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Kinetics of Methyl Ketone and Levulinic Acid Oxidative Scission Over Supported Vanadium Oxide Catalysts

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Abstract

Levulinic acid (LA) is a platform chemical derived from lignocellulosic biomass. Among the various applications LA has in industrial commodities and specialty chemicals, we previously reported a novel pathway that converts LA to maleic anhydride (MA) in high yields through methyl a-carbon oxidative scission over supported vanadium oxide catalysts. However, the high selectivity of methyl scission during LA oxidation appears to be unexpected according to the trends observed during the analogous oxidative scission of methyl ketones (e.g., 2-butanone and 2-pentanone). The impacts of vanadium oxide structures, metal oxide substrates, and methyl ketone molecular structures on both selectivity and reactivity of the oxidative scission were investigated in order to understand the origins of the high MA yield resulting from LA oxidation. Surprisingly, none of the aforementioned significantly increased the selectivity of methyl scission. However, further analysis of the oxidation route from LA to MA identified a new reaction intermediate—protoanemonin—and clarified its significance for the observed high MA yield.

Reactivity data demonstrated that the rate-limiting step for the oxidative scission of LA over supported vanadium oxide is the methyl scission of protoanemonin to MA. A mechanism study of analogous methyl ketone scission was carried out to investigate the fundamentals of LA oxidation. The observed mechanistic insights suggested that the oxidative scission of methyl ketones involves both Eley-Rideal and Mars van Krevelen mechanisms. Accordingly, this joint mechanism is proposed for the first time. The active site for the methyl ketone oxidative scission was identified using pyridine poisoning, NH3 poisoning, and water co-feeding. The results suggest that adsorbed methyl ketones
on acidic sites (Lewis and Bronsted) and redox sites (V-O-M) are able to react with gas-
phase oxygen, cleaving into two fragments. The alkyl fragment can form ketones or
aldehydes with the oxygen of either. In contrast, the carbonyl fragment can form surface
acetate with lattice oxygen and desorb as acetic acid only if the lattice oxygen is in the V-
O-M bond bridge.
Kinetics of Methyl Ketone and Levulinic Acid Oxidative Scission Over Supported Vanadium Oxide Catalysts

by

Ran Zhu

B.S., Iowa State University, 2013
M.S.E., University of Pennsylvania, 2014

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CHAPTER 1

Introduction
1.1 Background: Petroleum and Its Drawbacks

The use of fossil fuel energy to power steam engines facilitated the industrial revolution, which enabled meteoric growth in the world economy. Demand for petroleum products has continued to increase since the 19th century and reached 101.04 million barrels per day in 2019.¹ This reliance on petroleum brings with it unwanted byproducts, namely greenhouse gases, the most common of which is carbon dioxide. During the pre-industrialization era, natural greenhouse gases adsorbed and reflected back heat that radiated from earth's surface to space, resulting in an average temperature on earth that is suitable for living beings. As increasing quantities of petroleum products are consumed by humans to produce heat, energy, and transportation technology, the consequently emitted greenhouse gases (Figure 1.1)² are trapped in the atmosphere and re-emit more energy to the earth’s surface, causing severe environmental problems, such as global warming and global climate change.³-⁴

![Figure 1.1. Global CO₂ concentration since AD 1. The blue line at the early 19th century indicates the beginning of the industrial revolution.](image)

In addition to the environmental considerations mentioned above, concerns about the economic
impact of the current demand for petroleum products have persisted since the 1970s. As crude oil resources are unevenly distributed throughout the world, unstable geopolitics, declining oil reserves, and rising demand for oil have led to an unbalanced supply of and demand for crude oil, driving fluctuations in crude oil prices. The WTI (West Texas Intermediate) crude oil price reached a maximum of $135 per barrel in June 2008, low points of $35 per barrel in February 2009 and $30 in January 2016, and a minimum of $19 per barrel in March 2020. Volatility in crude oil prices is inherent, and it negatively impacts the chemical and energy industries that rely on crude oil as their primary feedstock.

Environmental and economic concerns regarding human reliance on petroleum have stimulated demand for renewable energy, chemicals, fuels, and materials, driving innovations in alternative energy and hydrocarbon resources. While the transportation and energy sectors may eventually commit to decarbonization, a sustainable carbon source is essential for chemical industries. This carbon alternative would need to be compatible with current carbon-based transportation and power infrastructure, enabling industry to smooth the transition to an efficient and environmentally friendly system. Biomass, the only sustainable neutral carbon source on earth, might be the most promising successor to petroleum.
1.2 Biomass as a Sustainable Resource

Biomass consists of plant and animal materials, which are among the most abundant materials on earth. The primary products of plant biomass are C6- and C5-sugars (cellulose and hemicellulose), lignin, lipids, starches, and terpenes. Terpenes, lipids, and starches have a high energy content but low production capacity; therefore, they are employed to synthesize products with a high added value.6 Marketing limitations, together with ethical considerations, have directed the search for a long-term, large-scale replacement of petroleum toward lignocellulose (cellulose, hemicellulose, and lignin). Biofuels generated from lignocellulose have been proposed as a suitable resource, especially for transportation fuels. In the United States, transportation fuels account for nearly 76% of all petroleum products consumed and are entirely transformed into CO₂.7 This extensive use of transportation fuels such as gasoline, diesel, and jet fuel, resulted in nearly 5,130 million tons of CO₂ output in 2019 and can be directly linked with a rise in CO₂ levels in the atmosphere.1 Meanwhile, plant biomass is primarily generated from CO₂ and H₂O through photosynthesis, using sunlight as an energy source. Therefore, biomass refining has the potential to offer a closed carbon cycle, in contrast with the one-way consumption associated with conventional petroleum products.

The main drawback of lignocellulose as an alternate transportation fuel is the redundant oxygen present in its polymeric molecular structures. This necessitates biorefinery that inevitably involves destruction and deoxygenation of the original macromolecule; this process involves breaking it down into fragments and reconstructing the long alkyl carbon chain from those
fragments. Biorefinery is often expensive, energy-inefficient, and nonselective. For example, the pyrolysis of biomass takes place in anaerobic conditions, mostly in an inert gas or even hydrogen;\(^8\) direct deoxygenation often requires tungsten compounds or acidic zeolites, as well as high pressures and temperatures;\(^9\) hydroprocessing requires hydrodesulfurization catalysts introduced under high levels of hydrogen pressure to hydrogenated unsaturated groups, as well as hydrocracking large molecules;\(^{10-11}\) gasification requires a high reaction temperature and a large amount of water;\(^{12}\) and this is followed by the final step of purification to meet environmental standards and other product specifications.\(^{13}\) In contrast, petroleum, especially when derived from fossil fuels, is an unparalleled transportation fuel precursor. According to data collected by the U.S. Energy Information Administration (Figure 1.2)\(^{14}\), net petroleum imports have decreased continuously since 2005, and a balance of consumption and production is expected in the short term. Furthermore, the recent average WTI crude oil price (2015–2020) of $60 per barrel (calculated excluding the influence of the pandemic), together with innovation in
electric vehicles, has significantly squeezed the biofuel market.

Under these circumstances, one might consider utilizing the functionality inherent in biomass to generate existing chemicals that directly compete with petroleum derivatives. The conventional production of functional intermediates from oil requires dehydrogenation and heteroatom insertion, which are often conducted at high temperatures under oxygen atmosphere. However, these conditions are also suitable for the undesired combustion or total oxidation of hydrocarbons, which forms carbon dioxide, resulting in a product selectivity optimization conundrum. One promising alternative is leveraging the abundant functional groups existing in biomass components to produce building blocks that can be utilized to produce novel chemicals or families of industrial commodities, such as solvents, polymers, and plastics. For example, the production and application of biomass-based levulinic acid (LA) is an idea that has potential.

One of the essential processes involved in the initial upgrading of lignocellulose is acid-catalyzed hydrolysis, which is usually conducted at a mild temperature (100–250°C). Acid-catalyzed hydrolysis transforms the two main components of lignocellulose, hemicellulose (20–40%) and cellulose (40–50%), into small molecules, such as xylose, furfural, glucose, 5-hydroxymethylfurfural, and levulinic acid. Lignin and humins, which comprise 15–30% of lignocellulose, remain as solid residues from hydrolysis. It is worth noting that lignin is a cross-linked and aromatic-based heteropolymer consisting of three monolignols (paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol), which are connected by a C-C and ether bond.
1.3 Levulinic Acid as a Future Target for Producing Building Blocks

Among the simpler molecules produced from hemicellulose and cellulose, levulinic acid, a C5 keto acid consisting of a ketone group and a carboxylic acid group, has been selected as one of the “top 10” target chemicals among biorefinery carbohydrates.\(^{20}\) It can be derived from both cellulose and hemicellulose (Scheme 1.1). The hemicellulose\(^{21}\) refinement process begins with the dilution of acid hydrolysis to produce xylose, followed by dehydration to furfural, hydrogenation to furfuryl alcohol, and final hydration to levulinic acid (LA).\(^{22}\) Levulinic acid production from cellulose begins with the production of glucose by means of hydrolysis. The following steps involve isomerization of glucose to fructose, dehydration of fructose to 5-hydroxymethylfurfural (HMF), and the final hydration of HMF to produce LA and formic acid.\(^{23}\)

Recent studies have simplified the multistep conversion of cellulose to LA into a single aqueous system consisting of solid acid catalysts with LA yields higher than 50%.\(^{23-25}\) In contrast to many
promising biorefinery strategies that are only replicable on a laboratory scale, the feasibility of converting lignocellulose to LA has been demonstrated by a proof of concept, and it has been industrialized by many chemical companies.\textsuperscript{26}

The various applications of LA (Figure 1.3) support its recognition as one of the top bio-based platform chemicals, and some of its derivatives are themselves platform chemicals. Derivatives produced from LA include but are not limited to tetrahydrofuran (THF),\textsuperscript{27} 2-methyl-THF,\textsuperscript{27} 5-nonanone,\textsuperscript{28} ethyl-levulinate,\textsuperscript{29} a-angelicalactone,\textsuperscript{30} sodium levulinate,\textsuperscript{30} acrylic acid,\textsuperscript{31} and 1,4-butanediol,\textsuperscript{32} which have been used as solvents, fuels, flavorings, fragrances, anti-freeze agents, resins and plasticizers.\textsuperscript{33} The production of $\gamma$-valerolactone (GVL)\textsuperscript{34} and succinic acid\textsuperscript{35} from LA is especially attractive because these two chemicals are themselves platform chemicals. The hydrogenation of LA produces $\gamma$-valerolactone (GVL), which can serve as fuel extender,
flavoring, and solvent.\textsuperscript{36} The ring opening of GVL can generate 1,4-pentanediol via hydrogenation, $\gamma$-hydroxyamides or amino in the presence of amines, isomers of pentenoic acids when exposed to acid catalysts, and methyl pentanoate through transesterification.\textsuperscript{37} The iodoform reaction of LA generates succinic acid, which is another DOE “top 10” chemical.\textsuperscript{20} Among the various chemical pathways that produce LA derivatives, Jesse Bond and Anargyros Chatzidimitriou have reported a novel pathway from LA to maleic anhydride (MA) using a vanadium oxide catalyst supported on metal oxides (VO$_x$/MeO).\textsuperscript{38}

Maleic anhydride has a furan basis, with two carbonyl groups at positions two and five. These abundant functionalities allow MA to participate in many types of reactions, providing various pathways to chemicals such as unsaturated polyester resins, 1,4-butanediol, maleic acid, fumaric acid, and alkenylsuccinic anhydrides.\textsuperscript{39} The conventional production of MA uses benzene or butane. Although the oxidation of benzene over vanadia-molybdena catalyst can offer a better MA yield, the relatively low price of butane makes it an ideal resource for maleic anhydride production.\textsuperscript{40} The highest maleic anhydride yields from the oxidation of butane over vanadium phosphorus oxide catalysts are 57–65%. Because this reaction takes place at high temperatures (653–673K) and under aerobic conditions, parallel combustion is always a problem; it decreases the quantity of MA produced. Therefore, the oxidation of LA over VO$_x$/MeO at a milder temperature (548–598K), which results in an unoptimized MA yield of 70%, provides a significant opportunity for further improvement.
1.4 Project Overview

The fundamentals of LA oxidative scission to MA remain unclear. The hypothesized reaction pathway from LA to MA starts with the terminal scission of LA between the terminal carbon and the carbonyl carbon, producing formaldehyde and succinic acid. Subsequent dehydration turns succinic acid into succinic anhydride, which in turn produces MA and water through further oxidative dehydrogenation. This hypothesis is based on the oxidative scission of methyl ketones (2-butane or 2-pentanone), which are monofunctional molecules of LA. However, within the two scission pathways of methyl ketones (methyl and alkyl), the selectivity of internal scission (~90–95%), which cleaves the C-C between the carbonyl carbon and its a-carbon in the methylene bridge, dominates the reaction distribution, resulting in a contradiction when compared with observations regarding the oxidation of LA. When LA is compared with 2-pentanone, the additional carboxylic acid present in LA, which by itself would not further react over VOₓ/MeO, is the only structural difference between the two compounds.

Therefore, we have proposed three possible factors that explain the unique selectivity of MA formed via the oxidative scission of LA. These factors are i) the interaction between the probe molecules and the catalyst surface, ii) the intramolecular interaction within LA, and iii) the
combination of both. In keeping with this hypothesis, the interaction between ketones and keto acids is our first target. However, the fundamental chemistry of heterogeneous ketone oxidative scission is unclear. We have, therefore, studied the reaction and contrasted the various structure-function relationships involved in ketone oxidative scission over VOₓ/MeO (Chapter Two).

Then, the origin of selective MA production from the oxidative scission of LA is studied and discussed in Chapter Three. In Chapter Four, the oxidative scission of methyl ketones is revisited, and mechanistic insights from kinetics and spectroscopic studies are observed and discussed. The influences of acidity, basicity, and hydration on catalyst performance in aerobic ketone oxidative scission are illustrated in Chapter Five. Finally, Chapter Six addresses future works regarding i) microkinetic modeling of methyl ketone oxidative scission based on the macro kinetics data observed and the mechanism proposed in Chapter Four, and ii) a steady-state isotopic transient kinetic analysis (SSITKA) study that identifies the proposed influence of vanadium speciation on the intrinsic activity of methyl ketone oxidative scission.
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CHAPTER 2

Influence of Vanadate Structure and Support Identity on Catalytic Activity in the Oxidative Scission of Methyl Ketones

2.1 Abstract

Oxidative ketone scissions are an interesting class of reactions; they yield aldehyde and carboxylic acids as products, and they proceed over reducible oxides in the presence of molecular oxygen. This chemistry can be leveraged in the production of bio-based maleic anhydride (MA) from levulinic acid (LA) over supported vanadium oxides. Here, we probe the role of active site structure and support identity in dictating the rate of ketone oxidation. Specifically, we have prepared supported vanadium oxides in a range of loadings on SiO$_2$, $\gamma$-Al$_2$O$_3$, TiO$_2$ and CeO$_2$, and we have quantified their intrinsic activity in the oxidative scission of 2-pentanone. FT-Raman spectroscopy and temperature programmed surface oxidation (TPSO) of adsorbed methanol were employed to probe vanadium speciation and oxidation site densities. Our analysis suggests that the intrinsic activity of supported vanadates is sensitive to both vanadium oxide structure and support identity.
2.2 Introduction

Lignocellulosic biomass is abundant, carbon-based, and renewable; as such, it is often touted as a sustainable alternative to petroleum. That said, biomass is largely comprised of carbohydrates and lignin, which are heavily oxygenated relative to fossil resources.\textsuperscript{1} This creates the classic challenge of biorefining: most large-market, petroleum-based commodities (e.g., fuels) are composed of carbon and hydrogen, and matching their properties from biomass requires extensive oxygen removal.\textsuperscript{2} More often than not, deep deoxygenation is costly relative to conventional oil refining, which makes it difficult for biomass to compete as a fuel precursor alongside inexpensive crude. To foster development of bio-based technologies in the current landscape, it is essential to identify scenarios where biomass might offer a competitive advantage.

Within a refinery or petrochemical facility, \textit{introducing} chemical functionality to inert alkanes is challenging and expensive. One may, for example, point to the energy demand of aromatic production (naptha reforming) or the difficult selectivity control during partial hydrocarbon oxidation as cost drivers in the production of chemical intermediates.\textsuperscript{3, 4} In certain cases, it may be advantageous to initiate production of specialty or commodity chemicals by leveraging the inherent reactivity of biomass.\textsuperscript{5} Indeed, with the challenges in commercial development of biofuels increasingly apparent, several bio-based strategies aimed at the production of alkenes, dienes, aromatics, and oxygenates have recently come to the forefront.\textsuperscript{6-10} Along these lines, we have reported a catalytic pathway for the production of bio-based maleic anhydride (MA), which is based on the oxidative scission of the ketone moiety in levulinic acid (LA) over supported vanadium oxides (Scheme 2.1). The process begins with a sugar derivative (LA), and it offers relatively mild processing and good selectivity compared to conventional butane oxidation.\textsuperscript{11} The
present article is focused on understanding the role of vanadium oxide structure and support identity in dictating reactivity during ketone oxidation.

![Scheme 2.1](image)

**Scheme 2.1:** The oxidation of levulinic acid (4-oxopentanoic acid) yields maleic anhydride. Transforming levulinic acid into maleic anhydride requires oxidative scission of levulinic acid’s C4-C5 bond. This is a specific example of a generic ketone oxidation.

Over reducible oxides, oxidative chemistries frequently proceed through a Mars-van-Krevelen mechanism, wherein atomic oxygen is transferred to adsorbed species by concurrent reduction of lattice heteroatoms. This forms reaction products, which desorb to expose an oxygen vacancy. Molecular oxygen then facilitates re-oxidation of the lattice to complete the catalytic cycle.\(^\text{12,13}\)

Because lattice oxygen plays such a critical role in Mars-van-Krevelen mechanisms, rates of heterogeneously-catalyzed oxidations are often sensitive to changes in the nature of the oxygen-heteroatom bonds that comprise the active site;\(^\text{14-16}\) however, there have been few prior investigations aimed at developing the structure-function relations that govern oxidative scission of ketones; accordingly, we take steps to do so here.

At vanadium oxide surfaces, oxygen atoms can be found in one of three bonding environments: vanadyl oxygens (V=O), vanadium-oxygen-vanadium bonds (V-O-V), and vanadium-oxygen-support bonds (V-O-M, where M is the heteroatom cation in the solid oxide support).\(^\text{17,18}\) The oxygen distribution depends on the local structure adopted by vanadium oxides, of which one can identify three broad categories: isolated, tetrahedral vanadate monomers; oligomeric, surface
vanadates that extend in one or two dimensions; and bulk, three-dimensional crystallites (e.g., \( \text{V}_2\text{O}_5 \)).\(^{19}\) The vanadium oxide distribution is sensitive to the nature of the metal oxide support, the vanadium loading, the vanadium precursor, and the synthetic methodology.\(^{20-22}\) As the character of the lattice oxygen population changes with the identity of the vanadium phase, so may catalytic reactivity. Further, it is clear that changing the identity of the support cation, M, will perturb the electronic structure of the V-O-M bond, which can make its reduction more or less facile. If reduction or re-oxidation of the V-O-M vanadium is kinetically significant, this perturbation will directly impact oxidation kinetics.\(^{21}\) In order to probe how intrinsic rates of ketone oxidation respond to changes in vanadate structure and support cation identity, we have prepared twenty catalysts by depositing vanadium at five different fractions of the theoretical monolayer coverage (0.0, 0.1, 0.5, 1.0 and 1.5) onto four oxide supports of varying cation reducibility (\( \text{SiO}_2 \), \( \gamma\)-\( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \) and \( \text{CeO}_2 \)). Physical and chemical properties of each catalyst were determined by FT-Raman spectroscopy, \( \text{N}_2 \) physisorption, and temperature-programmed surface oxidation (TPSO) of methanol. In order to build connections between active site structure and catalytic function, we have additionally quantified the activity of each catalyst during oxidation of 2-pentanone, which is a suitable probe reaction for investigating fundamental aspects of oxidative ketone scission.
2.3 Materials and Methods

2.3.1 Reagents

Cerium nitrate hexahydrate (Acros Organics, 99.5%), γ-alumina (Strem Chemicals, 95%),
titanium dioxide (Acros Organics, Aeroxide® P25), amorphous silica (Sigma-Aldrich, Davisil
Grade 633), ammonium metavanadate (Sigma-Aldrich, ≥99.5%) and oxalic acid (Acros
Organics, 98%) were used in catalyst synthesis. Vanadium pentoxide (Acros Organics, 98%+) was
used as supplied. 2-pentanone (Acros Organics, 99%) was used as a probe molecule.
Formaldehyde (Sigma-Aldrich, 37wt.% in H2O, 10-15% methanol as stabilizer), dimethyl ether
(Aldrich Chemistry, ≥99%), acetaldehyde (Sigma-Aldrich, ≥99.5%), acetic acid (Acros Organics,
99.8%), propionaldehyde (Acros Organics, 99%+), propionic acid (Acros Organics, 99%), n-
butyric acid (Acros Organics, 99%+), CO (Airgas, 1%, 1% Ar, balance He) and CO2 (Airgas,
1%, 1% Ar, balance He) were used for calibration of analytical instruments. Methanol (Fisher,
Optima 99.9%) was employed for TPSO experiments. Water was purified in house by sequential
reverse osmosis, UV oxidation, and double ion exchange to >18.2 MΩ cm resistivity
(Spectrapure). He (Airgas, Ultra High Purity) and O2 (Airgas, Ultra High Purity) were used as
diluent and oxidant during reactor operation. Air (Airgas, Ultra Zero Grade) was used for ex-situ
calcination of all catalyst samples.

