(02\)00323-1](https://doi.org/10.1016/S0920-5861(02)00323-1).
- Yadav, G.D., Mewada, R.K., Wagh, D.P., Manyar, H.G., 2022. Advances and future trends in selective oxidation catalysis: a critical review. *Catal. Sci. Technol.* 12 (24), 7245–7269. <https://doi.org/10.1039/D2CY01322C>.
- Yoshida, H., Yuliat, L., Hamajima, T., Hattori, T., 2004. Valence of highly dispersed cerium oxide species on silica quantitatively estimated by Ce LIII-edge XANES. *Mater. Trans.* 45 (7), 2062–2067. <https://doi.org/10.2320/matertrans.45.2062>.
- Zhang, L., Bi, X., Guan, X., Li, X., Liu, Q., Barry, B.D., Liao, P., 2013. Chemoselective oxidative C (CO)-C (methyl) bond cleavage of methyl ketones to aldehydes catalyzed by CuI with molecular oxygen. *Angew. Chem., Int. Ed.* 52, 11303–11307. <https://doi.org/10.1002/ange.201305010>.
- Zhu, R., Chatzidimitriou, A., Bond, J.Q., 2018. Influence of vanadate structure and support identity on catalytic activity in the oxidative cleavage of methyl ketones. *J. Catal.* 359, 171–183. <https://doi.org/10.1016/j.jcat.2018.01.006>.
- Zhu, R., Chatzidimitriou, A., Liu, B., Kerwood, D.J., Bond, J.Q., 2019. Understanding the origin of maleic anhydride selectivity during the oxidative scission of levulinic acid. *ACS Catal.* 10 (2), 1555–1565. <https://doi.org/10.1021/acscatal.9b04289>.
- Zhu, R., Liu, B., Wang, S., Huang, X., Schuarc, R.L., He, W., et al., 2021. Understanding the mechanism (s) of ketone oxidation on $VO_x/\gamma-Al_2O_3$. *J. Catal.* 404, 109–127. <https://doi.org/10.1016/j.jcat.2021.09.003>.