2.3.2 Catalyst synthesis

Cerium oxide was synthesized by calcination of cerium nitrate hexahydrate in static air at 823K
(5K min⁻¹, 4 h). CeVO₄ samples were synthesized using an established co-precipitation
method. Specifically, an alkaline (NaOH) solution of ammonium metavanadate was reduced by
sodium borohydride and subsequently reacted with cerium nitrate to precipitate CeVO₄.
Vanadium oxides were supported on SiO$_2$, γ-Al$_2$O$_3$, TiO$_2$, and CeO$_2$. Vanadium mass loadings were varied on each support to achieve fractions (0.0 – 1.5) of the theoretical monolayer coverage of VO$_x$ units for that support.

Supported vanadium oxides were prepared by incipient wetness impregnation of ammonium metavanadate dissolved in aqueous oxalic acid. The molar ratio of ammonium metavanadate to oxalic acid was 1:2, and the molar concentration of ammonium metavanadate was varied as necessary to achieve desired vanadium loadings.$^{21,25,26}$ Resultant solids were dried at 338K, crushed to break aggregates, calcined under flowing air at 723K (60 sccm, 3 K min$^{-1}$, 4 h), crushed into fine particles, and graded through standard mesh sieves. Treating samples at 723K in air is sufficient to decompose precursor salts, resulting in deposition of vanadium (+5) oxides on the support surface.$^{27,28}$ All characterization and reaction experiments were performed using catalyst particles in the 45-90 µm range. In this manuscript, we refer to quantities defined in Equations 2.1 – 2.3, which specify vanadium loadings in several dimensions.

\[
V_A = \frac{N_V \cdot N_A}{m_S \cdot S_A S} \quad (2.1)
\]

\[
V_M = \frac{N_V}{N_V \cdot MW_V + m_S} \quad (2.2)
\]

\[
V_W = V_M \cdot MW_V \cdot 100 \quad (2.3)
\]

In these equations, $V_A$ is the areal density of atomic vanadium (V nm$^{-2}$); $V_M$ is the molar loading of vanadium per unit mass of catalyst (µmol V g$^{-1}$); $V_W$ is the mass percentage of vanadium in a given catalyst; $N_V$ is the total moles of vanadium in a given catalyst preparation; $N_A$ is Avogadro’s number; $m_S$ is the mass of support used in a given catalyst synthesis; $S_A S$ is the
support surface area per unit mass determined by N\textsubscript{2} physisorption; and MW\textsubscript{v} is the atomic mass of vanadium.

2.3.3 Surface area and pore size measurements:

Surface areas and average pore sizes for each catalyst and support were determined by N\textsubscript{2} physisorption at 77K (Micromeritics, ASAP 2020). Prior to N\textsubscript{2} dosing, samples were outgassed under vacuum for 4 hours at 523K. Total surface areas were determined by BET analysis. Average pore diameters were determined from BJH analysis of the desorption branch of N\textsubscript{2} uptake isotherms.\textsuperscript{29, 30}

2.3.4 Raman spectroscopy

Raman spectra were acquired using a Bruker FRA 106 FT-Raman spectrometer equipped with an Nd:YAG laser emitting at 1064 nm. Prior to spectral acquisition, samples were dehydrated ex situ in a home-built cell. 50 – 60 mg of powdered catalyst were loaded into a quarter inch borosilicate tube and held in place with two quartz wool end plugs. Samples were then calcined under a flow of zero-grade air (723K, 3 K min\textsuperscript{-1}, 4h, 60 sccm) that was further dried by passing through a moisture trap (Agilent, MT200-4). After cooling to room temperature under continuous purge, the cell was pressurized (2.4 bar, absolute pressure), sealed using block valves, and transferred into the FT-Raman sample chamber. Spectra were obtained at a resolution of 2 cm\textsuperscript{-1} at room temperature using a laser power of 200 mW with an accumulation of 200 scans. Before each measurement, the instrument focus was tuned using an external V\textsubscript{2}O\textsubscript{5} standard. Full width at half maxima (FWHM) were computed for individual Raman bands by fitting each peak to a normal distribution function, which generates regressed values for the peak location and standard deviation (σ) for the distribution. For Gaussian peaks, the FWHM is calculated as a function of
standard deviation (Equation 2.4):

$$FWHM = 2\sqrt{2 \cdot \ln(2) \cdot \sigma}$$  \hspace{1cm} (2.4)

2.3.5 Temperature programmed surface oxidation

The oxidative capacity of each catalyst was quantified using temperature programmed surface oxidation (TPSO) of chemisorbed methanol.\textsuperscript{25, 26, 31, 32} 100 – 400 mg of powdered catalyst were supported between two quartz wool plugs inside of a 1/2" quartz tube, which was then positioned inside of a high-temperature ceramic furnace (Omega, CRFC). Samples were calcined under zero-grade air (50 sccm, 723 K, 4 h) and subsequently cooled to 373 K. The process gas was then switched from air to a Helium/Methanol blend (100 sccm, 22 Torr methanol, balance He), which was prepared by vaporizing a continuous flow of liquid methanol into a Helium sweep. The methanol feed was controlled using a syringe pump (Cole Parmer series 100) and introduced to the He stream through a capillary tube. The catalyst sample was contacted with methanol until reaching its saturation uptake (typically within 30 minutes), which was determined by monitoring the effluent methanol concentration using an online, mass-selective residual gas analyzer (RGA, Stanford Instruments RGA 100). After surface saturation, the sweep gas was switched to 100 sccm of a Helium blend containing 1% argon (internal standard), and the sample was purged until no further evolution of methanol was observed (≈ 60 min). The cell temperature was then ramped to 773 K at a rate of 10 K min\(^{-1}\). During the temperature ramp, MS signals corresponding to formaldehyde (\(m/z = 29\)), carbon monoxide (\(m/z = 28\)), carbon dioxide (\(m/z = 44\)), dimethyl ether (\(m/z = 45\)), methanol (\(m/z = 31\)) and argon (\(m/z = 40\)) were monitored continuously. RGA response factors were determined, relative to the argon internal standard, for each species. All MS signals were corrected for fragmentation interferences. Temperature in the
furnace was measured using a type K thermocouple (Omega) and controlled using a PID temperature controller (Love Controls, Series 16A).

Total oxidation site densities were determined from quantities of evolved formaldehyde (HCHO), carbon monoxide (CO), and carbon dioxide (CO₂), which are all products of methanol oxidation. Unfortunately, as methanol TPSO was performed under inert atmospheres and high temperatures, there is ambiguity in assigning the precise stoichiometries leading to formation of HCHO, CO, and CO₂. For example, HCHO can form by either oxidative or non-oxidative dehydrogenation of methanol. In turn, CO might form either through oxidative or non-oxidative dehydrogenation of formaldehyde. This uncertainty further propagates into the stoichiometry of CO₂ evolution. In our analysis, we have assumed that each carbon atom observed in the reactor effluent is generated from one molecule of chemisorbed methanol, and that hydrogen atoms not recovered in formaldehyde are oxidized fully to form water. The former assumption is straightforward, while the latter is based on the fact that we observed limited evolution of molecular H₂ (m/z = 2.0) relative to observed quantities of HCHO and CO during control experiments. Since methanol TPSO was conducted under an inert atmosphere (He), stoichiometric quantities of oxygen must be provided by reduction of the catalyst. Accordingly, as summarized in Equations 2.5 – 2.7, we take evolution of formaldehyde (HCHO) to indicate titration of a single accessible oxygen atom, carbon monoxide (CO) to indicate titration of two accessible oxygen atoms, and carbon dioxide (CO₂) to indicate titration of three accessible oxygen atoms. Weighing evolved quantities of HCHO, CO, and CO₂ in this manner, we estimate the total number of redox accessible oxygen atoms per gram of catalyst.

\[
\text{CH}_3\text{OH} + O \rightarrow \text{HCHO} + \text{H}_2\text{O}
\]  

(2.5)
\[ \text{CH}_3\text{OH} + 2\text{O} \rightarrow \text{CO} + 2\text{H}_2\text{O} \] (2.6)

\[ \text{CH}_3\text{OH} + 3\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \] (2.7)

2.3.6 Catalytic activity testing

Although our motivating interest is the oxidation of levulinic acid, we have examined, as a model system, the catalytic activity of each material in the oxidative scission of 2-pentanone. There are several reasons for doing so. First, levulinic acid and its dominant oxidation product (maleic anhydride) have low vapor pressures, which complicates partial pressure control and online chromatographic analysis, both of which are essential to rigorous kinetic analysis of gas-phase reactions. In contrast, vaporization of 2-pentanone is facile, and it produces a suite of C\textsubscript{1} – C\textsubscript{4} monofunctional hydrocarbons that have relatively high vapor pressures and are easily resolved and quantified by online GC analysis. Second, levulinic acid is thermally unstable. Under oxidative reaction conditions, it is consumed in parallel by a number of facile, non-oxidative pathways, which complicates quantitative determination of oxidation reaction rates. 11

2-pentanone, on the other hand, is consumed primarily by oxidative scission pathways. Finally, whether one considers levulinic acid oxidation or 2-pentanone oxidation, the central chemistry involves oxidative scission of the C-C bond between the ketone carbonyl and one of its alpha carbons. Accordingly, 2-pentanone oxidation captures the fundamental essence of ketone oxidation, and any insights generated regarding oxidative scission of ketones are broadly applicable to levulinic acid oxidation.

2-pentanone oxidation was carried out in the gas phase using an up flow, packed bed reactor. To mitigate exothermicity, sieved catalyst powders (45 – 90 µm) were diluted 1:4 in sieved quartz powder (45 – 90 µm). The diluted catalyst bed was positioned at the midpoint of a 7 ½” x ¼”
stainless steel tube and held in place with two quartz wool plugs. The upstream section of the reactor tube was filled with quartz chips. The packed bed was then placed inside of a high temperature furnace and connected to the gas manifold using compression fittings. Prior to subjecting catalysts to ketone oxidation conditions, each bed was calcined in situ at 723 K for 4 hours under an O₂/He (1:5) gas mixture.

Reactor gas feeds were comprised of 2-pentanone vaporized into an O₂/He blend. As shown in Figure 2.1, the O₂/He blend was prepared by combining O₂ and He in desired ratios using mass flow controllers (Brooks 5850S). It was subsequently fed, alongside liquid 2-pentanone, into a ½” stainless steel vaporizer that was packed with quartz granules and held at 393K. 2-pentanone was introduced into the vaporizer through a capillary tube, and its flow rate was controlled using a syringe pump (Cole Parmer series 100). This configuration provided complete vaporization of 2-pentanone over the range of partial pressures and space velocities reported here. The vaporizer effluent was fed into a 6-port valve, which was used to direct the process stream either into the packed bed reactor or to a bypass. During startup, the process gas was fed into the bypass and monitored by online GC until reaching steady state, while the reactor tube was purged with an O₂/He mixture. Subsequently, the 6-position valve was switched to divert the process stream into the packed bed reactor. The time of this switch is defined herein as zero time-on-stream. Feed mole fractions were controlled at 0.015 2-pentanone, 0.164 O₂, and 0.821 He. All reactions were carried out at a total system pressure of 915 Torr, and the pressure gradient across the catalyst bed was always less than 100 Torr or roughly 11% of the inlet pressure. Space velocities were adjusted to maintain 2-pentanone conversions below 4% for all catalysts under all reaction conditions. Reported reaction temperatures reflect the internal reactor temperature, which was measured immediately downstream of the catalyst bed using an inline, Type K thermocouple.
Comparison to control experiments revealed that, for the range of feed rates and conversions reported here, the temperature gradient across the catalyst bed was always less than 1°C. The above observations suggest the differential reactor approximation is reasonable; accordingly, we take kinetic data reported here to reflect reaction rates obtained under isothermal conditions at 466K and under an atmosphere of 13.7 Torr 2-pentanone, 150 Torr O₂, and 751 Torr He.

For product analysis, the reactor effluent was passed to an online GC through a stainless steel transfer line that was maintained at 423K, which was sufficient to prevent condensation of all species at their representative partial pressures. Species concentrations were determined using an HP 5890 GC equipped with two inlets, two columns, and two detectors. A Restek ShinCarbon ST Micropacked Column connected to a TCD detector was used for resolution and quantification of O₂, CO, and CO₂. An HP-INNOWAX column coupled to an FID detector was used for resolution and quantification of all other species, which included carboxylic acids, aldehydes, and ketones. Temperatures in the reactor and all auxiliary heated zones were monitored with K-type thermocouples (Omega) and controlled using PID temperature controllers (Love Controls Series 16A). Carbon balances closed to within 5%.

**Figure 2.1.** Reactor setup for oxidation of 2-pentanone: a) vaporizer at 393K, b) syringe pump, c) mass flow controllers, d) 6-port valve and transfer lines at 433K, e) mass flow controllers, f) gas chromatograph, g) reactor at 466K, h) exhaust.
As illustrated in Scheme 2.2, there are three primary pathways of 2-pentanone oxidation; further, the products formed therein are generally susceptible to secondary oxidation. Since we have controlled only partial pressures for oxygen and 2-pentanone, the only meaningful kinetic analysis is one that considers rates of primary reactions consuming 2-pentanone; however, the prevalence of secondary and tertiary reactions makes their quantification nontrivial. To aid in our analysis, we generated Scheme 2.2 through a set of control experiments designed to distinguish stable products from those that undergo further conversion. This topic will be detailed in a forthcoming manuscript; however, we briefly summarize key aspects here in order to justify the convention we have used in defining primary rates of 2-pentanone oxidation.

The three primary pathways that consume 2-pentanone are (1) direct combustion to form CO$_2$ and H$_2$O, neither of which undergoes further conversion; (2) oxidative scission of the C$_2$-C$_3$ bond (alkyl scission) to form acetic acid and propionaldehyde; and (3) the oxidative scission of the C$_1$-C$_2$ bond (methyl scission) to form butyric acid and formaldehyde. Under the conditions reported
here, we observe less than ≈ 10% selectivity to direct combustion pathways. With respect to alkyl scission products acetic acid is stable, while propionaldehyde is consumed by both direct oxidation to form stable propionic acid, and oxidative scission to produce acetaldehyde and formic acid. Formic acid decomposes to water and carbon oxides. Acetaldehyde does not undergo further C-C scission under our reaction conditions; however, it is oxidized to form acetic acid. In contrast, methyl scission of 2-pentanone forms butyric acid and formaldehyde. As with acetic and propionic acid, butyric acid is stable under our reaction conditions. Formaldehyde is oxidized to formic acid, which forms water and carbon oxides. Due to their facile oxidation/decomposition, neither formaldehyde nor formic acid were observed in our system; their presence in this landscape is inferred through analysis of plausible ketone oxidation mechanisms. Finally, control experiments revealed trace background activity resulting in formation of acetaldehyde, propionaldehyde, and acetic acid. As all of these species are observed during 2-pentanone oxidation over supported vanadates, background molar flow rates for each compound were determined for each reaction condition and subtracted from extensive production rates of acetaldehyde, propionaldehyde and acetic acid prior to evaluation of reaction rates (Equations 2.8 and 2.9).

From Scheme 2.2, the total rate of alkyl scission for 2-pentanone \((R_I)\) can be determined based on background-corrected molar flowrates of acetaldehyde \((F_A)\), propionaldehyde \((F_P)\), acetic acid \((F_{AA})\), and propionic acid \((F_{PA})\) as shown in Equation 2.8.

\[
R_I = \frac{F_A + F_P + F_{AA} + F_{PA}}{2}
\]  

(2.8)

Butyric acid is stable even under our most severe conditions. Accordingly, from Scheme 2.2, one can establish the rate of methyl scission \((R_I)\) based solely on observed quantities of butyric acid
as shown in Equation 2.9:

\[ R_f = F_{BA} \]  

Under all reported conditions and excluding direct combustion of 2-pentanone, selectivity toward the alkyl scission pathway is >95%; thus, to streamline discussion, we present only the rate of alkyl oxidative scission \((R_f)\). Based on our analysis, kinetic trends observed for methyl scission are identical to those observed for alkyl scission; accordingly, little is gained from a parallel consideration of methyl scission rates in this analysis.

In comparing catalytic activities, we employ site-time yields (STY), which are defined as the measured rate of alkyl oxidative scission of 2-pentanone \((R_f)\) per unit oxidation site (Equation 2.10). As such, they approximate a turnover frequency. The total number of oxidation sites in a catalyst bed is computed as the product of catalyst mass loading \((m_{cat})\) and the oxidation site density determined by methanol TPSO \((\rho_S)\).

\[ STY = \frac{R_f}{m_{cat} \cdot \rho_S} \]  

Catalysts in this system always undergo a period of deactivation, and they generally reach steady state within 50 hours on stream. As different catalysts on different supports may undergo different extents of deactivation, it is difficult to directly compare steady state activities in two different systems. Accordingly, we report only initial rates of reaction at zero-time on stream, which were estimated by fitting experimentally measured decay profiles to a first order deactivation model. Finally, we are confident that data reported here reflect intrinsic kinetics and are not obscured by mass and heat transfer artifacts. We provide a complete assessment of transport limitations in the online supporting information and references therein.\(^{39-45}\)
2.4 Results and Discussion

Vanadium loadings are summarized in Table 2.1. The molar loading of vanadium at monolayer coverage was calculated as the product of the support surface area and the areal density of dispersed VO$_x$ sites at monolayer coverage; thus, a low areal vanadate density does not necessarily mean a low vanadium loading. For example, because of its relatively low hydroxyl surface density, silica will accommodate a lower monolayer coverage of vanadium oxides ($\approx 2.3$ VO$_x$ nm$^{-2}$)$^{28}$ than supports with higher hydroxyl densities, such as $\gamma$-Al$_2$O$_3$, TiO$_2$, and CeO$_2$ ($\approx 8$ – 9 VO$_x$ nm$^{-2}$)$^{19,22,25}$ however, SiO$_2$ has a relatively high surface area per unit mass, which facilitates substantial mass percentages of vanadium despite a low hydroxyl density. As the solid oxides employed here are a somewhat heterogeneous class of materials, “monolayer coverages” reported in the literature are not taken as rigorously quantitative; rather, they are used to provide benchmarks that guide the vanadium loadings required to achieve vanadate densities above and below monolayer coverage. Vanadium speciation is sensitive to coverage; thus, this approach should yield catalysts where vanadium oxides exist in a range of local environments, which aids in connecting structure and function.$^{20,46}$ For convenience, catalysts are nominally described using their theoretical fraction of monolayer coverage (0.0, 0.1, 0.5, 1.0, and 1.5).
Table 2.1. Vanadium content of supports, bulk vanadates, and supported vanadium oxides.\textsuperscript{19, 25, 28, 47} The BET surface areas for the supports used in these syntheses were: \( \text{SiO}_2 \) (490 m\(^2\) g\(^{-1}\)), \( \text{Al}_2\text{O}_3 \) (231 m\(^2\) g\(^{-1}\)), \( \text{TiO}_2 \) (49 m\(^2\) g\(^{-1}\)), and \( \text{CeO}_2 \) (75 m\(^2\) g\(^{-1}\)).

<table>
<thead>
<tr>
<th>Support</th>
<th>Fraction of Monolayer</th>
<th>Vanadium Loading</th>
<th>(wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(V nm(^{-2}))</td>
<td>mol V g(^{-1})</td>
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<tr>
<td>( \text{SiO}_2 )</td>
<td>0.1</td>
<td>0.23</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.16</td>
<td>862</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.30</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.45</td>
<td>2236</td>
</tr>
<tr>
<td>( \gamma\text{-Al}_2\text{O}_3 )</td>
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<td>0.799</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3.99</td>
<td>1347</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>7.99</td>
<td>2399</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12.0</td>
<td>3245</td>
</tr>
<tr>
<td>( \text{TiO}_2 )</td>
<td>0.1</td>
<td>0.812</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.00</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>8.00</td>
<td>614</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12.0</td>
<td>897</td>
</tr>
<tr>
<td>( \text{CeO}_2 )</td>
<td>0.1</td>
<td>0.857</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.25</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>8.49</td>
<td>962</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>12.8</td>
<td>1382</td>
</tr>
</tbody>
</table>

To probe vanadium speciation, we employed Raman spectroscopy, which is useful in distinguishing dispersed (1D and 2D) vanadium oxide phases from those present as bulk crystallites.\textsuperscript{13, 20, 48-51} Figures 2.2-2.5 present Raman spectra for all catalysts and supports indicated in Table 2.1. This series focuses on the spectral window from 600 – 1200 cm\(^{-1}\), as this is the most informative region for gauging the relative populations of dispersed and bulk phases;\textsuperscript{52} moreover, specific features within this region reveal additional details regarding the extent of oligomer formation in networks of surface vanadium oxides.\textsuperscript{53-55} Spectra in Figures 2.2-2.5 were normalized to the support features indicated in the figure captions;\textsuperscript{50, 56-58} accordingly, spectra within a given support series may be taken as a semi-quantitative assessment of vanadium coverage and speciation. For reference, full scale versions of each spectrum are presented in Figures S2.2 – S2.5 of the online supporting information. In addition, Figure S2.6 of the online supporting information shows full scale spectra of the bulk structures (V\(_2\)O\(_5\) and CeVO\(_4\)) indicated in subsequent analysis.
Raman spectra for our VO\textsubscript{x}/SiO\textsubscript{2} samples are presented in Figure 2.2, and our discussion highlights trends observed with increasing vanadium loading. First, the spectrum for the SiO\textsubscript{2} support (0.0) has broad bands at 600, 800 and 980 cm\textsuperscript{-1}. The band at 600 cm\textsuperscript{-1} corresponds to tricyclosiloxane rings, which are produced by the condensation of surface hydroxyls;\textsuperscript{59-61} the band at 800 cm\textsuperscript{-1} is associated with Si-O-Si bonds;\textsuperscript{62-64} and the band at 980 cm\textsuperscript{-1} is assigned to the stretching mode of surface silanols (Si-OH).\textsuperscript{62-64} As vanadium loadings increase, (0.1), SiO\textsubscript{2} bands remain evident; however, we also note the appearance of a band at 1042 cm\textsuperscript{-1}, which is assigned to the stretching mode of the V=O in the dispersed vanadate species.\textsuperscript{65-67} For VO\textsubscript{x}/SiO\textsubscript{2} samples, this band is generally attributed to an isolated VO\textsubscript{4} in a tetrahedral coordination environment.\textsuperscript{55,66,68} As vanadium loading continues to increase (0.5 – 1.5), we observe...
increasing intensity of the 1042 cm\(^{-1}\) band alongside decreasing intensity of the bands at 600 cm\(^{-1}\), 800 cm\(^{-1}\), and 980 cm\(^{-1}\). This stands to reason as increased vanadate coverages should be facilitated by conversion of surface silanols and/or siloxanes into Si-O-V bonds. At vanadium loadings above the theoretical monolayer coverage (1.5), we observe formation of prominent bands at 700 and 997 cm\(^{-1}\), which are associated with bulk V\(_2\)O\(_5\) crystallites.\(^{69,70}\) As these bands are absent at and below 1.0 loadings, we conclude that samples prepared from 0.1 to 1.0 vanadium loadings have primarily dispersed vanadium oxide phases with minor fractions of bulk vanadates, while those prepared above 1.0 have both dispersed and bulk phases. Interestingly, as one transitions from 0.1 to 1.5 vanadium loadings, the intensity of the band at 1042 cm\(^{-1}\) increases without substantial broadening or peak shift. This suggests that, despite a clear increase in vanadium oxide surface density, the nature of the dispersed vanadate phase (e.g., monomeric vs. oligomeric) changes little in this set of materials.\(^{71}\) With increased vanadium loading, we also observe the appearance of bands at 920 cm\(^{-1}\) and 1080 cm\(^{-1}\); unfortunately, there has thus far been no conclusive structural assignment for these bands. Most likely, they are attributed to Si-O\(^-\) and Si-(O\(^-\))\(_2\) species perturbed by the formation of V-O-Si bonds\(^ {48,72}\) or, perhaps, to the V-O-Si bond itself.\(^{15,73,74}\) We see no definitive evidence of bands associated with V-O-V bonds, which should be observed in the 750 cm\(^{-1}\) – 820 cm\(^{-1}\) range for VO\(_x\)/SiO\(_2\) samples.\(^{15}\) Note that the broad feature at 800 cm\(^{-1}\) in the 1.5 sample may be attributed either to vibrational modes of SiO\(_2\) (see 0.0) or to bulk V\(_2\)O\(_5\) (see Figure S2.6); as such, we cannot take this band as a definitive polyvanadate signature. Based on this observation and the fact that increasing vanadium loading leads to neither broadening nor shift of the 1042 cm\(^{-1}\) band, we conclude that surface vanadates are mostly likely present as VO\(_4\) monomers in this set of VO\(_x\)/SiO\(_2\) samples. At coverages above 1.0, we also observe evidence of V\(_2\)O\(_5\) crystallites.
Figure 2.3. Raman spectra of supported vanadates on γ-Al2O3, VOx/Al2O3. Due to the absence of support bands, VOx/Al2O3 spectra were normalized to spectral intensity at 1100 cm⁻¹. a) inset highlighting weak Raman bands in 0.1 and 0.5 monolayer samples.

Figure 2.3 summarizes Raman spectra obtained for VOx/Al2O3 samples. γ-Al2O3 exhibits strong fluorescence, which dominates Raman spectra for 0.0, 0.1, and 0.5 samples. That said, a small band at 1024 cm⁻¹ is evident in the 0.1 monolayer sample, and this band is shifted to 1037 cm⁻¹ in the 0.5 monolayer sample (see inset). Raman bands in the region from 1020 cm⁻¹ to 1040 cm⁻¹ are assigned to methyl V=O stretching modes in the dispersed vanadium phase.⁵⁴, ⁷³, ⁷⁵, ⁷⁶ The clear shift in the band position from 1024 cm⁻¹ to 1037 cm⁻¹ is most likely attributed to a transition from monomeric VO₄ in the 0.1 sample (1024 cm⁻¹) to polymeric vanadates in the 0.5 sample (1037 cm⁻¹).¹⁸ This conclusion is supported by the co-emergence of a broad band at 930 cm⁻¹, which is attributed to a V-O-V stretching mode.¹³, ⁴⁹, ⁷⁷ We additionally note that, for 0.1 and 0.5 samples, there is no band at 997 cm⁻¹, which suggests that vanadium distributions in low-loading
samples are comprised entirely of surface vanadates rather than a mixture of surface and bulk vanadium oxides. Transitioning to 1.0 and 1.5 monolayer samples, the band at 930 cm\(^{-1}\) (V-O-V) is shifted to 945 cm\(^{-1}\), and its intensity increases. This suggests increased oligomerization of surface vanadium oxides in 1.0 and 1.5 samples. Further, the Raman bands at 700, 800, and 997 cm\(^{-1}\) become more pronounced in the 1.0 and 1.5 monolayer samples, which clearly indicates formation of bulk V\(_2\)O\(_5\) crystallites at and above theoretical monolayer loadings.\(^{69,70}\) To summarize, in the VO\(_x\)/Al\(_2\)O\(_3\) series, Raman spectra suggest that, as vanadium loadings increase, there is a transition from dispersed monomeric vanadium oxides (0.1), to polymeric vanadates (0.5), to a mixture of polymeric vanadates and bulk V\(_2\)O\(_5\) crystallites (1.0 and 1.5).

![Raman spectra of supported vanadates on TiO\(_2\), VO\(_x\)/TiO\(_2\). The spectra were normalized to the TiO\(_2\) band at 640 cm\(^{-1}\).](image)

**Figure 2.4.** Raman spectra of supported vanadates on TiO\(_2\), VO\(_x\)/TiO\(_2\). The spectra were normalized to the TiO\(_2\) band at 640 cm\(^{-1}\).

Raman spectra are summarized for the VO\(_x\)/TiO\(_2\) samples in Figure 2.4. In all samples, the prominent bands at 640 and 796 cm\(^{-1}\) are assigned to vibrations associated with the anatase phase.
of TiO$_2$. As VO$_x$ loadings increase on the TiO$_2$ support, we observe a band at 1030 cm$^{-1}$ (0.1), which is assigned to V=O stretching modes in dispersed vanadium oxides on the TiO$_2$ surface. At higher loadings (0.5 – 1.5), this band’s intensity increases slightly, and it shifts to 1037 cm$^{-1}$, which likely reflects increasing oligomerization of surface vanadium oxides. This is supported by the concurrent emergence of a band at 920 cm$^{-1}$ (0.5), which is attributed to V-O-V stretching modes in 2-dimensional polyvanadates. As vanadium loadings increase further (1.0 and 1.5), the intensity of this band increases, and it shifts to higher wavenumber, both of which are consistent with increased oligomerization of surface vanadium oxides. Bands at 700 and 997 cm$^{-1}$, which are associated with V$_2$O$_5$ crystallites, are clearly observable alongside the 1037 cm$^{-1}$ band for 1.0 and 1.5 samples. Similar to the VO$_x$/Al$_2$O$_3$ series, we conclude that, as vanadium loading on TiO$_2$ increases from 0.1 to 1.5, there is a transition from monomeric tetrahedral vanadates, to polymeric vanadates, to a mixture of 2D (surface) and 3D (bulk crystalline) phases.
Finally, we consider Raman spectra for a series of VO\textsubscript{x}/CeO\textsubscript{2} samples (Figure 2.5). In this spectral region, CeO\textsubscript{2} (0.0) has no strong Raman bands. At the lowest vanadium loading (0.1), we observe broad Raman bands at 700 cm\textsuperscript{-1} and 830 cm\textsuperscript{-1}, both of which are associated with the formation of V-O-Ce bonds.\textsuperscript{51,80} Further, we observe a more prominent band at 1010 cm\textsuperscript{-1}, which has a shoulder at 1024 cm\textsuperscript{-1}. As in preceding discussions, bands in the 1010 cm\textsuperscript{-1} – 1050 cm\textsuperscript{-1} region are associated with V=O stretching modes in dispersed vanadium oxides.\textsuperscript{53,81,82} The lower end of this wavenumber range is generally attributed to monomeric vanadates, while shifts to higher wavenumber are associated with increasing oligomerization in the dispersed vanadate phase.\textsuperscript{83} Accordingly, we conclude that the vanadium oxide distribution in the 0.1 sample includes both monomers and oligomers; however, the size of the shoulder relative to that of the main band suggests limited formation of an oligomer network. With increased vanadium loading (0.5), Raman bands corresponding to the V-O-Ce bond shift to higher wavenumbers (720 cm\textsuperscript{-1}).
and 840 cm\(^{-1}\)). Further, the vanadyl band at 1015 cm\(^{-1}\) is broadened and shifted to \(\approx 1030\) cm\(^{-1}\), which suggests increased oligomer formation.\(^{55,83}\) In parallel, we observe concurrent appearance of a broad feature near 930 cm\(^{-1}\), which is attributed to vibrational modes of V-O-V bonds and is thus consistent with increasing polyvanadate formation.\(^{19,49,53}\) Finally, in the 0.5 sample, we begin to observe formation of a CeVO\(_4\) phase, which is clearly indicated by pronounced Raman bands at 789, 801 and 863 cm\(^{-1}\).\(^{84-86}\) As loading increases further in 1.0 and 1.5 samples, we observe extensive formation of CeVO\(_4\) aggregates, evidenced by the strong bands as 789 cm\(^{-1}\), 801 cm\(^{-1}\), and 863 cm\(^{-1}\). Further, in these high loading samples, the surface vanadate distribution is dominated by polymeric species, which are indicated by V=O signatures at 1024 cm\(^{-1}\), 1037 cm\(^{-1}\), and 1050 cm\(^{-1}\) and by V-O-V modes at 950 cm\(^{-1}\). All of these bands are shifted to higher wavenumbers relative to those observed in monomer-rich distributions, which is consistent with increasing polyvanadate formation.

A meaningful discussion of oxidative scission rates measured over catalysts that have varied supports and vanadium speciation necessitates approximation of turnover frequencies such that activity can be compared on a unit active site basis. This requires quantification of oxidation site densities in each material. To do so, we rely on methanol TPSO. Table 2.2 compiles evolved oxidation products and total oxidative capacity for all catalyst/support systems and bulk structures indicated by analysis of Raman spectra (V\(_2\)O\(_5\) and CeVO\(_4\)). For reference, BET surface areas for all materials are additionally compiled in Table 2.2.
Table 2.2. BET surface areas and oxidation site densities for all catalysts, supports, and bulk vanadates.

<table>
<thead>
<tr>
<th>Support</th>
<th>Fraction of Monolayer</th>
<th>Surface Area (m² g⁻¹)</th>
<th>HCHO (µ mol g⁻¹)</th>
<th>CO (µ mol g⁻¹)</th>
<th>CO₂ (µ mol g⁻¹)</th>
<th>Total O (µ mol g⁻¹)</th>
<th>Total O (µ mol µmol⁻¹ V⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.0</td>
<td>490</td>
<td>68</td>
<td>112</td>
<td>9</td>
<td>319</td>
<td>--</td>
</tr>
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Products from methanol TPSO include formaldehyde, carbon monoxide and carbon dioxide, and each product arises from methanol oxidation. Water is assumed as a co-product, and the requisite oxygen is assumed to come from reduction of the catalyst. Accordingly, we take the weighted sum of evolved quantities (Equations 2.4 – 2.7) to give the total number of oxygen atoms that are both accessible and bound to a heteroatom that is feasibly reducible under TPSO conditions. Before proceeding, we offer the caveat that this titration method will interrogate sites that are active for methanol oxidation, and these sites are not necessarily identical to those participating in oxidative ketone scission. Further, methanol TPSO provides no clear way to distinguish between distinct types of reducible surface sites. Specifically, methanol oxidation is structure insensitive, and methanol TPSO cannot resolve whether oxidation occurs at a single monomeric VO$_x$ site or at a vanadium center within an oligomeric phase. Finally, it is clear from data in Table 2.2 that supports (SiO$_2$, $\gamma$-Al$_2$O$_3$, TiO$_2$, and CeO$_2$) and bulk vanadium oxides (V$_2$O$_5$, CeVO$_4$) have latent oxidative capacity, which might arise either from inherent support reducibility or from the presence of reducible contaminants. Methanol TPSO lumps all of this complexity into a single site count, and it is important to bear these potentially confounding artifacts in mind when using this method to define site-time yields.

We next highlight meaningful trends in TPSO data. First, the total oxidation site density generally increases with vanadium loading. Despite the aforementioned uncertainty, this suggests that the bulk of oxidative capacity arises from vanadium species; however, the trend does not apply universally. Oxidation site counts often decrease as one exceeds theoretical monolayer loadings, and VO$_x$/CeO$_2$ catalysts display a contrasting trend in which oxidation site counts decrease with increasing vanadium loading. As discussed in detail below, these trends reflect both support contributions and changes in accessible vanadia surface area as speciation shifts
from dispersed vanadium oxides to bulk aggregates.

The final column of Table 2.2 reports oxygen availability normalized by the total quantity of vanadium in each sample. Essentially, this presents a vanadium-normalized “dispersion” of oxidation sites. Methanol oxidation is generally accepted to occur through a Mars-van-Krevelen mechanism, which is predicated upon reduction of vanadium centers via transfer of lattice oxygen to surface adsorbates.\textsuperscript{13,88} The number of oxygen atoms contributed by a single vanadium center is dependent upon how deeply it is reduced during the catalytic cycle. For example, an isolated VO\textsubscript{4} cluster could theoretically donate 4 oxygen atoms under conditions that are sufficiently reducing to form vanadium metal; however, this is implausible under the inert atmosphere of our TPSO experiments. In this case, vanadium atoms are reduced by donation of oxygen atoms to surface bound hydrocarbons, and formation of zerovalent vanadium seems unlikely. Typically, for a Mars-van-Krevelen mechanism, vanadium centers are assumed to cycle between V (5+) (e.g., a VO\textsubscript{4} site) and V (3+) (e.g., a VO\textsubscript{3} site), which suggests that each vanadium atom will contribute one oxygen atom per catalytic cycle.\textsuperscript{88,89} Accordingly, we expect that the upper limit of oxidation site dispersions should be 1.0 for 1D or 2D vanadium oxides as 100% of the vanadium centers are theoretically accessible in these cases. That said, Table 2.2 indicates that dispersions are always greater than one for 0.1 monolayer samples. Since deep reduction of VO\textsubscript{x} clusters is unlikely, we attribute oxidation site dispersions above 1.0 to a substantial contribution of the support, and we again note that each support considered here has latent oxidative capacity during methanol TPSO. Consistent with this interpretation, apparent dispersions for 0.1 monolayer catalyst samples increase in the order VO\textsubscript{x}/SiO\textsubscript{2} \approx VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} < VO\textsubscript{x}/TiO\textsubscript{2} < VO\textsubscript{x}/CeO\textsubscript{2}, a trend which likely reflects the increase in support reducibility as one moves from generally non-reducible SiO\textsubscript{2} and \gamma-Al\textsubscript{2}O\textsubscript{3} to readily reducible CeO\textsubscript{2}. 
For each VOₓ/support family, oxygen dispersions decrease monotonically with vanadium loading, and the extent of the decrease is support dependent. For example, the VOₓ/SiO₂ series has dispersions ranging from 1.3 – 0.7, while the VOₓ/CeO₂ series is far more extreme, ranging from 5.1 – 0.14. As noted above, dispersions larger than 1.0 are attributed to support contributions to the site count, which increase with support reducibility. Dispersions below 1.0 are attributed to the formation of bulk crystallites, which include V₂O₅ (SiO₂, γ-Al₂O₃ and TiO₂) and CeVO₄ (CeO₂). Both bulk structures have low surface areas (Table 2.2), which means that the majority of their oxidation sites are inaccessible to adsorbates. Specifically, TPSO results indicate that there are, respectively, 0.0013 and 0.020 accessible oxygen atoms per vanadium atom in V₂O₅ and CeVO₄. Raman spectra broadly indicate that bulk structures become increasingly prevalent at high vanadium loadings and that the onset and extent of bulk phase formation is support-dependent and increases in the order VOₓ/SiO₂ < VOₓ TiO₂ < VOₓ/ γ-Al₂O₃ ≈ VOₓ/CeO₂. This observation suggests that vanadium dispersions (i.e., the number of accessible oxidation sites per unit vanadium atom) should decrease in the same order, which is consistent with trends in oxidation site dispersions determined by methanol TPSO (Table 2.2).

The catalytic activity of each material during the oxidative scission of 2-pentanone is summarized in Figure 2.6. Rates are presented as site time yields, which represent the rate of oxidative scission of 2-pentanone (alkyl) per accessible lattice oxygen atom titrated by methanol TPSO (Table 2.2). All rates reflect initial reaction rates, i.e., those at zero time on stream. Error bars indicate 95% confidence intervals on the initial rate of reaction estimated from each decay profile. Although all supports considered in this study display some oxidative capacity, only CeO₂ is intrinsically active for 2-pentanone oxidation. This underscores the aforementioned concern that the spectrum of active sites sampled by methanol TPSO may not contribute equally
to the oxidative scission of ketones, making it somewhat challenging to precisely define a site-time yield. Based on Figure 2.6, we conclude that observed rates of ketone oxidation over VOx/SiO2, VOx/γ-Al2O3, and VOx/TiO2 are attributed entirely to vanadium oxides, whereas reactivity observed over VOx/CeO2 is likely comprised of separate contributions from CeOx, VOx, and CeVOx phases. We next focus on establishing the intrinsic reactivity of surface vanadium oxides in each catalyst system.

**Figure 2.6.** 2-pentanone alkyl oxidation turnover frequencies over VOx supported on SiO2, γ-Al2O3, TiO2, and CeO2. T = 466K, 10 Torr 2-pentanone.

In Figure 2.6, one observes that samples in the VOx/SiO2 series display site time yields ranging from $2.9 \pm 0.2 \times 10^{-4}$ s$^{-1}$ (0.1 monolayer) to $5.1 \pm 0.3 \times 10^{-4}$ s$^{-1}$ (0.5 monolayer). Values scatter around a mean of $4.1 \pm 1.0 \times 10^{-4}$ s$^{-1}$, suggesting that, in the VOx/SiO2 series, vanadium loading has little influence over site-time yields in the span of 0.1 – 1.5 monolayer loadings. This is consistent with our Raman analysis, which suggests that surface vanadium oxides in this VOx/SiO2 series are primarily monomeric and relatively insensitive to vanadium loading.

Assuming that all reactivity can be attributed to dispersed vanadium oxides, there is no reason to
anticipate a change in activity as a function of vanadium loading in this system. For all other catalyst series (excluding bare CeO$_2$), site time yields clearly increase as a function of vanadium loading, generally reaching a plateau in the 1.0 – 1.5 monolayer range. There are two plausible explanations for this, which are addressed in detail below.

The first explanation is that oxidative scission is a structure sensitive reaction, and that intrinsic reactivity changes as vanadium distributions shift from monomer-rich to oligomer-rich on γ-Al$_2$O$_3$, TiO$_2$, and CeO$_2$. Specifically, oxidative ketone scission may require a pair of VO$_x$ centers in close proximity. This mechanistic detail could manifest as an increase in observed site-time yields as vanadium speciation shifts away from isolated monovanadates and toward polyvanadates. At and above the monolayer limit, polyvanadates comprise the dominant dispersed vanadium oxide phase in all our samples, which should lead to a plateau in site-time-yields near monolayer coverage since the nature of surface sites become insensitive to vanadium loading in this regime. We further note that evidence of structure sensitivity over VO$_x$/Al$_2$O$_3$, VO$_x$/TiO$_2$, and VO$_x$/CeO$_2$ does not conflict with a lack thereof in our VO$_x$/SiO$_2$ samples. Raman analyses of the former materials show clear transitions from monomeric to polymeric vanadates in the range of 0.1 to 1.5 vanadium loadings, while Raman analysis of VO$_x$/SiO$_2$ suggests surface vanadates are primarily monomeric at all vanadium loadings. In general, pronounced sensitivity to the proximity of vanadium active sites is not widely reported for oxidative chemistries; however, the majority of prior reports consider alcohol oxidation$^{19, 87, 89}$ and alkane oxidative dehydrogenation$^{18, 21, 90, 91}$ which require transfer of a single lattice oxygen to complete the catalytic cycle. In contrast, although elementary mechanisms and rate controlling steps are not well-established for oxidative ketone scission, it is clear that transforming a ketone into carboxylic acid and aldehyde co-products requires transfer of two oxygen atoms. It is therefore
plausible that intrinsic rates of ketone oxidation might be higher at vanadium site pairs (e.g., in polyvanadates) than they are at isolated VO₄ monomers.

The second explanation for increasing site time yields as a function of vanadium loading is that oxidation site counts inferred from methanol TPSO include contributions from both the support and from vanadium oxides (Table 2.2); however, only vanadium oxides (with the exception of CeO₂) are active for oxidative scission under our reaction conditions. Because the supports are generally inert to oxidative ketone scission, active oxidation sites are over-counted by methanol TPSO when the support is partially exposed. This is especially problematic at low vanadium loadings as, in these cases, one expects sparse VOₓ coverages and large fractions of exposed support surface area. This is supported by our observation of oxygen dispersions well above 1.0 for all of the 0.1 monolayer samples (Table 2.2). Inflated site counts would lead to artificially low site time yields on sparsely covered surfaces. As the VOₓ coverage increases up to and beyond monolayer coverage, one expects that the majority of the exposed surface area becomes dominated by polymeric VOₓ species rather than the bare support (on VOₓ/Al₂O₃, VOₓ/TiO₂, and VOₓ/CeO₂ specifically). At high loadings of vanadium, all sites counted by methanol TPSO are thus part of a relatively uniform population of surface sites (i.e., those in polyvanadates). As the support no longer contributes to active site counts, observed site time yields no longer vary with vanadium loading.

Unfortunately, the characterization methods employed here are unable to quantitatively resolve the surface distribution of mono- and polyvanadate species, which makes it difficult to answer the question of whether reactivity indeed scales with the proximity of VOₓ clusters. However, with the exception of the VOₓ/SiO₂ series, we can state with some confidence that a) the accessible surface area in 1.0 and 1.5 monolayer catalyst samples is likely dominated by
vanadium oxides rather than exposed support and b) the distribution of accessible surface vanadium oxide sites in 1.0 and 1.5 monolayer samples is polyvanadate rich. (Note that VO_x/SiO_2 is excluded from this group since Raman spectra do not provide definitive evidence of polyvanadate formation on VO_x/SiO_2, whereas it is clearly indicated at high vanadium loadings on VO_x/Al_2O_3, VO_x/TiO_2, and VO_x/CeO_2.) Accordingly, we take site time yields estimated for VO_x/Al_2O_3, VO_x/TiO_2, and VO_x/CeO_2 in the high coverage limit to represent the intrinsic reactivity of dispersed, polymeric VO_x sites on each support. Based on the average of site time yields estimated at 1.0 and 1.5 monolayer coverages, intrinsic activities of supported vanadium oxides increase in the following order: VO_x/γ-Al_2O_3 (6.8 ± 0.1 x 10^{-4} s^-1) < VO_x/TiO_2 (15 ± 2.7 x 10^{-4} s^-1) ≈ VO_x/CeO_2 (17 ± 0.8 x 10^{-4} s^-1). This result is in line with the frequent observation that support reducibility is a strong predictor of reactivity in heterogeneously catalyzed oxidations.22, 92-94 An increase in intrinsic reactivity with the reducibility of the support cation suggests that reduction of the V-O-M bond is kinetically significant, which implies a Mars-van-Krevelen redox mechanism. Finally, it is worth noting that bare CeO_2 is intrinsically active for 2-pentanone oxidation, presenting a site time yield of 6.7 ± 1.0 x 10^{-4} s^-1. This is roughly a factor of 2 lower than that observed on vanadium oxide sites dispersed onto a CeO_2 support (17 ± 0.8 x 10^{-4} s^-1).

Despite their low surface areas and oxidation site counts (Table 2.2), bulk V_2O_5 and CeVO_4 have appreciable intrinsic activity during ketone oxidation. Under identical conditions to those used to generate Figure 2.6, measured site time yields of 2-pentanone oxidation over V_2O_5 and CeVO_4 are 25 ± 2.0 x 10^{-4} s^-1 and 21 ± 0.9 x 10^{-4} s^-1. On a per-active site basis, bulk vanadate structures thus have comparable intrinsic reactivity to the most active of our supported vanadates. Raman spectra (Figures 2.2-2.5) also indicate that catalysts with high vanadium loadings are rich in bulk
structures. Rates reported here are estimated based on species production rates, which are extensive quantities that reflect the sum of background reactivity, support reactivity, reactivity associated with dispersed vanadium oxides, and reactivity associated with bulk vanadium oxides. We have corrected data for background reactivity and have demonstrated (Figure 2.6) that, with the exception of CeO₂, supports do not contribute substantially to measured rates of oxidative scission under our reaction conditions. However, because bulk vanadate phases display a high intrinsic activity toward oxidative scission, and because Raman spectra indicate extensive formation of bulk phases in many samples, it is reasonable to ask whether they contribute substantially to measured reactivity in our system.

Based on their low surface areas and poor oxidation site accessibility, it is tempting to dismiss potential contributions of bulk structures outright; however, this depends on crystallite sizes for the bulk structures on the various supports. Nanoscale particles of either bulk phase could have appreciable surface area relative to their volume and thus display a higher oxidation site dispersion than the bulk samples that we have characterized in Table 2.2. We have not quantitatively assessed particle size distributions for bulk vanadium oxide structures present in supported catalysts; however, detailed analysis of Raman spectra is sufficient to exclude substantial bulk vanadate contributions to reactivity. In general, the width of Raman peaks scales inversely with the size of crystalline domains.⁹⁵-⁹⁹ Single crystals display the lower limit on peak width, large bulk particles approach this limit, and small nanostructures show substantial broadening relative to this limit. Accordingly, Table 2.3 summarizes full width at half maxima (FWHM) for V₂O₅ and/or CeVO₄ phases where they are observed on VOₓ/SiO₂, VOₓ/γ-Al₂O₃, VOₓ/TiO₂, and VOₓ/CeO₂.
Table 2.3. FWHM of peaks corresponding to V2O5 or CeO4 at 148, 285, 997,863 cm⁻¹ for all the catalysts and the bulk structures. nr = not resolved; -- = not detected.

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<th>Peak (cm⁻¹)</th>
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<th>CeVO₄</th>
<th>γ-Al₂O₃</th>
<th>TiO₂</th>
<th>CeO₂</th>
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<td>1.0</td>
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<td>0.1</td>
</tr>
<tr>
<td>148</td>
<td>11</td>
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<td>9</td>
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</table>

A detailed analysis of peak widths indicates little difference between V₂O₅ and or CeVO₄ bands in supported catalysts and those in bulk samples, which suggests similarly sized crystalline domains. Therefore, where bulk structures are present in supported catalysts, their oxidation site densities can be reasonably approximated by those measured on bulk samples: 14 µmol g⁻¹ for V₂O₅ and 78 µmol g⁻¹ for CeVO₄. Based on these site densities, if one assumes the entire mass content of vanadium in VOₓ/SiO₂, VOₓ/γ-Al₂O₃ and VOₓ/TiO₂ series are present as bulk V₂O₅, one predicts oxidation site counts that range from 0.1 – 1.1 µmol g⁻¹. Experimentally, methanol TPSO indicates oxidation site densities that are at least two orders of magnitude larger than this (Table 2.2), which suggests a minimal contribution from the bulk phase in VOₓ/SiO₂, VOₓ/γ-Al₂O₃ and VOₓ/TiO₂ catalysts. Similarly, if one assumes the entire vanadium content in the VOₓ/CeO₂ series is present in bulk CeVO₄ structures, one predicts oxidation site densities ranging from 2.1 to 27.5 µmol g⁻¹. These values are, in the most extreme case, an order of magnitude smaller than observed oxidation site densities, again suggesting that the bulk phase does not contribute substantially to measured site densities or reactivity in VOₓ/CeO₂ samples.
2.5 Conclusions

In the loading ranges considered here, VO₅ supported on SiO₂, γ-Al₂O₃, and TiO₂ exist as a diverse population of bulk V₂O₅ nanoparticles and dispersed, mono- and polyvanadates, whereas VO₅/CeO₂ exhibits surface mono- and polyvanadates and a bulk CeVO₄ phase. Based on methanol TPSO and reactivity data, we conclude that both bulk V₂O₅ and CeVO₄ have considerable intrinsic reactivity toward the oxidative scission of 2-pentanone; however, their low surface areas translate to poor dispersion of reducible oxidation sites, and they have low activities per unit mass. When bulk structures are present alongside surface vanadates in a supported vanadium oxide, they do not contribute substantially to total site counts or rates of oxidative scission. Likely, this is due to the persistence of relatively large crystalline domains, which limits oxidation site accessibility and thus their extensive contributions to reactivity. When using methanol TPSO to assess oxidative capacity, exposed support surface area can contribute substantially to the total oxidation site count; however, SiO₂, γ-Al₂O₃, and TiO₂ are inert toward 2-pentanone oxidation under our reaction conditions. CeO₂ displays innate activity during the oxidative scission of 2-pentanone, but it is less active than vanadium oxides dispersed on the surface of CeO₂. We observe that site time yields for the oxidative scission of 2-pentanone increase with the extent of polyvanadate formation across multiple supports, which provides some evidence of structure sensitivity in this reaction; however, this conclusion is tempered by uncertainty in the use of methanol TPSO for the titration of oxidation sites. Measured site time yields in 2-pentanone oxidation also appear support-dependent, increasing in the order VO₅/γ-Al₂O₃ < VO₅/TiO₂ < VO₅/CeO₂, which likely reflects the underlying trend in support reducibility.
2.6 Supporting Information

This study considers rates measured over supported vanadium oxides having varied vanadium loadings (active sites) for each support. Site time yields (STY) were estimated based on measured rates of oxidative scission and the number of active sites as determined by TPSO of adsorbed methanol. On the majority of our catalyst series, we observe variation in STY with vanadium loading. This may indicate reaction rates that are controlled by mass or heat transfer; however, it is also possible that oxidative scission of ketones is a structure sensitive reaction or that other artifacts obscure a true site-time yield. The possibility of a structure sensitive reaction makes it difficult to apply a Madon-Boudart type test in this system as changing the vanadium loading will generally also change the structure of supported vanadates. In order to exclude the possibility that transport limitations obscure true reaction rates in this system, we tabulate theoretical criteria for maintaining kinetic control. Further, we consider the effect of particle size on measured reaction rates in our most demanding system.

Threshold criteria were evaluated at the maximum rate of oxidative scission observed for each support under reaction conditions (T = 466K, P = 915 Torr, P_{2-P} = 14 Torr). Data used in estimating mass and heat transfer coefficients are summarized in Table S2.1. In certain cases, there is flexibility in assigning a parameter value. For example, the reaction enthalpy listed in Table 2.1 represents that for complete combustion of 2-pentanone to CO₂ and H₂O. Although we observe very little actual yield of CO₂ under our reaction conditions, this represents the most constrained situation for heat transfer—that of a strongly exothermic combustion. Throughout our analysis, we have employed this approach of using relatively conservative values that we believe represent the most difficult scenarios for maintaining kinetic control. We assume that if criteria are satisfied under these conditions, they are also satisfied at the remainder of
Since the 2-pentanone partial pressure was maintained at a dilute 14 Torr for all reactions, bulk properties of the flowing gas were evaluated with assumption that the process gas is binary mixture of helium (763 Torr) and oxygen (153 Torr). The total gas flowrate was 60 ml min⁻¹ at
STP, which corresponds to $1.3 \times 10^{-6} \, \text{m}^3 \, \text{s}^{-1}$ at our reaction temperature and pressure. Diffusivity of helium and oxygen gas mixture were computed under reaction conditions based on the work of Wasik and McCulloh.\textsuperscript{40} Mass and heat transfer coefficients were obtained using methods in \textit{Transport Processes and Unit Operations} by Geankoplis\textsuperscript{41} and in \textit{Unit Operations of Chemical Engineering} by McCabe, Smith, and Harriott.\textsuperscript{44} Mean free path, average velocity and Knudsen diffusion were computed using correlations in \textit{Kinetics of Catalytic Reactions} by Vannice.\textsuperscript{45} We have estimated the diameter of 2-pentanone based on its density, molecular weight, and assumption of spherical molecular shape. Thermal conductivity of the gas mixture was calculated using Wilke’s rule.\textsuperscript{39} The apparent activation energy for combustion was estimated from yields of combustion products observed in our system over a range of reaction temperatures. In addition to the generic system parameters summarized in table S2.1, table S2.2 lists maximum observed rates for each support alongside the different physical properties. Since our computed mean free path is larger than the pore diameters in our catalyst supports, we assume that the effective diffusivity in a given system is equal to the Knudsen diffusivity. Although there is considerable uncertainty in estimating a diffusivity, we note that these values are in the range of $1.0 \times 10^{-6} \, \text{m}^2 \, \text{s}^{-1}$, which is relatively conservative for gas diffusion.
Table S2.2. Parameters used in evaluating criteria for each support.

<table>
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<tr>
<th>Parameter</th>
<th>SiO$_2$</th>
<th>γ-Al$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CeO$_2$</th>
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<td>Pore Size (Å)</td>
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<td>75</td>
<td>320</td>
<td>160</td>
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<tr>
<td>Density (g m$^{-3}$)</td>
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<td>2.4 × 10$^6$</td>
<td>2.5 × 10$^6$</td>
<td>4.3 × 10$^6$</td>
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<tr>
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<td>3.8 × 10$^{-6}$</td>
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</tr>
<tr>
<td>Thermal conductivity (W m$^{-1}$K$^{-1}$)</td>
<td>1.4</td>
<td>23</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>$r''$ (μmol g$^{-1}$ min$^{-1}$)</td>
<td>42</td>
<td>29</td>
<td>27</td>
<td>31</td>
</tr>
<tr>
<td>$r''$ (mol m$^{-3}$ s$^{-1}$)</td>
<td>1.1</td>
<td>1.2</td>
<td>1.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Mass and heat transfer threshold criteria were calculated through equation S2.1-S2.4, and results are summarized in Table S2.3. Equation S2.1 was taken from *Kinetics of Catalytic Reactions* by Vannice,$^{45}$ and equation S2.2 – S2.4 were taken from *The Microkinetics of Heterogeneous Catalysis* by Dumesic.$^{43}$

Weisz-Prater Criteria for excluding intraparticle diffusion limitations for a second order reaction:

$$\frac{r'' \cdot r_p^2}{C_s \cdot D_e} < 0.3 \quad (S2.1)$$

Criteria for excluding interphase mass transfer limitations:

$$\frac{r'' \cdot r_p}{C_s k_c} < 0.15 \quad (S2.2)$$

Criteria for excluding intraparticle Heat Transfer Limitations

$$\frac{|\Delta H_{rxn}| \cdot r'' \cdot r_p^2}{\lambda T_s} \cdot \frac{E_A}{RT_s} < 0.75 \quad (S2.3)$$

Criteria for excluding interphase heat transfer limitations:

$$\frac{|\Delta H_{rxn}| \cdot r'' \cdot r_p}{h T_b} \cdot \frac{E_A}{RT_b} < 0.15 \quad (S2.4)$$
Table S2.3. Summary of threshold criteria for 2-pentanone alkyl oxidative scission reactions over each support at the highest measured rates

<table>
<thead>
<tr>
<th>Support</th>
<th>Mass Transfer</th>
<th>Heat Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intraparticle</td>
<td>Interphase</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.4 x 10⁻¹</td>
<td>6.9 x 10⁻⁵</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.8 x 10⁻²</td>
<td>7.2 x 10⁻⁵</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.0 x 10⁻²</td>
<td>7.0 x 10⁻⁵</td>
</tr>
<tr>
<td>CeO₂</td>
<td>2.8 x 10⁻²</td>
<td>1.4 x 10⁻⁴</td>
</tr>
</tbody>
</table>

According to tabulated criteria, even under the most constraining conditions (i.e., highest measured initial rates of reaction), threshold criteria are met in this system. However, the Weisz-Prater criterion for SiO₂ supported catalyst is approaching the threshold value. This is attributed to the fact that VOₓ/SiO₂ catalysts at 1.0 and 1.5 monolayer loadings had the highest measured oxidation site densities of any catalyst tested in this study and thus the highest measured rates of oxidation per unit volume of catalyst; thus, the VOₓ/SiO₂ system is the most demanding for satisfying kinetic control. Because threshold criteria cannot definitively exclude the possibility of intraparticle diffusion limitations, it was necessary to probe them experimentally.

Figure S2.1. Deactivation profiles of 2-pentanone oxidative scission reaction over 1.0 monolayer VOₓ/SiO₂ catalyst with two different particle sizes: a) methyl scission, b) alkyl scission.
To do so, we measured the rate of 2-pentanone oxidative scission on two VO\textsubscript{x}/SiO\textsubscript{2} catalysts of different particle sizes prepared at 1.0 monolayer loading. Specifically, we measured the rate of oxidative scission on the 1.0 monolayer VO\textsubscript{x}/SiO\textsubscript{2} sample in a sieve cut of particles ranging in diameter from 45-90 μm (T = 466K, P\textsubscript{2-P} = 14 Torr). A second 1.0 monolayer VO\textsubscript{x}/SiO\textsubscript{2} sample was pelletized, crushed, and sieved to obtain a larger particle size distribution (90-120 μm), which was then employed for oxidative scission of 2-pentanone under identical conditions. Figures S2.1a and S2.1b illustrate the deactivation profiles of the same catalyst with two different size ranges, and it is clear that oxidation rates are independent of particle size in this range. Initial rates for methyl and alkyl bond scission were estimated by fitting a first order decay model to the temporal profiles shown in Figures S2.1 and S2.2. Since 2-pentanone oxidative scission is exothermic, the high conversion at zero time on stream will generate heat, resulting in a rise in temperature downstream of the catalyst bed (about 3-4 K at our condition), suggesting non-isothermal operation during initial startup. The bed temperature stabilizes after roughly 150 minutes, whereafter a maximal gradient of 1K across the bed is indicated; consequently, only data measured after 150 minutes were used in estimating the initial reaction rate. Over the 90 – 120 μm sieve cut, the alkyl scission rate (R\textsubscript{A}) was 0.61 ± 0.04 μmol s\textsuperscript{-1}g\textsuperscript{-1} and the methyl scission rate (R\textsubscript{T}) was 0.022 ± 0.002 μmol s\textsuperscript{-1}g\textsuperscript{-1}. Comparing with the smaller sized catalyst (D\textsubscript{p} = 45-90 μm), the alkyl scission rate was 0.59 ± 0.04 μmol s\textsuperscript{-1}g\textsuperscript{-1} and the methyl scission rate was 0.025 ± 0.003. All estimations are indistinguishable within statistical precision, and we conclude that the rates measured on the two samples have no dependence on particle size and are therefore free of intraparticle transport limitations. As this material presented the highest rate per volume in the set of catalysts considered here, we assume this conclusion extends to all other materials considered in this study.
2.6.1 Raman spectra

Figure S2.2. Raman spectra of supported vanadates on SiO$_2$, VOx/SiO$_2$. The spectra were normalized to the peak intensity of the broad SiO$_2$ band at 460 cm$^{-1}$. 
Figure S2.3. Raman spectra of supported vanadates on γ-Al₂O₃, VOx/γ-Al₂O₃. Due to the absence of support bands, VOx/Al2O3 spectra were normalized to spectral intensity at 1100 cm⁻¹.
Figure S2.4. Raman spectra of supported vanadates on TiO$_2$ and VOx/TiO$_2$. The spectra were normalized to the TiO2 band at 640 cm$^{-1}$. 
Figure S2.5. Raman spectra of supported vanadates on CeO$_2$ and VOx/CeO$_2$. The spectra were normalized to the ceria band at 467 cm$^{-1}$
Figure S2.6. Raman spectra of crystal V$_2$O$_5$ and CeVO$_4$. The V$_2$O$_5$ spectrum was normalized to band at 147 cm$^{-1}$ and the CeVO$_4$ spectrum was normalized to band at 860 cm$^{-1}$. 
2.7 References


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68. Oyama, S. T.; Went, G. T.; Lewis, K. B.; Bell, A. T.; Somorjai, G. A., Oxygen chemisorption and laser Raman spectroscopy of unsupported and silica-supported vanadium


84. Banares, M.; Martinez-Huerta, M.; Gao, X.; Fierro, J.; Wachs, I., Dynamic behavior of supported vanadia catalysts in the selective oxidation of ethane: In situ Raman, UV–Vis DRS
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CHAPTER 3
Understanding the Origin of Maleic Anhydride Selectivity During the Oxidative Scission of Levulinic Acid

3.1 Abstract

Biomass-derived levulinic acid (LA) is a green platform chemical, and we have previously reported a novel oxidative scission pathway that transforms levulinic acid into maleic anhydride (MA) over supported vanadates in good yield. This reaction is curious because it requires oxidative scission of the terminal (methyl) ε-carbon in levulinic acid whereas ketone oxidations are typically selective toward internal (alkyl) bond scission. In order to probe the origin of this unique selectivity, we consider trends observed during the oxidative scission of ketones, keto-acids, and keto-acid analogs, and we highlight the influences of steric hindrances, α-carbon substitution, and the presence of a secondary carboxylic acid functionality. We further consider the role of cyclic intermediates, namely angelicalactones, in mediating selectivity during the oxidative scission of levulinic acid. Our kinetic analysis is supported by FTIR spectroscopy, which reveals the formation of hydrogen-deficient surface intermediates prior to the onset of oxidative scission. We further paired short-contact time selectivity analysis with GCMS and NMR spectroscopy to identify a previously undisclosed reaction intermediate—protoanemonin—that forms during the oxidative scission of both levulinic acid and α-angelicalactone. We conclude that facile oxidative dehydrogenation of α-angelicalactone to form protoanemonin is the major driving force for the high selectivity toward methyl scission during levulinic acid oxidation. We also note that protoanemonin is an intriguing polyfunctional molecule that appears to be uniquely suited to bio-based production, and we have observed that it can be synthesized in yields from 50% - 75% during periods of transient reactor operation.
3.2 Introduction

We have reported that the vapor-phase, aerobic oxidation of levulinic acid affords maleic anhydride (Scheme 3.1) in good yield (>70%). Based on consideration of the relevant literature, this is an unexpected result. From an oxidative scission perspective, levulinic acid (4-oxopentanoic acid) can be viewed as a methylketone. During oxidation, it can only form maleic anhydride through methyl scission—specifically, though the oxidative scission of the C₄-C₅ bond between the carbonyl carbon and its methyl α-carbon. However, prior accounts of simple methylketone oxidation report only trace selectivity toward methyl scission, which makes a high yield of maleic anhydride noteworthy. The obvious difference between levulinic acid and a methylketone is that levulinic acid is bifunctional, i.e., it is a keto-acid. It is reasonable to expect that the presence of the carboxyl group underlies the stark differences in methyl scission selectivity; however, the mechanistic origins remains unclear. Aerobic ketone oxidation using homogeneous catalysts is well-studied in condensed media, but analogous insights for heterogeneously-catalyzed oxidations are sparse.

Our aim here is to resolve the origin of the unexpectedly high selectivity toward methyl scission during the vapor-phase, oxidation of levulinic acid over vanadium oxides. We do so primarily by comparing the oxidative scission of levulinic acid and various analogs that have been selected to interrogate specific impacts of ketone structure and secondary functionality. Kinetic analysis is supported by FTIR and NMR spectroscopies, which we use to provide insights into the nature of bulk and surface species formed during various oxidation reactions.
3.3 Materials and Methods

3.3.1 Reagents

We quantify rates and selectivities during the oxidative scission of 2-propanone (Acros, 99%), 2-propanone-d₆ (Aldrich, 99.9% D), 2-butanone (Acros 99%), 2-pentanone (Acros, 99%), 2-hexanone (Acros 98%), 2-heptanone (Acros, 98%), 2-octanone (Acros, 99%), 3-methyl-2-pentanone (Sigma 97%), 4-methyl-2-pentanone (Sigma, 99%), 3,3-dimethyl-2-pentanone (Oakwood, 96%), 4,4-dimethyl-2-pentanone (Acros, 99%), levulinic acid (Acros, 98%), and α-angelicalactone (Alfa Aesar, 98%). Additional reference samples were used for species identification and instrument calibration. These include ethanoic acid (Acros, 98%), propanoic acid (Acros 99%), butanoic acid (Acros 99%), pentanoic acid (Acros, 99%), hexanoic acid (Acros, 99%), heptanoic acid (98%, Acros), 2-methyl butanoic acid (Sigma, 98%), 2,2-dimethyl butanoic acid (Acros, 99%), 3,3-dimethyl butanoic acid (Sigma, 98%), maleic anhydride (TCI, 99%), 1,3-cyclopentanedione (Acros, 99%), 4-cyclopentene-1,3-dione (Aldrich, 95%), ethanal (Sigma, ≥99.5%), propanal (Acros, 99%), butanal (Acros, 99%), pentanal (Acros, 98%), hexanal (Alpha Aesar, 98%), α′-angelicalactone (TCI, 98%), CO (Airgas, 1%, 1% Ar, He balance) and CO₂ (Airgas, 1%, 1% Ar, He balance). Our catalyst synthesis method used γ-Al₂O₃ (Strem, 95%), ammonium metavanadate (Sigma, 99.5%), and oxalic acid (Acros, 99%). β-angelicalactone was not available commercially, so it was synthesized by mixing triethylamine (Acros, 99%) with α-angelicalactone in 1:1 molar ratio and stirring at room temperature for 16 hours. This resulted in a two-phase mixture with a dense lower phase containing angelicalactone isomers in a molar ratio of 2:8 (a:b). It was extracted and used to acquire FTIR reference spectra, calibrate GC retention times, and obtain reference MS fragmentation patterns.
For quantitative analysis, the FID response factor for $\beta$-angelicalactone was taken to be equal to that of its isomer, $\alpha$-angelicalactone. Water was purified by reverse osmosis, UV oxidation, and ion exchange to a resistivity >18.2 M$\Omega$-cm (Spectrapure). O$_2$ (Airgas, Ultra High Purity) and He (Airgas, Ultra High Purity) were used as oxidant and diluent during reactor operation. Air (Airgas, Ultra Zero) was used for ex-situ calcination of catalyst samples.

3.3.2 Catalyst synthesis

Experiments were carried out using a VO$_x$/\gamma-Al$_2$O$_3$ catalyst prepared at a loading of 8.0 V nm$^{-2}$ by impregnation of aqueous vanadium oxalate onto a $\gamma$-Al$_2$O$_3$ support (231 m$^2$ g$^{-1}$) that was pre-calcined under zero-grade air (723K, 3 K min$^{-1}$ ramp, 4h hold, 60 ml min$^{-1}$). Ammonium metavanadate and oxalic acid were dissolved in water at 343K at 1:2 molar ratio.$^{13-14}$ The solution was then added to the calcined $\gamma$-Al$_2$O$_3$ at a loading of 1.1 mL solution per gram of $\gamma$-Al$_2$O$_3$. The resulting slurry was dried in an oven at 338 K for 16 hours and then calcined under flowing air (723K, 3 K min$^{-1}$ ramp, 4h hold, 60 ml min$^{-1}$).$^{15}$ The catalyst was then crushed and sieved. All samples utilized here had a particle size range of 45-90 $\mu$m.

3.3.3 Oxidative scission reactions

Rates and selectivities for oxidative scission were measured at steady state in a packed bed reactor.$^{16}$ 50 – 100 mg of VO$_x$/\gamma-Al$_2$O$_3$ were diluted to 20 wt.% in quartz granules (45-90 $\mu$m) and placed between quartz wool plugs at the center of a 6” long ½” OD stainless steel tube. The tube upstream of the catalyst bed was filled with quartz chips, and an inline type-K thermocouple was positioned in the void space downstream of the catalyst bed to monitor the internal temperature. All transfer lines were heat traced and held at 500K, which was sufficient to prevent
condensation and/or crystallization of all species at their representative partial pressures. Effluent concentrations were measured using an inline gas chromatograph (HP 5890). It was equipped with two inlets, two columns, and two detectors. We used an HP-INNOWax column paired with an FID detector for analysis of hydrocarbons, and we used a Restek ShinCarbon ST Micropacked column paired with a TCD detector for analysis of carbon oxides. Reaction products were qualitatively identified by matching GC retention times with those of reference standards, by comparison with NIST libraries using GC-MS (Agilent 7890 + 5975C MSD), and/or by solution NMR (Bruker Avance III HD 400MHz). Carbon balances for all experiments closed to ≥95%, and monitoring of internal and external bed temperatures confirmed isothermal operation.

VOₓ/γ-Al₂O₃ deactivates during oxidative scission, and reactors typically reach steady state within 20 hours on stream. Unfortunately, the rate and extent of deactivation vary with the identity of the probe molecule, which demands caution when comparing steady-state rate measurements between different probe molecules. To address this, each experiment was initialized with 2-pentanone oxidation (466K or 550K, WHSV = 1.95 h⁻¹, 12.3 Torr 2-pentanone, 133 Torr O₂, He balance). The system was allowed to reach steady state, and effluent flowrates were quantified. Subsequently, we made a step change in probe molecule identity while holding all other parameters constant. The system was again allowed to reach steady state, and effluent flowrates were again quantified. Finally, the probe molecule was switched back to 2-pentanone, and the system was permitted to return to steady state. Doing so allowed us to correct for catalyst deactivation and/or induction caused by a change in probe molecule identity, ensuring a common basis for comparing oxidation rates for varying probe molecules. We did not characterize deactivation modes, but catalyst activity was fully restored by calcination in He/O₂ mixture (133
Torr O₂, He balance) at 450°C, implicating either carbon deposition or reduction of the lattice. Upon regeneration, catalyst beds retained their initial reference activity indefinitely (>10 cycles).

3.3.4 FTIR spectroscopy

We employed in situ transmission FTIR to probe the nature of surface species during ketone oxidation (Nicolet 6700, DTGS detector). We used a home built-cell constructed from a vacuum tee (McMaster-Carr, 1½” OD) with electrical feedthroughs and CaF₂ windows. The cell was configured to accommodate an aluminum sample holder positioned orthogonal to the IR beam. The sample holder was drilled to accept two cartridge heaters (McMaster, 1/8”×1 ¼”) and a type K thermocouple, which were used with a PID controller (Love Controls, Series 16A) to regulate temperature. To allow gas flow or sample evacuation, two ¼” tubes were welded onto the vacuum tee body; each was equipped with a ¼” bellows valve. Prior to introducing the catalyst sample, the cell was purged under continuous air flow (Peak Scientific, PG28L), and the sample holder was heated to 723K (3 K min⁻¹, 4h hold, 100 ml min⁻¹). The sample holder was then cooled to 573K and purged for 30 minutes with a He/O₂ blend (Airgas, 15% O₂, 85% He, 100 ml min⁻¹) that was purified by passing sequentially through a liquid nitrogen trap and a molecular sieve trap (Agilent, MT200-4). FTIR spectra were then acquired at 5 minute intervals until the system reached steady state. The final spectrum was used as the background reference, and the sample holder was cooled to ambient temperature. Subsequently, 15 mg of sample (VOₓ/γ-Al₂O₃ or γ-Al₂O₃) were pressed into a wafer using a hydraulic press (Specac M26855), secured in the aluminum sample holder, and subjected to an identical calcination procedure to that described for the empty cell. Reference spectra of the calcined catalyst and support were obtained at each reaction temperature. Probe molecules were next introduced by vaporizing species into the
He/O\textsubscript{2} carrier at a pressure of 0.2 Torr, which proved sufficiently high to generate detectable coverages of surface species and sufficiently low to minimize gas-phase bands and avoid condensate formation. Probe molecules were introduced through capillary tubing into a temperature-controlled vaporizer comprised of a stainless-steel tee that was heat-traced, insulated, and packed with quartz wool. Liquid flow was controlled using a syringe pump (Cole Parmer series 100). Maleic anhydride is a high-melting solid, so it was introduced by sublimation. Specifically, we passed the carrier through a temperature-controlled saturation chamber containing solid maleic anhydride. After exposing the catalyst to the probe molecule, FTIR spectra were acquired at 5 minute intervals until reaching steady state. The sample temperature was then increased by 60 K (3K/min), and the process was repeated until reaching 473K. The catalyst pellet was changed for each probe molecule. Both the cell body and transfer lines were heat-traced and held at sufficient temperatures to prevent condensation of probe molecules and their oxidation products at representative partial pressures.

3.3.5 NMR spectroscopy

We used NMR to determine the structure of a previously unidentified reaction intermediate observed during the oxidation of levulinic acid and \( \alpha \)-angelicalactone. NMR spectra were recorded at 300 K on Bruker AVANCE III HD 400MHz spectrometer equipped with a liquid nitrogen-cooled Prodigy probe. NMR samples were prepared by bubbling vapor-phase reaction products through a cold trap containing perdeuterated 2-propanone (2-propanone-d\textsubscript{6}, C\textsubscript{3}D\textsubscript{6}O). Attempts to isolate and purify the unknown reaction product induced polymerization and precipitation, which prevented a detailed structural assignment. It was thus necessary to record spectra for unrefined reaction products. We enriched the mixture in the target molecule by
operating reactors under conditions that gave high selectivity to the unknown intermediate (confirmed by GC). We also obtained reference spectra for all known species present in appreciable concentrations in the product mixture. These were ethanoic acid, α-angelicalactone, and maleic anhydride. Each was separately dissolved in an aliquot of the C3D6O solution containing reaction products, which permitted resolution of peaks associated with known compounds from those associated with the unidentified intermediate. 1D 1H spectra were obtained at a spectral width of 20 ppm in 16 scans with a relaxation delay of 1s and 65536 data points. Proton spectra were referenced to the 2-propanone methyl hydrogen peak at 2.05 ppm. 1D 13C spectra were acquired at a spectral width of 239 ppm in 256 scans with a relaxation delay of 2s and 65536 data points. Carbon spectra were referenced to the 2-propanone methyl carbon at 29.93 ppm. 1H-13C HSQC spectra were collected using the Bruker pulse sequence hsqcetgfpsisp 2.3, which includes multiplicity editing during the selection step. HSQC spectra had 2048 x 256 data points with spectral widths of 13 ppm in the 1H dimension and 165 ppm in the 13C- dimensions. 4 scans were acquired during each t1 increment. HSQC data were apodized by a cos² function in both dimensions with zero-filling in the remote dimension to give a final data set of 1000 x 1000 points. Spectra were analyzed using Bruker’s Topspin 3.6.1 software. Qualitative peak assignments were made using comparisons to reference standards and, where necessary, predicted NMR spectra generated using ChemDraw 18.0.

3.3.6 Contact time experiments

To distinguish between primary and sequential reaction products during the oxidative scission of levulinic acid and α-angelicalactone, we measured product selectivities as a function of contact
time ($\tau$), which is defined per Eq. 3.1 as the catalyst mass ($m_C$) divided by the influent mass flowrate of the probe molecule ($\dot{m}_R$).

$$\tau = \frac{m_C}{\dot{m}_R}$$  \hspace{1cm} (3.1)

Contact time experiments were performed at 550K under 5 Torr of levulinic acid or $\alpha$-angelicalactone and 133 Torr O$_2$ in a He balance. To separate lactone isomers, we used a Restek RTX-1701 column in GC-FID described in Section 2.3; otherwise, the reactor and analytical equipment were identical to the previously described system (Section 1.3). Each experiment was initialized by feeding the probe molecule into the reactor and allowing it to reach steady state. Subsequently, the contact time was varied by changing the inlet flowrates of all species as necessary to maintain constant feed partial pressures, and the system was again permitted to reach steady state. We observed that contact time had no significant impact on catalyst deactivation; accordingly, contact times were varied progressively without returning to initial conditions, and deactivation corrections were not employed. This approach is acceptable since the probe molecule identity remained fixed for the duration of the experiment, and we discuss only the evolution of selectivity as a function of contact time rather than making a comparison of rates as a function of time on stream. Where it was necessary to increase or decrease contact time beyond the range permitted by modulation of inlet flowrates, we varied the mass of catalyst.
3.4 Results and Discussion

For each probe molecule, we report rates and selectivities for the oxidative scission of the C-C bonds between the carbonyl carbon and each of its α-carbons (Scheme 3.2). We focus primarily on asymmetric methylketones, where one α-carbon is a methyl group and the other is an alkyl chain. We thus refer to the two scission pathways as “methyl scission” and “alkyl scission.” Regardless of the pathway, oxidative ketone scission yields two primary products: a carboxylic acid that is formed by oxidation of the reacting ketone’s carbonyl carbon, and an aldehyde or ketone that is formed by oxidation of its cleaved α-carbon.\(^{17-20}\) Ketones and aldehydes can undergo secondary reactions at typical operating conditions, which prevents one from equating their production rates with the primary rate of oxidative scission. In contrast, the carboxylic acids initially formed through oxidative scission are stable, and we use their production rates to define mass-normalized rates of methyl and alkyl scission (Eq. 3.2 and Eq. 3.3).\(^{16}\)

\[
R_m = \frac{F_{C_{n+1}COOH}}{m_c}
\]

(Scheme 3.2: Methyl and alkyl oxidative scission pathways for methylketones.)
\[ R_A = \frac{F_{el}}{m_c} \]  

(3.3)

\[ S_M = \frac{R_M}{R_M + R_A} \]  

(3.4)

\[ S_A = \frac{R_A}{R_M + R_A} \]  

(3.5)

Table 3.1: Oxidative scission rates and selectivities toward methyl and alkyl scission for linear and branched methylketones.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Oxidative Scission Rate (μmol g⁻¹min⁻¹)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Alk</td>
</tr>
<tr>
<td>1</td>
<td>2-propanone</td>
<td>1.7</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>2-butanone</td>
<td>0.5</td>
<td>12.5</td>
</tr>
<tr>
<td>3</td>
<td>2-pentanone</td>
<td>0.5</td>
<td>7.9</td>
</tr>
<tr>
<td>4</td>
<td>2-hexanone</td>
<td>0.3</td>
<td>7.4</td>
</tr>
<tr>
<td>5</td>
<td>2-heptanone</td>
<td>0.3</td>
<td>6.8</td>
</tr>
<tr>
<td>6</td>
<td>2-octanone</td>
<td>0.3</td>
<td>7.1</td>
</tr>
<tr>
<td>7</td>
<td>3-Me-2-P</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>3,3-diMe-2-P</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>4-Me-2-P</td>
<td>0.7</td>
<td>6.2</td>
</tr>
<tr>
<td>10</td>
<td>4,4-diMe-2-P</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Methyl (Me); Alkyl (Alk); 2-pentanone (2-P).

T = 468K, \( P_{\text{Ketone}} \) = 12.3 Torr; \( P_{\text{O}_2} \) = 133 Torr; Helium balance.
Methyl scission produces carboxylic acid fragments that vary with the structure and chain length of the probe molecule. The rate of methyl scission \( (R_M) \) is thus uniquely defined for each probe molecule as the effluent molar flowrate of the \( C_{n-1} \) carboxylic acid divided by the mass of catalyst \( (m_C) \) in the packed bed reactor (Eq. 3.2), where \( n \) is the total number of carbon atoms in the probe molecule. Conversely, alkyl scission of a methylketone always produces ethanoic acid (acetic acid) as a primary product; accordingly, the rate of alkyl scission \( (R_A) \) for all species is given by the effluent flowrate of ethanoic acid \( (F_{EA}) \). As shown in Eq. 3.4 and Eq. 3.5, rates of methyl and alkyl scission are used to define selectivities toward methyl \( (S_M) \) and alkyl scission \( (S_A) \). Oxidative C-C scission is irreversible under our reaction conditions; therefore, scission selectivity is kinetically controlled.\(^1\) Except for 2-propanone (acetone), all probe molecules are asymmetric, and carboxylic acids formed through methyl and alkyl scission pathways are easily resolved by gas chromatography.

We begin by summarizing trends in the oxidative scission of linear and branched methylketones at 468K (Table 1). All rates were obtained over 8.0 V/nm\(^2\) loading \( \text{VO}_x/\gamma-\text{Al}_2\text{O}_3 \)\(^{13-15}\) under differential conditions.

2-propanone is a linear, symmetric ketone with indistinguishable methyl groups in each \( \alpha \)-position. Scission of either \( \alpha \)-carbon forms ethanoic acid, which is produced at a rate of 3.4 \( \mu \text{mol g}^{-1} \text{ min}^{-1} \). Assuming that each \( \alpha \)-carbon contributes half to the total ethanoic acid production rate, we infer an intrinsic methyl scission rate of 1.7 \( \mu \text{mol g}^{-1} \text{ min}^{-1} \). In contrast, \( \text{C}_4-\text{C}_8 \) methylketones are asymmetric, permitting independent quantification of methyl and alkyl scission rates. We observe a threefold decrease in methyl scission rate upon transitioning from 2-propanone (1.7 \( \mu \text{mol g}^{-1} \text{ min}^{-1} \)) to 2-butanone (0.5 \( \mu \text{mol g}^{-1} \text{ min}^{-1} \)). Thereafter, rates of methyl scission are
comparable for 2-pentanone (0.5 μmol g⁻¹ min⁻¹), 2-hexanone (0.3 μmol g⁻¹ min⁻¹), 2-heptanone (0.3 μmol g⁻¹ min⁻¹), and 2-octanone (0.3 μmol g⁻¹ min⁻¹). In total, methyl scission rates decrease significantly between 2-propanone (C₃) and 2-butane (C₄) and then become insensitive to chain length in the C₄ – C₈ range, where we observe a mean rate of 0.38 ± 0.3 μmol g⁻¹ min⁻¹ (95% confidence interval). Relative to the methyl scission rate established for 2-propanone (1.7 μmol g⁻¹ min⁻¹), extending the chain by a single carbon (2-butane) increases the rate of alkyl scission by an order-of-magnitude (12.5 μmol g⁻¹ min⁻¹). Subsequent chain extension to 2-pentanone decreases the alkyl scission rate to 7.9 μmol g⁻¹ min⁻¹, whereas further chain extension only slightly reduces alkyl scission rates for 2-hexanone (7.4 μmol g⁻¹ min⁻¹), 2-heptanone (6.8 μmol g⁻¹ min⁻¹), and 2-octanone (7.1 μmol g⁻¹ min⁻¹). The mean alkyl scission rate for C₅ – C₈ methyl ketones is 7.3 ± 1.5 μmol g⁻¹ min⁻¹ (95% confidence interval), and only 2-butane falls outside this range, suggesting that alkyl scission rates, like methyl scission rates, initially decrease with chain length but become insensitive in the C₅ – C₈ range.

From our delineation of methyl and alkyl scission rates, we highlight three important observations. First, transitioning from methyl scission (2-propanone) to alkyl scission (2-butane) confers an order-of-magnitude increase in oxidation rate. This implies that a secondary α-carbon is far more susceptible to oxidation than a primary α-carbon. Second, within a given category of α-carbons (i.e., considering the scission of either primary or secondary α-carbons), oxidative cleavage rates initially show a strong, inverse scaling with chain length (C₃ – C₅) and thereafter are insensitive to the size of the molecule (≥C₅). We do not expect alkyl chain length to significantly influence free energies of activation or reaction for the elementary scission and bond formation steps that comprise ketone oxidation, so we tentatively attribute this effect to reduced coverages for increasingly bulky probe molecules. We have not confirmed this by
measuring adsorption isotherms; however, it is reasonable to expect that repulsive lateral interactions become significant at lower coverages for larger molecules and that this impact is more pronounced when extending a short chain ketone (e.g., 2-propanone vs. 2-butanone) than when extending a long chain ketone (e.g., 2-heptanone vs. 2-octanone). Finally, rates of alkyl scission are always roughly an order of magnitude higher than rates of methyl scission. This results in an alkyl scission selectivity of ≈95%, which is independent of the probe molecule and aligns with the preference for alkyl scission that is typically reported over vanadium oxides.

We next consider the impact of branching and carbon substitution in the α- and β-positions of the alkyl side chain. Adding a methyl substituent to the 3-position of 2-pentanone creates a tertiary α-carbon in the alkyl side chain. This increases the rate of alkyl scission five-fold relative to that observed for linear C₅ – C₈ methylketones (40 μmol g⁻¹ min⁻¹ vs. 7.3 ± 1.8 μmol g⁻¹ min⁻¹). On the other hand, the rate of methyl scission for 3-methyl-2-pentanone is indistinguishable from methyl scission rates in C₄ – C₈ linear methylketones (0.5 μmol g⁻¹ min⁻¹ vs. 0.38 ± 0.3 μmol g⁻¹ min⁻¹). An enhanced alkyl scission rate alongside a static methyl scission rate improves alkyl scission selectivity to 99% for 3-methyl-2-pentanone. Dimethyl substitution at the 3-position of 2-pentanone (3,3-dimethyl-2-pentanone) creates a quaternary α-carbon. After rigorous subtraction of trace ethanoic acid associated with feed impurities (3,3-dimethyl-2-pentanone was available at a purity of 96%), we found no evidence that 3,3-dimethyl-2-pentanone undergoes alkyl scission, so we conclude that oxidative cleavage is completely suppressed for a quaternary α-carbon. In contrast, its rate of methyl scission is identical to the average observed for C₄–C₈ linear methylketones (0.3 μmol g⁻¹ min⁻¹ vs. 0.38 ± 0.3 μmol g⁻¹ min⁻¹). Since no alkyl scission is observed, 3,3-dimethyl-2-pentanone oxidation is 100% selective toward methyl scission. To probe the impact of substitution at the β-position, we consider the oxidative scission of 4-methyl-
2-pentanone and 4,4-dimethyl-2-pentanone. Data reveal a monotonic increase in methyl scission selectivity with increasing substitution at the β-carbon. Specifically, we observe methyl scission selectivities of 5% for 2-pentanone, 10% for 4-methyl-2-pentanone and 34% for 4,4-dimethyl-2-pentanone. The shift in selectivity arises from a simultaneous increase in methyl scission rates and suppression of alkyl scission rates. This suggests that steric restrictions play an important role in dictating oxidative cleavage selectivity.

The rate of oxidative scission increases monotonically with degree of substitution for primary, secondary, and tertiary α-carbons, yet scission is entirely suppressed for a quaternary α-carbon. For oxidative scission to occur, it is clear that the α-carbon must be bound to at least one hydrogen atom. This stands to reason as, macroscopically, oxidative scission of methylketones converts an sp³ α-carbon (e.g., CH₃) into an sp² carbonyl (e.g., HCHO), which requires elimination of an α-hydrogen. Because fragmentation is completely suppressed for a quaternary α-carbon, we further argue that scission of the α-CH bond must mechanistically precede scission of the α-CC bond. Finally, our observation that rates are enhanced by carbon substitution indicates that the rate controlling step involves either formation or consumption of an intermediate that is stabilized by increased electron density at the α-carbon, e.g., an α-radical or a α-cation (or, in this case, their surface analogs). These conclusions align with mechanisms that have been previously suggested for ketone oxidation in solution. First, whether they are acid-, base-, or radical-initiated, homogeneous ketone oxidations proceed through a sequence of α-hydrogen elimination followed by α-CC scission. Second, they all ultimately involve homolytic reactions that form a radical at the α-carbon. This radical reacts with dioxygen to form either a peroxy or a hydroperoxy species, which subsequently attacks the electrophilic carbonyl carbon to drive C-C scission.
α-hydrogen elimination clearly plays an important role in ketone oxidation over VOₓ/γ-Al₂O₃. Further, one expects that the rate of α-CH scission will be sensitive to the degree of α-carbon substitution. This sensitivity may underlie our observation that ketone oxidation rates depend on the degree of α-carbon substitution, so it is worth considering whether α-CH scission is rate controlling. The relationship between the kinetics of α-CH scission and the degree of α-carbon substitution is dictated by the nature of C-H scission, which can occur in one of three ways: homolytic bond scission to form a hydrogen atom and a carbon radical; heterolytic deprotonation to form a proton and a carbanion; and heterolytic hydride elimination to form a hydrogen anion and a carbocation. VOₓ/γ-Al₂O₃ purportedly has surface acid, base, and redox functionality; and it can facilitate Brønsted and Lewis interactions as well as single electron oxidations.²⁶⁻²⁸ Thus, it can potentially catalyze any C-H scission pathway, and we accordingly consider their kinetic significance.

α-hydrogen deprotonation is possible and perhaps even likely on an amphoteric solid oxide;²⁹ however, alkyl scission rates that increase with α-carbon substitution argue against rate control by deprotonation of the α-hydrogen. The pKa for a C-H bond increases with the degree of carbon substitution.³⁰ We take pKa as a proxy for C-H deprotonation energies, so we infer that these will also increase with carbon substitution. Within a given class of reactions, kinetic barriers scale linearly with reaction enthalpies;³¹⁻³³ thus, deprotonation barriers should increase with pKa, and deprotonation rates should decrease with carbon substitution. This is exactly the trend observed in reactions that are limited by deprotonation of the α-hydrogen, such as aldol condensation in alkaline media.³⁴⁻³⁵ For this reason, we conclude that if α-CH scission is rate controlling, it must either occur through homolytic scission to form an α-radical or hydride elimination to form an α-carbenium (or surface analogs thereof). C-H bond dissociation energies decrease with carbon
substitution, and proton affinities for alkenes (negative enthalpies of protonation) increase with carbon substitution. Again assuming that kinetic barriers scale linearly with reaction enthalpies, one expects that rates of both homolytic C-H scission and heterolytic hydride elimination will increase with carbon substitution; thus, rate control by either would be consistent with our observations. To further interrogate the kinetic significance of $\alpha$-CH scission, we compare rates of oxidative scission for 2-propanone and perdeuterated 2-propanone (Figure 3.1), and we clearly observe that deuterium substitution at the $\alpha$-carbon has no impact on the rate of oxidative scission.

The lack of a primary kinetic isotope effect indicates that, although it is mechanistically required to precede $\alpha$-CC scission, $\alpha$-CH scission is likely not kinetically significant. Though less definitive, the lack of a secondary kinetic isotope effect may argue that the rate determining step does not involve the $\alpha$-carbon at all—this despite our observation that increasing substitution at the $\alpha$-carbon enhances the overall rate of oxidation. Our rationale is that $\alpha$-CH scission appears to precede $\alpha$-CC scission; thus the $\alpha$-carbon undergoing oxidation is initially hydrogen deficient and may be loosely described as having $sp^2$ hybridization. As it undergoes the $\alpha$-CO bond formation and/or $\alpha$-CC bond scission steps necessary to effect oxidative cleavage and

**Figure 3.1:** Rates of oxidative scission of 2-propanone and 2-propanone-d6. (470 K, $P_{\text{Pr}}=12.3$ Torr, $P_{\text{O}_2}=133$ Torr, He Balance).
ultimately form a carbonyl, one might anticipate transitions between sp\(^2\) and sp\(^3\) hybridization at the α-carbon. It is therefore not unreasonable to expect a modest secondary kinetic isotope effect if either α-CC scission or α-CO bond formation are rate controlling. Additional work is necessary to fully resolve rate control in this system, but based on a clear lack of kinetic isotope effects upon deuterium substitution at the α-carbon, we tentatively attribute the observation that oxidative scission rates increase with α-carbon substitution to a thermodynamic effect. Most likely, the rate controlling step in ketone oxidation simply involves consumption of a species whose equilibrium bulk and/or surface concentrations are enhanced by increasing substitution at the α-carbon.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Oxidative Scission Rate (μmol g(^{-1})min(^{-1}))</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Alk</td>
</tr>
<tr>
<td>1</td>
<td>2-P</td>
<td>7</td>
<td>140</td>
</tr>
<tr>
<td>2</td>
<td>LA</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>α-AL</td>
<td>29</td>
<td>5</td>
</tr>
</tbody>
</table>

Methyl (Me); Alkyl (Alk); 2-pentanone (2-P); levulinic acid (LA); α-angelicalactone (α-AL).

T = 550K, PKetone = 12.3 Torr; PO\(_2\) = 133 Torr; Helium balance.

Having mapped reactivity and selectivity trends during the oxidative scission of monofunctional ketones, we next consider levulinic acid oxidation. Levulinic acid is far less susceptible to oxidative scission than its monofunctional analogs (Table 1, 468K); accordingly, we carried out its oxidation at 550K, and we benchmarked our observations against 2-pentanone oxidation at the same temperature (Table 2). We note that levulinic acid reacts by other pathways at this temperature, so conversions here are not strictly differential (see subsequent contact time analysis). The total oxidative scission rate for 2-pentanone increases from 8.4 μmol g\(^{-1}\) min\(^{-1}\) at
468K (Table 1) to 147 μmol g⁻¹ min⁻¹ at 550K (Table 2); however, selectivities toward alkyl scission (95%) and methyl scission (5%) are identical to those observed at lower temperatures. Transitioning to levulinic acid, the rate of methyl scission (30 μmol g⁻¹ min⁻¹) is significantly higher than that observed for 2-pentanone (7 μmol g⁻¹ min⁻¹), whereas the rate of alkyl scission is profoundly diminished (11 μmol g⁻¹ min⁻¹ vs. 140 μmol g⁻¹ min⁻¹). This gives rise to alkyl and methyl scission selectivities of 27% and 73%, respectively. Based on data in Table 1, this is difficult to reconcile with the fact that levulinic acid has a secondary α-carbon in its alkyl side chain. With no other structural differences, perturbations in the rates of both methyl scission (5-fold increase) and alkyl scission (10-fold decrease) are clearly attributable to the presence of the carboxyl group in levulinic acid, and we next attempt to resolve possible origins.

Our analysis of monofunctional ketone oxidation (Table 1) indicates that steric hindrances at the alkyl chain α-carbon can improve methyl scission selectivity by simultaneously enhancing methyl scission rates and suppressing alkyl scission rates. That said, the impact is relatively minor, and a significant steric effect—an increase in methyl scission selectivity from 5% to 34%—was only observed in the case of a bulky dimethyl substituent at the β-position (i.e., immediately adjacent to the α-carbon). It thus seems unlikely that a carboxyl group at the γ-position (relative to the ketone) could impose sufficient steric hindrances to shift selectivity strongly toward methyl scission. Alternatively, we have demonstrated that rates of oxidative scission increase with electron density (alkyl substitution) at the α-carbon. One may propose that the carboxyl group of levulinic acid draws electron density away from the alkyl α-carbon and consequently suppresses its rate of scission; however, one expects a relatively weak impact since any such induction effects are screened at the α-carbon by an intervening methylene group. It thus seems unlikely that induction effects would make alkyl scission less favorable than methyl
scission in levulinic acid. A final possibility is that the carboxyl group enables formation of unique bulk and/or surface structures that are less susceptible to alkyl scission and/or more susceptible to methyl scission than analogous monofunctional ketones.

We have thus far considered that oxidative ketone scission must occur through open chain, enol-mediated pathways, which are commonly reported for ketone oxidations in solution and on reducible oxide surfaces. If levulinic acid oxidation follows an open chain pathway, then its dominant oxidation product, maleic anhydride, must form through a sequence of methyl scission (to form succinic acid) followed by dehydration and oxidative dehydrogenation (Figure 3.2).

It is worth considering whether the cyclization and oxidative scission steps actually happen in reverse. Specifically, levulinic acid will readily undergo intramolecular dehydration form cyclic angelicalactone isomers (α, α’, and β). Levulinic acid dehydration is both kinetically facile and thermodynamically favorable under our reaction conditions, making it plausible that dehydration precedes oxidative scission in this system. Accordingly, we measured the rate of
oxidative scission for α-angelicalactone at identical conditions to levulinic acid and 2-pentanone (Table 2). At $29 \, \mu \text{mol g}^{-1} \text{min}^{-1}$, the methyl scission rate for α-angelicalactone is nearly identical to that observed for levulinic acid and significantly higher than that observed for 2-pentanone. In contrast, its alkyl scission rate ($5 \, \mu \text{mol g}^{-1} \text{min}^{-1}$) is further suppressed relative to levulinic acid, causing a small increase in methyl scission selectivity (85%). These results suggest that levulinic acid and α-angelicalactone proceed through common oxidative scission pathways and that these pathways may be distinct from those governing 2-pentanone oxidation. We further probe this hypothesis using in situ transmission FTIR spectroscopy, which provides insight into the nature of surface species formed upon exposing 8.0 V/nm$^2$ loading VOₓ/γ-Al₂O₃ to 2-pentanone (2-P), levulinic acid (LA), α-angelicalactone (α-AL), and maleic anhydride (MA) under O₂ (Figure 3.3).

At 473K, full-scale spectra for α-angelicalactone and levulinic acid are nearly identical (Figure 3.3a), indicating that common surface intermediates form during the oxidation of both molecules. Further, comparison with the 2-pentanone spectrum suggests that these intermediates are different from those formed during oxidation of a monofunctional ketone. At 473K, the 2-pentanone spectrum is dominated by carboxylate (O-C-O) stretching modes (1454 and 1564 cm$^{-1}$) and a CH deformation mode (1354 cm$^{-1}$). Based on a comparison with reference spectra (Figure S 3.15), these bands are all associated with surface-bound acetate. This is consistent with the facile production of ethanoic acid via alkyl scission of 2-pentanone, which occurs readily at 468K (Table 1). Analogous spectra for levulinic acid and α-angelicalactone also show carboxylate signatures, however, a comparison with a reference spectrum indicates that these features are distinct from their dominant oxidative scission product, adsorbed maleic anhydride (Figure 3.3a). This aligns with our observation that levulinic acid and α-angelicalactone do not
undergo appreciable oxidative scission below ≈500K. Accordingly, we suggest that these bands are associated with distinct surface intermediates that mechanistically precede the oxidative scission of α-CC bonds.

We next highlight the region between 2800 and 3300 cm\(^{-1}\), where we observe various C-H stretching modes that change with the identity of the probe molecule and the reaction temperature (Figure 3.3b). In the case of 2-pentanone, alkyl C-H stretching modes (2800-3000 cm\(^{-1}\)) dominate at all reaction temperatures.\(^{49}\) In contrast, during the oxidation of levulinic acid and α-angelicalactone, we observe both alkyl C-H stretching modes (2800 – 3000 cm\(^{-1}\)) and alkenyl C-H stretching modes (3050-3200 cm\(^{-1}\)).\(^{50}\) At low temperatures, alkyl and alkenyl C-H bands co-exist, which is consistent with chemisorbed angelicalactones or their open-chain analogs (enol tautomers of levulinic acid). As temperatures increase, the alkyl C-H bands disappear almost entirely, and the spectra become dominated by alkenyl C-H bands. We further note that the alkenyl bands observed during the oxidation of levulinic acid and α-angelicalactone change qualitatively (and in a similar way) as a function of reaction temperature. Both species

**Figure 3.3:** FTIR spectra of 2-pentanone (2-P), levulinic acid (LA), α-angelicalactone (α-AL), and maleic anhydride (MA) over VOx/γ-Al\(_2\)O\(_3\) at a) T = 473K; b) the zoomed in version of C-H stretching region at various reaction temperature. \(P_{\text{probe molecule}} = 0.2\) Torr, \(P_{\text{O}_2} = 133\) Torr, He balance.
display the same alkenyl bands at low temperatures (3143 cm\(^{-1}\) and 3116 cm\(^{-1}\), 353K).

Subsequently, the bands shift and intensify, ultimately manifesting as a broad feature at 3090 cm\(^{-1}\) (473K). The similarity of the bands indicate that levulinic acid and α-angelicalactone likely form the same surface intermediates under oxidizing conditions. Further, the loss of alkyl C-H stretching modes alongside increasingly prominent alkenyl features indicates that these surface intermediates are hydrogen-deficient relative to both levulinic acid and α-angelicalactone. These observations are potentially consistent with the formation of their dominant oxidation product, maleic anhydride, which has no sp\(^3\) carbons and thus no alkyl C-H bonds; however, comparison with reference spectra (Figure 3.3b) indicates that these new alkenyl C-H bands are distinct from the relatively well-defined alkenyl C-H stretching modes observed for chemisorbed maleic anhydride. Again, this is consistent with our observation that neither levulinic acid nor α-angelicalactone undergo appreciable oxidative scission below roughly 500K; accordingly, we conclude that, during the oxidation of levulinic acid and α-angelicalactone, dehydrogenation reactions form increasingly hydrogen-deficient surface species prior to the onset of oxidative scission reactions that form maleic anhydride.

We further investigate reaction networks by analyzing trends in carbon selectivity as a function of contact time during the oxidation of levulinic acid and α-angelicalactone. Before doing so, we discuss carbon balance closure and observed reaction products. During oxidation of both species, we confirmed the presence of maleic anhydride, α-angelicalactone, β-angelicalactone,\(^{12}\) ethanoic acid, CO, CO\(_2\), and methyl vinyl ketone by comparison of retention times and/or GCMS fragmentation patterns with reference standards. GCMS analysis also indicated the formation of two additional species. The first had a total molecular mass of 98 (C\(_5\)H\(_6\)O\(_2\)) and a fragmentation pattern that matched that of 1,3-cyclopentanedione, while the other had a total molecular mass of
96 (C₅H₄O₂) and a fragmentation pattern that matched 4-cyclopentene-1,3-dione. Based on these GCMS assignments, we previously reported these cyclic diones as minor products of levulinic acid oxidation; however, those assignments were incorrect.¹ Detailed analysis of the fragmentation pattern for the 98 m/z species suggests that its structure is far more consistent with α'-angelicalactone, which we confirmed by matching its retention time and fragmentation pattern with that of a commercial standard. A detailed analysis of the fragmentation pattern for the 96 m/z species was inconclusive, and we were further unable to match its retention time with a commercial standard of 4-cyclopentene-1,3-dione. Accordingly, we used NMR to determine its structure.

![Figure 3.4](image)

**Figure 3.4:** a) ¹³C-NMR spectrum and b) ¹H-NMR spectrum for a representative a product mixture obtained during the oxidation of levulinic acid/α-angelicalactone. Samples dissolved in C/D₆O.

Figure 3.4 presents ¹³C- NMR and ¹H-NMR for a product mixture obtained from α-angelicalactone oxidation under conditions that were selective toward the unidentified 96 m/z species. Its associated peaks are labelled by their chemical shift; they were assigned by elimination. All reference and full range spectra are provided in the online supporting information (Figures S 3.1-S 3.8). The ¹³C- spectrum contains five peaks assigned to the unknown compound (Figure 3.4a). Based on comparisons with reference spectra and general
correlations between chemical shift and carbon environment, we assign the peaks at 98.3, 122.2, 145.1, and 156.3 ppm to 4 distinct carbon atoms present in C=C double bonds, and we assign the peak at 167.4 ppm to a carbon atom in an acid anhydride or lactone structure. In the $^1$H-NMR spectrum (Figure 3.4b), we observe 4 distinct hydrogen atoms that give rise to peaks (5.05, 5.21, 6.35 and 7.74 ppm) with varying degrees of splitting. Most likely, these are attributable to four distinct alkenyl hydrogens. These assignments are reinforced by the $^1$H-$^{13}$C HSQC spectrum (Figure S 3.9), which indicates that two hydrogens (5.05 ppm and 5.21 ppm) are bound to a primary alkene carbon (98.3 ppm), while two additional hydrogens (6.35 ppm and 7.74 ppm) are bound to distinct secondary alkene carbons (122.2 and 145.1 ppm) in an oxolene group. Considering these structural insights alongside a total molecular mass of 96 amu (GCMS) and the indication from FTIR that levulinic acid and $\alpha$-angelicalactone form increasingly hydrogen-deficient intermediates under reaction conditions, we conclude that the unknown is the dehydrogenated analog of $\beta$-angelicalactone, specifically, 5-methylidenefuran-2-one (protoanemonin). A simulated 13C spectrum for protoanemonin was generated using ChemDraw 18.0, and it agrees well with our proposed assignments (Figure 3.5).

Before considering the role of protoanemonin during levulinic acid oxidation, we note that it is a polyfunctional molecule comprised of a lactone ring alongside a conjugated diene. Protoanemonin has previously been discussed in the plant science and medical literature, where there was some historical interest in its antimicrobial properties. Relevant to future
biorefining opportunities, we highlight that dienes and lactones are routinely leveraged in polymer chemistry, making protoanemonin a unique and intriguing platform for bio-based polymers.\(^{59}\) To date, only one account of protoanemonin synthesis has been reported using levulinic acid as a starting material (with one other account describing its synthesis from \(\beta\)-acetylacrylic acid, i.e., dehydrogenated levulinic acid).\(^{60}\) It was accomplished in good yield using a conventional organic methodology, namely through a sequence of acid-catalyzed reactive distillation\(^{61}\) of levulinic acid to form \(\alpha\)-angelicalactone followed by bromination and dehydrobromination of \(\alpha\)-angelicalactone to form protoanemonin.\(^{62}\) Here, our attempts at yield optimization were limited to enriching protoanemonin concentration for the benefit NMR analysis; however, even with this cursory effort, we achieved transient protoanemonin yields between 55\% and 75\% via simple, direct, gas-phase oxidation of \(\alpha\)-angelicalactone (e.g., see Figure 3.6). We believe these yields are sufficiently high to suggest scalability and industrial feasibility. The reaction is not thermodynamically limited, which motivates future efforts at improving selectivity via catalyst and process design. We note that our attempts to isolate and purify dilute protoanemonin (<10 Torr) generally induced polymerization. We are also presently unable to source a commercial standard for protoanemonin. These factors prevented us from

![Figure 3.6: Conversion of \(\alpha\)-angelicalactone and corresponding yields to protoanemonin and maleic anhydride over VO\(\gamma\)-Al\(\theta\)O\(_3\). \(P_{\text{H}_2} = 8\) Torr, \(P_{\text{O}_2} = 133\) Torr, \(T=528\)K.](image)
obtaining a precise GC-FID response factor. We thus assumed that protoanemonin has the same FID response factor as its isomer, 4-cyclopentene-1,3-dione (C_5H_4O_2). Carbon balances closed to within 10%, suggesting a reasonable approximation; however, we acknowledge that there is uncertainty in our reported yields and production rates for protoanemonin.

We next analyze the evolution of product selectivity as a function of contact time during levulinic acid oxidation. We do not restrict consideration to oxidative scission, and selectivities were calculated for all products on a carbon basis \( (S_{C,j}) \) as shown in Eq. (3.6). Here \( F_j \) is the molar flowrate of species \( j \), \( N_{C,j} \) is the number of carbon atoms in a molecule of species \( j \), and the index “\( j \)” excludes the reacting molecule.

\[
S_{C,j} = \frac{F_j N_{C,j}}{\sum_i F_i N_{C,i}}
\]  

(3.6)

We focus our discussion on cyclic structures—angelicalactones (\( \alpha \), \( \alpha' \), and \( \beta \)), protoanemonin, and maleic anhydride, and we exclude the remaining products for clarity. Presented carbon
selectivities do not necessarily sum to 1; however, carbon balances fully closed for each experiment.

Figure 3.7a shows that, during levulinic acid oxidation, only two products, \( \alpha \)-angelicalactone and \( \alpha' \)-angelicalactone, have positive \( y \)-intercepts. These translate to non-zero selectivities at the zero conversion limit, which indicates that both \( \alpha \)-angelicalactone and \( \alpha' \)-angelicalactone are formed through reactions that directly consume levulinic acid. Selectivities toward both \( \alpha \)- and \( \alpha' \)-angelicalactone decrease as a function of contact time, which implies that they are each consumed by secondary reactions. In contrast, \( \beta \)-angelicalactone selectivity extrapolates to zero at the \( y \)-intercept, indicating that it is not a primary product of levulinic acid conversion. \( \beta \)-angelicalactone selectivity then increases to a maximum at a contact time of 20 minutes before diminishing at longer contact times. Its selectivity increase mirrors the decrease in selectivity toward \( \alpha \)- and \( \alpha' \)-angelicalactones, which indicates that \( \beta \)-angelicalactone forms through reactions that consume the \( \alpha \)-isomers. The decay in \( \beta \)-angelicalactone selectivity indicates that it is further converted through tertiary pathways. During levulinic acid oxidation, selectivities to protoanemonin and maleic anhydride both extrapolate to a zero \( y \)-intercept and subsequently increase alongside the decrease in \( \beta \)-angelicalactone selectivity. This indicates that both protoanemonin and maleic anhydride form through tertiary pathways via consumption of \( \beta \)-angelicalactone; however, their relationship is unclear based on analysis of levulinic acid oxidation selectivity alone. To aid in resolution, we consider the analogous selectivity trends observed during \( \alpha \)-angelicalactone oxidation (Figure 3.7b). In this case, both \( \alpha' \) and \( \beta \)-angelicalactone are primary products (positive \( y \)-intercept) that form directly by consumption of \( \alpha \)-angelicalactone. \( \beta \)-angelicalactone selectivity decreases with contact time, indicating subsequent consumption by secondary reactions. Protoanemonin has a zero \( y \)-intercept, and its
selectivity increases with contact time alongside a decrease in β-angelicalactone selectivity. We therefore conclude that protoanemonin forms as a secondary product of reactions that consume β-angelicalactone. Subsequently, protoanemonin selectivity decreases, indicating that it is converted by a tertiary pathway. Maleic anhydride selectivity also extrapolates to a zero y-intercept (i.e., it is not a primary product). Further, its selectivity increases with the onset of protoanemonin formation and continues to increase alongside the decay in protoanemonin selectivity at higher contact times. This strongly suggests that maleic anhydride forms through a tertiary reaction that consumes protoanemonin directly. Finally, the selectivity plateau observed for maleic anhydride suggests that it is a stable product under our experimental conditions.

Based on the above delineation of primary and sequential reaction products, we propose that, during levulinic acid oxidation, maleic anhydride forms through the network shown in Scheme 3.3. Initially, levulinic acid dehydrates to form α- and α’-angelicalactones. Subsequent isomerization forms β-angelicalactone, which undergoes oxidative dehydrogenation at its C₄-C₅ bond to form protoanemonin. Protoanemonin has a single C=C unsaturation adjacent to the ring oxygen, which is similar to the enol-type structures that are widely thought to precede oxidative scission of ketone α-carbons; accordingly, we propose that maleic anhydride forms through oxidative scission of the C₄=C₅ bond in protoanemonin. If one follows the logic that enol-like structures must precede oxidative C-C scission, then protoanemonin, once formed, is susceptible only to scission between the C₄=C₅ bond. This corresponds to the bond between the carbonyl carbon and its α-methyl carbon in both levulinic acid and α-angelicalactone, i.e., the one that is cleaved in order to form maleic anhydride. Intermediate formation of protoanemonin therefore provides a plausible explanation for suppressed alkyl scission rates and the corresponding high
selectivity toward methyl scission observed during the oxidation of levulinic acid and α-angelicalactone.

A limited susceptibility of protoanemonin is reasonable, and it explains why protoanemonin should have a high selectivity toward methyl scission; however, it does not immediately explain why the oxidation of levulinic acid and angelicalactone are so selective toward methyl scission. In either case, protoanemonin formation must proceed through α’- or α-angelicalactone. Both α-isomers have C=C bonds adjacent to the ring oxygen, which, following the rationale presented for protoanemonin, should make them susceptible to oxidative scission, yet we observe no succinic anhydride (scission of C₄=C₅ bond in the α’-isomer) and very little acetate/ethanoic acid (scission of the C₃=C₄ bond in the α-isomer) during the oxidation of either levulinic acid or α-angelicalactone. The lack of succinic acid can be reasonably attributed to the fact that the α’-isomer is thermodynamically unfavorable and generally present in low concentrations; however, the α-isomer is favorable, and we frequently observe product distributions that are rich in α-angelicalactone. Considering this alongside the apparent oxidation susceptibility of the C₃=C₄ bond in α-angelicalactone, it is not immediately clear why alkyl scission rates approach zero (Table 2) during the oxidation of both levulinic acid and α-angelicalactone. We argue that the answer lies in the relative rates and equilibrium positions for dehydration, isomerization, oxidative dehydrogenation, and oxidative scission.

Under our typical operating conditions, levulinic acid is nearly equilibrated with α- and α’-angelicalactones,⁴⁵ indicating that its dehydration occurs rapidly. The migration of C=C bonds is also facile over solid oxides,⁶³-⁶⁴ which explains why we observe angelicalactone distributions that are rich in the thermodynamically preferred isomers (α- and β-) instead of those formed
directly by dehydration ($\alpha$- and $\alpha'$-). Subsequent oxidative dehydrogenation of $\beta$-angelicalactone forms protoanemonin and water, which is thermodynamically favorable and may be considered irreversible.\textsuperscript{65-67} If levulinic acid dehydration and C=C bond migration are facile, it is reasonable to assume that any $\beta$-angelicalactone consumed by oxidative dehydrogenation is rapidly offset by isomerization of $\alpha$-$\alpha'$-isomers and further dehydration of levulinic acid. In a system where levulinic acid dehydration, C=C bond migration, and oxidative dehydrogenation are facile (but oxidative scission is not kinetically accessible), one expects a high concentration of the thermodynamic product, which is protoanemonin. Once formed, protoanemonin cannot revert to $\beta$-angelicalactone, and it is susceptible only to oxidative scission at the $C_4=C_5$ bond; thus, the balance between methyl scission and alkyl scission should be dictated by the relative rates of oxidative scission of the $C_3=C_4$ bond in $\alpha$-angelicalactone and oxidative dehydrogenation of the $C_4-C_5$ bond in $\beta$-angelicalactone. If oxidative dehydrogenation of $\beta$-angelicalactone is rapid relative to oxidative scission of $\alpha$-angelicalactone, one will preferentially form protoanemonin and observe a high methyl scission selectivity. If the converse is true, one should observe appreciable selectivity to acetate/ethanoic acid via $C_3=C_4$ scission of $\alpha$-angelicalactone.

\textbf{Scheme 3.3:} The pathway for maleic anhydride formation during the oxidation of levulinic acid.
To test this interpretation, we fed $\alpha$-angelicalactone and 2-pentanone into the oxidation reactor at identical conditions ($T = 473\, \text{K}, P_{\text{probe molecule}} = 10\, \text{Torr}, P_{\text{O}_2} = 133\, \text{Torr}$). During the oxidation of angelicalactone, we observed an initial protoanemonin formation rate of $442\, \mu\text{mol g}^{-1}\text{min}^{-1}$ with no evolution of maleic anhydride. Protoanemonin is a secondary product in this system, and we measured this production rate at 92% conversion of $\alpha$-angelicalactone and 75% yield of protoanemonin, i.e., at near-complete angelicalactone conversion (all isomers). $442\, \mu\text{mol g}^{-1}\text{min}^{-1}$ thus reflects an average rate of oxidative dehydrogenation over the catalyst bed, and we take it as a lower limit on the intrinsic rate of oxidative dehydrogenation of $\beta$-angelicalactone at the reactor inlet. At identical conditions, 2-pentanone undergoes oxidative alkyl scission at a rate of $118\, \mu\text{mol g}^{-1}\text{min}^{-1}$, which we measured at 16% conversion. This production rate reasonably approximates a differential rate of reaction, and we take it as an upper limit on the rate of oxidative scission for a secondary $\alpha$-carbon at the reactor inlet. We further assume that the rate of alkyl scission in 2-pentanone is a reasonable proxy for the expected rate of oxidative scission for the $\text{C}_3=\text{C}_4$ bond in $\alpha$-angelicalactone since both have a secondary $\alpha$-carbon. We therefore conclude that oxidative dehydrogenation of the $\text{C}_4$-$\text{C}_5$ bond in $\beta$-angelicalactone can be reasonably expected to occur roughly 4-times more quickly than the oxidative scission of a secondary $\alpha$-carbon. If, as speculated, the balance between methyl scission and alkyl scission is determined by the ratio of the rate of oxidative dehydrogenation of $\beta$-angelicalactone to the oxidative scission of a secondary $\alpha$-carbon, one expects methyl scission and alkyl scission will be observed in a roughly 4:1 ratio. This aligns remarkably well with our observed selectivities during the oxidation scission of levulinic acid (73% methyl vs. 27% alkyl) and $\alpha$-angelicalactone (85% methyl vs. 15% methyl) at 550K.
3.5 Conclusion

We have examined the influences of ketone structure and secondary function on rates and selectivity during oxidative scission over 8.0 V/nm² loading VOₓ/γ-Al₂O₃. Oxidative scission reactions are moderately sensitive to steric effects, and we observe that α-hydrogen elimination is a necessary precursor to oxidative scission of the α-CC bond. This criteria can be met for primary, secondary, and tertiary α-carbons, for which oxidative scission rates increase with degree of the α-carbon substitution. Interestingly, we observe neither primary nor secondary kinetic isotope effects during the oxidative scission of 2-propanone and 2-propanone-d₆, which may argue that the rate determining step in ketone oxidation does not involve formation or scission of a bond at the α-carbon (at least not on VOₓ/γ-Al₂O₃).

Similarities in selectivity and surface intermediates formed during the the oxidation of levulinic acid and α-angelicalatone suggest the two species undergo a common oxidation pathway that is distinct from that of a typical methylketone. Specifically, both molecules appear to undergo dehydrogenation reactions that form identical surface intermediates prior to oxidative C-C scission—behavior that is not observed during 2-pentanone oxidation. A detailed analysis of product selectivities at very short contact times reveals that levulinic acid rapidly dehydrates to form α, α′, and β-angelicalatones, which are thermodynamically favored relative to levulinic acid under our reaction conditions. β-angelicalactone undergoes irreversible oxidative dehydrogenation to form protoanemonin, which we conclusively identified using NMR spectroscopy. Once formed, protoanemonin is only susceptible to oxidation via scission of its methyl α-carbon, i.e., the C₄=C₅ bond, to form maleic anhydride. Importantly, oxidative dehydrogenation of β-angelicalactone is sufficiently fast to limit the extent of oxidative scission
of the C₃=C₄ bond in α-angelicalactone, which minimizes selectivity toward alkyl scission.

Ultimately, we attribute the high yield of maleic anhydride during levulinic acid oxidation to a kinetically and thermodynamically favorable cascade of reactions that occur quickly relative to the oxidative scission of a α-carbon. This cascade leads to protoanemonin, which forms irreversibly and is susceptible only to oxidation via α-methyl scission to form maleic anhydride.

As a final note, our attempt to resolve the origin of maleic anhydride selectivity lead us to isolate protoanemonin via direct, gas-phase oxidation of levulinic acid and α-angelicalactone. Protoanemonin has both lactone and diene functionality, and it is an interesting platform for the synthesis of novel bio-polymers. Its unique structure and function may offer performance advantages relative to conventional petrochemical monomers. To our knowledge, this is the first reported synthesis of protoanemonin using the heterogeneously-catalyzed, gas-phase, aerobic oxidation of relatively accessible bio-based commodities like levulinic acid or α-angelicalactone. Further, we have demonstrated the technology in a flow process, and we have observed yields in the range of 50% – 75% during periods of transient operation. Protoanemonin yields are not thermodynamically limited, suggesting potential feasibility and motivating further optimization of angelicalactone dehydrogenation.
3.6 Support Information

3.6.1 NMR spectra

Figure S 3.1 shows the $^{13}$C spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($C_3D_6O$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); however, they include contributions from other reaction products as it was not possible to operate at 100% yield, nor was it possible to easily isolate the unknown subsequent to collection.

Figure S3.1: $^{13}$C NMR for mixed reaction products dissolved in 2-propanone-d6 ($C_3D_6O$).
Figure S3.2 shows the $^{13}$C spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone (C$_3$D$_6$O) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced acetic acid standard, permitting independent resolution of peaks associated with acetic acid.

Figure S3.2: $^{13}$C NMR for mixed reaction products dissolved in 2-propanone-d6 (C$_3$D$_6$O) with an acetic acid standard.
Figure S 3.3 shows the $^{13}$C spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($\text{C}_3\text{D}_6\text{O}$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced $\alpha$-angelicalactone standard, permitting independent resolution of its associated peaks.

**Figure S3.3:** $^{13}$C NMR for mixed reaction products dissolved in 2-propanone-d6 ($\text{C}_3\text{D}_6\text{O}$) with an $\alpha$-angelicalactone standard.
Figure S 3.4 shows the $^{13}$C spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($\text{C}_3\text{D}_6\text{O}$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced maleic anhydride standard, permitting independent resolution of its associated peaks.

**Figure S3.4:** $^{13}$C NMR for mixed reaction products dissolved in 2-propanone-d6 ($\text{C}_3\text{D}_6\text{O}$) with a maleic anhydride standard.
Figure S 3.5 shows the $^1$H spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($C_3D_6O$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); however, they include contributions from other reaction products as it was not possible to operate at 100% yield, nor was it possible to easily isolate the unknown subsequent to collection.

Figure S3.5: $^1$H NMR for mixed reaction products dissolved in 2-propanone-d6 ($C_3D_6O$).
Figure S 3.6 shows the $^1$H spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone (C$_3$D$_6$O) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced acetic acid standard, permitting independent resolution of its associated peaks.

**Figure S3.6**: $^1$H NMR for mixed reaction products dissolved in 2-propanone-d6 (C$_3$D$_6$O) with an acetic acid standard.
Figure S 3.7 shows the $^1$H spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($C_3D_6O$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced $\alpha$-angelicalactone standard, permitting independent resolution of its associated peaks.

**Figure S3.7:** $^1$H NMR for mixed reaction products dissolved in 2-propanone-d6 ($C_3D_6O$) with an $\alpha$-angelicalactone standard.
Figure S 3.8 shows the $^1$H spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone ($\text{C}_3\text{D}_6\text{O}$) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS); this sample includes an externally introduced maleic anhydride standard, permitting independent resolution of its associated peaks.

**Figure S3.8:** $^1$H NMR for mixed reaction products dissolved in 2-propanone-d6 ($\text{C}_3\text{D}_6\text{O}$) with a maleic anhydride standard.
Figure S 3.9 shows the $^1$H-$^{13}$C HSQC spectrum for a mixture of reaction products obtained by bubbling the reactor effluent gas through deuterated acetone (C$_3$D$_6$O) under conditions of optimal selectivity toward the targeted unknown compound (96 m/z according to GCMS).

Figure S3.9: $^1$H-$^{13}$C HSQC for mixed reaction products dissolved in 2-propanone-d6 (C$_3$D$_6$O).
3.6.2 In situ FTIR spectra

Figure S3.10: FTIR spectra of calcined $\gamma$-Al$_2$O$_3$ at various reaction temperatures. $P_{O_2}$=133 Torr and He balanced.

Figure S3.11: FTIR spectra of calcined VO$_x$$\gamma$-Al$_2$O$_3$ (8 V/nm$^2$) at various temperatures. $P_{O_2}$=133 Torr and He balanced.
Figure S3.12: FTIR spectra of VO$_2$/$\gamma$-Al$_2$O$_3$ (8 V/nm$^2$) exposed to 0.2 Torr 2-pentanone during steady-state oxidation at various temperatures. P$_{O_2}$=133 Torr and He balanced.

Figure S3.13: FTIR spectra of VO$_2$/$\gamma$-Al$_2$O$_3$ (8 V/nm$^2$) exposed to 0.2 Torr levulinic acid during steady-state oxidation at various temperatures. P$_{O_2}$=133 Torr and He balanced.
Figure S3.14: FTIR spectra of VO$_x$/γ-Al$_2$O$_3$ (8 V/nm$^2$) exposed to 0.2 Torr α-angelicalactone during steady-state oxidation at various temperatures. P$_{O_2}$=133 Torr and He balanced.

Figure S3.15: FTIR spectra of VO$_x$/γ-Al$_2$O$_3$ (8 V/nm$^2$) exposed to 0.15 Torr acetic acid during steady-state oxidation at various temperatures. P$_{O_2}$=133 Torr and He balanced.
Figure S3.16: FTIR spectra of \( \text{VO}_x/\gamma-\text{Al}_2\text{O}_3 \) (8 V/nm²) exposed to 0.2 Torr maelic anhydride during steady-state oxidation at various temperatures. \( P_{\text{O}_2}=133 \) Torr and He balanced.
3.7 References


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CHAPTER 4

The Role of Gas Phase Oxygen and Lattice Oxygen in the Oxidative Scission of Methyl Ketones over VO$_x$/γ-Al$_2$O$_3$
4.1 Introduction

Hydrocarbon selective oxidation is a key challenge in the process that converts chemical feedstocks into industrial commodities,\textsuperscript{1-2} and biomass conversion\textsuperscript{3-5} is crucial to industrial and academic research. We have previously published research on selective maleic anhydride production from the oxidation of levulinic acid over supported vanadium oxide catalysts.\textsuperscript{6} The final step in the process of converting levulinic acid into maleic anhydride (Scheme 4.1), in which protoanemonin is cleaved to produce maleic anhydride, has been demonstrated to be the rate-limiting step.\textsuperscript{7} Therefore, this scission process is of particular interest when optimizing reaction performance.

![Scheme 4.1](image)

Scheme 4.1. The aerobic oxidative scission of protoanemonin to maleic anhydride over vanadium oxide supported on gamma alumina.

The terminal enol structure in protoanemonin suggests that the mechanism involved in the rate-limiting step in the oxidative scission of levulinic acid is comparable to the homogenous aerobic oxidative scission of a ketone.\textsuperscript{8} Naturally developed metalloenzymes, which precede selective oxidation, frequently use copper-associated active sites,\textsuperscript{9-11} and the bionic oxidative scission of ketone by homogenous copper catalysis with gas phase oxygen in condensed media has been extensively studied.\textsuperscript{12-15} In contrast, little is known about the analogous chemistry of the aerobic oxidative scission process catalyzed by heterogeneous transition metal oxides. In order to reach a fundamental understanding of the chemical processes involved in the oxidative scission of levulinic acid, or protoanemonin, to maleic anhydride, this study investigates the aerobic
oxidative scission of methyl ketones, the monofunctional molecule of both levulinic acid and protoanemonin, over supported vanadium oxide on $\gamma$-Al$_2$O$_3$.

We therefore combined our studies on macrokinetic reaction order analysis, temperature programmed surface reactions, transient period analysis, surface chemistry with Fourier-transform infrared (FITR) spectroscopy, and diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy. The aim of this synergy is to approach a fundamental understanding of the mechanism enabling oxidative scission over supported vanadium oxide. The role of gas phase dioxygen and lattice oxygen is clarified. This study proposes a novel combination of the Eley-Rideal and Mars van Krevelen mechanisms, in addition to the structural insights it presents regarding the surface reaction intermediates.
4.2 Materials and Methods

4.2.1 Reagents

3-methyl-2-butanone (Acros, 98%) was used as a probe molecule during steady state ketone oxidation and temperature programmed surface reactions. Acetone (Fisher, Optima), acetic acid (Acros, 98%), isobutyric acid (Acros, ≥ 99%), acetaldehyde (Sigma, ≥ 99.5%), CO (Airgas, 1%, 1% Ar, He balance), and \( \text{CO}_2 \) (Airgas, 1%, 1% Ar, He balance) were used for instrument calibration. Water was purified via sequential reverse osmosis, UV oxidation, and ion exchange to achieve a resistivity ≥ 18.2 MΩ·cm (Spectrapure). \( \text{O}_2 \) (Airgas, Ultra High Purity) and He (Airgas, Ultra High Purity) were used as an oxidant and a diluent, respectively, during reactor operation. Air (Airgas, Ultra Zero) was used for ex-situ calcination of catalyst samples.

4.2.2 Catalyst synthesis

All experiments used VO\(_x\)/\( \gamma \)-Al\(_2\)O\(_3\) samples with vanadium loadings from 0.04 to 8.0 V nm\(^{-2}\). Catalysts were synthesized by incipient wetness impregnation\(^{16}\) of 1.2 mL of aqueous vanadium per gram of \( \gamma \)-Al\(_2\)O\(_3\) (205 m\(^2\) g\(^{-1}\), Advanced Materials, 97%). Prior to impregnation, \( \gamma \)-Al\(_2\)O\(_3\) was calcined under zero-grade air (723K, 3 K min\(^{-1}\), 4h hold, 60 ml min\(^{-1}\)). Next, ammonium metavanadate (Sigma, 99.5%) and oxalic acid (Acros, 99%) were dissolved in water at a 1:2 molar ratio (343K).\(^{17}\) Precursor concentrations were adjusted to achieve desired vanadium loadings.\(^{18-19}\) The resulting sample was dried in an oven at 338 K for 16 hours and subsequently calcined under flowing air (723K, 3 K min\(^{-1}\) ramp, 4h hold, 60 ml min\(^{-1}\)).\(^{20}\) The catalyst was then crushed and sieved. Only particles in the 45–90 μm range were used in this study.
4.2.3 Steady state 3-methyl-2-butanone oxidative scission rate and selectivity measurements

![Graph showing conversion as a function of 3-methyl-2-butanone contact time]

**Figure 4.1.** The plot of conversion as a function of 3-methyl-2-butanone contact time study.

Oxidative scission of 3-methyl-2-butanone was carried out over VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} in a packed bed reactor.\textsuperscript{21} Gas feeds were regulated by mass flow controllers (Brooks 5850S), and liquids were delivered through capillary tubing using a syringe pump (Cole Parmer, Series 100). Helium and O\textsubscript{2} were fed independently and mixed in a column packed with quartz chips. The gas feed was then combined with liquid 3-methyl-2-butanone in a stainless steel tee that was packed with quartz wool and maintained at 343K. This configuration achieved pulse-free vaporization of 3-methyl-2-butanone at all feed rates. Samples of VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} were diluted to 50 wt.% in quartz granules (45–90 μm) and supported between two quartz wool plugs. The catalyst bed was centered in a 6” x \( \frac{1}{2} \)” OD stainless steel tube. The upstream volume was packed with quartz chips, while the downstream volume was left unpacked to accommodate a type-K thermocouple, which was positioned on the downstream surface of the bed and used to monitor internal reactor temperature. Effluent species concentrations were quantified using an online gas chromatography (HP 5890) equipped with two inlets, two columns, and two detectors. We used an HP-INNOWax column paired with an FID detector to quantify oxygenated hydrocarbons, and
we used a Restek ShinCarbon ST Micropacked column paired with a TCD detector to quantify carbon oxides. Reaction products were periodically collected and analyzed offline using GC-MS (Agilent 7890 + 5975C MSD). Species were qualitatively identified by matching GC retention times with reference standards and by comparison of MS fragmentation patterns with those available in NIST libraries. All gas transfer lines were heat-traced and maintained at or above 423 K to prevent condensation. Carbon balances closed to ≥ 97%, and monitoring of internal and external bed temperatures confirmed isothermal operation. Kinetic data were obtained at or below 10% conversion of 3-methyl-2-butanone. In this range (Figure 4.1), we observe that ketone conversion increases linearly with contact time—defined here as the inverse of weight-hourly-space-velocity (Equation 4.1)—indicating that the differential reactor approximation is reasonable. Accordingly, reaction rates are defined as space-time yields, i.e., the effluent flowrate of oxidation products normalized by the mass of catalyst in the bed (Equation 4.2).

\[ \tau = \frac{m_{\text{cat}}}{\dot{m}_R} \]  
\[ r'_i = \frac{F_j}{m_{\text{cat}}} \]  

In the above equations, \( \tau \) represents contact time; \( m_{\text{cat}} \) is the total mass of the catalyst in the bed; \( \dot{m}_R \) is the mass flowrate of the reacting probe molecule; \( r'_i \) is the mass-normalized rate of reaction \( i \); and \( F_j \) is the molar flowrate of species \( j \), which is formed as a primary product of reaction \( i \). To aid in constructing a network that captures sequential and parallel reactions, we measured product selectivities as a function of fractional conversion (Equation 4.3 and Equation 4.4).
\[ X_R = \frac{\sum_{j \neq R} F_j \cdot N_{C,j}}{F_R \cdot N_{C,R}} \]  

\[ S_j = \frac{F_j}{\sum_{j \neq R} F_j} \]  

Here, \( X_R \) represents the fractional conversion of the reacting probe molecule defined on a carbon basis, \( F_j \) is the molar flowrate of reaction product \( j \), \( N_{C,j} \) is the number of carbon atoms in a molecule of species \( j \), \( F_R \) is the feed molar flowrate of the reacting probe molecule \( R \), and \( N_{C,R} \) is the number of carbon atoms in the reacting probe molecule \( R \). Selectivities were measured between 0 and 30% conversion by varying contact time over a VO\(_x\)/\( \gamma \)-Al\(_2\)O\(_3\) catalyst (8.0 VO\(_x\)/nm\(^2\)). Selectivity comparisons were made at 453K under 11 Torr of 3-methyl-2-butanone and 130 Torr of O\(_2\) in an He balance. Before varying contact times, the reactor was allowed to reach steady state at a reference condition (60 mL min\(^{-1}\), 16.4% O\(_2\), 1.45% 3-methyl-2-butanone, He balance, \( \approx \)20 hours). During the initial transient period, the catalyst lost roughly 35% of its activity; thereafter, we observed minimal deactivation. After the reactor reaching steady state, contact times were varied by changing the inlet flowrate of each species while maintaining constant partial pressures. Selectivity data reflect the steady state achieved after each perturbation in contact time. In this system, varying contact time has a minimal impact on catalyst stability; changing the contact time causes neither deactivation nor induction. Therefore, contact times were changed progressively without returning the system to reference conditions. Where necessary, the range of accessible contact times was expanded by changing the mass of the catalyst and repeating system initialization.
We followed a similar procedure to determine apparent reaction orders. The system was initialized by allowing the catalyst to reach steady state at the reference condition. Subsequently, the feed pressures of 3-methyl-2-butanone (6 to 91 Torr) and O\(_2\) (65–776 Torr) were varied alternately while maintaining all other operating conditions constant. For each condition, at least 4 steady state data points were collected, and we report the average here (3% standard deviation from the mean). At the end of each experiment, reactor operating conditions were returned to the reference state to assess changes in activity. We observed only minimal deactivation (≤ 5%) during an entire reaction order study (10 hours). Furthermore, reaction orders quantify relative changes in reaction rate following perturbations in partial pressure; this renders absolute reaction rates unnecessary for reaction order determination. For these reasons, we did not employ activity corrections in estimating reaction orders from steady state data.

Finally, we investigated the impact of vanadium loading. VO\(_x\)/Al\(_2\)O\(_3\) samples with vanadium contents ranging from 0.04 to 4.0 V nm\(^{-2}\) were loaded into the reactor. Their masses (35-350 mg) varied with the atomic percentage of vanadium, ensuring similar conversion ranges for each material. Catalysts were allowed to reach steady state over a period of 20 hours under the reference conditions described above. Each catalyst experienced different extents of deactivation; accordingly, we compare only initial rates of 3-methyl-2-butanone oxidative scission in this analysis. These rates were estimated by fitting a first order decay profile to oxidation rates measured as a function of time on stream; this method is described in greater detail in the online supporting information.
4.2.4 FTIR spectroscopy

Transmission FTIR spectra were acquired in situ using a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector. Spectra were collected over 120 scans at a resolution of 4 cm\(^{-1}\). The transmission cell—described in Chapter 3—was comprised of a vacuum tee with sealed CaF\(_2\) or KBr windows, electrical feedthroughs, and ports for introducing gas flow. Prior to each experiment, the empty cell was calcined in air at 723K (3 K min\(^{-1}\), 4h hold, 100mL min\(^{-1}\)) and then cooled to 413K under He (Airgas, UHP) or O\(_2\)/He (Airgas, 15% O\(_2\)). All gases were purified using a moisture trap (Restek 22015). Background spectra were recorded in the empty cell under the representative gas environment. For each experiment, 15 mg of VO\(_x\)/γ-Al\(_2\)O\(_3\) (8.0 V nm\(^{-2}\)) was pressed into a 2 cm pellet using a Specac hydraulic press (M26855). The pellet was then secured on an aluminum sample holder and positioned orthogonally to the IR beam. The cell was then sealed, calcined under air at 723K (3 K min\(^{-1}\), 4h hold, 100 mL min\(^{-1}\)), and cooled to 313K under He or O\(_2\)/He. Once the cooling step had begun, spectra were collected at 5 minute intervals until the end of the experiment. After the spectra of the calcined sample reached steady state at 313K, 3-methyl-2-butanone was vaporized into the gas stream at 0.15 Torr. This pressure level is high enough to facilitate the accumulation of detectable surface coverages during a reasonable timeframe, while still being low enough that gas-phase bands are absent from the spectra. Spectral acquisition continued until the system reached steady state at 313K. Subsequently, the sample temperature was increased in stages to 353K, 413K, 473K, 533K, 593K, and 653K using a ramp rate of 3 K min\(^{-1}\). Steady-state spectra were recorded at each temperature. The transmission cell and gas transfer lines were heated, insulated, and maintained at a sufficient temperature (393 K) to prevent condensation.
4.2.5 Transient experiments

Temperature-programmed surface reactions (TPSR) were performed in a quartz reactor held inside a tubular ceramic furnace (Omega). Gas delivery was regulated using mass flow controllers (Valco Instruments Co, Inc). Prior to entering the TPSR manifold, all gases were dried using a moisture trap (Restek, 22015). Liquid feeds (3-methyl-2-butane, acetic acid, calibration standards) were regulated by means of a syringe pump and introduced into a vaporization tee via capillary tubing. 200 to 300 mg of sample were supported between two quartz wool plugs and loaded into the reactor. An inline type K thermocouple was placed immediately upstream of the catalyst bed to permit in situ temperature measurement. A separate type-K thermocouple and PID controller (Love Controls, Series 16A) were used to monitor and regulate the furnace temperature. The reactor effluent was analyzed continuously using a mass-selective residual gas analyzer (Stanford Instruments, RGA 100). All transfer lines were maintained at 373K to prevent condensation.

Before each experiment, samples were calcined under air at 723K (60 mL min⁻¹, 3 K min⁻¹, 4 h) and subsequently cooled to 573K. The reactor was then purged with helium at 573 K (100 mL min⁻¹, 30 min) and cooled to 323K. The sample was next exposed to 5 Torr of the probe molecule until no further uptake was evident in the residual gas analyzer signal. The probe molecule flow was then shut off, and the catalyst bed was purged using the desired process gas (1% Argon/He or 1%Argon/15%O₂/He, 400 mL min⁻¹, 20 min) at 323K to remove physisorbed species. After purging, the system was stabilized at 323K under the reaction gas mixture (60 mL min⁻¹). Finally, the reactor temperature was ramped from 323K to 723K at a rate of 10 K min⁻¹. For subsequent experiments, the catalyst bed was regenerated in situ by calcination in air at 723K (60 mL min⁻¹, 3K min⁻¹, 4 hours). Replicate experiments using regenerated catalyst beds
were indistinguishable from results obtained with a fresh catalyst sample. Major species observed in the oxidative scission of 3-methyl-2-butane were independently tracked using the following mass-to-charge (m/z) ratios: oxygen (m/z = 32); H₂O (m/z = 18); carbon monoxide (m/z = 28); carbon dioxide (m/z = 44); 3-methyl-2-butane (m/z = 86); acetone (m/z = 58); acetaldehyde (m/z = 29); and acetic acid (m/z = 60). Argon (1%, m/z = 40) was employed as an internal standard. Many of the analytes present in this system have common chemical structures, which leads to the formation of identical fragments during ionization. Accordingly, impact factors at various mass-to-charge ratios were determined for each compound during calibrations, and the results were used to correct interferences in signals of interest. The same equipment was also used to analyze the transient period during reactor startup. Experiments were performed by calcining the catalyst in situ and cooling the reactor to reaction temperature under 15% O₂ in He until reaching a steady state effluent composition. At this point, the feed mixture was switched to 15% O₂, 1% Ar, and 1.5% 3-methyl-2-butane in He, while the reactor effluent was continuously monitored using GC and a mass selective residual gas analyzer.

4.2.6 UV-Vis spectroscopy

Diffuse Reflectance (DR) UV-Vis spectra were acquired using an EVOLUTION 300 UV-Vis spectrophotometer equipped with a Praying Mantis diffuse reflectance attachment and a High Temperature Reaction Chamber, both supplied by Harrick. Spectra were recorded against a Spectralon reference at wavelengths ranging from 200-800 nm. In a typical experiment, 200 mg of VOₓ/γ-Al₂O₃ (8.0 V nm⁻²) were loaded into a 5 mm sample holder and placed inside the reaction chamber. The catalyst was calcined in air at 723K (3 K min⁻¹, 100 mL min⁻¹, 4 h) and then cooled to 323K under a continuous flow of 15% O₂/He (100 mL min⁻¹), which was purified using a moisture trap (Restek, 22015). Spectra were thereafter obtained at 5 minute intervals.
until completion of the experiment. Once a steady state spectrum of the pristine sample was observed, 3-methyl-2-butanone (0.15 Torr) was introduced into the reaction chamber as described in FTIR experiments, and spectra were acquired until the reactor reached a steady state. The cell temperature was then increased by 50 K (2 K min$^{-1}$), and spectra were acquired until the reactor reached a steady state. This process was repeated until the reactor reached 473K. The spectra collected were transformed into Kubelka-Munk units using Equation 4.5.$^{22}$

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} \quad (4.5)$$
4.3 Results and Discussion

Our aim is to elucidate the mechanistic details of oxidative ketone scission over supported vanadates. This reaction network is sufficiently complex to warrant some preliminary discussion about competing reaction pathways, their impact on macroscopic trends, and strategies for their deconvolution. Oxidative ketone scission entails breaking the bond between the ketone carbonyl and one of its $\alpha$-carbons via oxygen insertion (Scheme 4.2). Each ketone has two $\alpha$-carbons, so, at a minimum, there are two primary cleavage pathways occurring in parallel. The scission of either $\alpha$-carbon will form two fragments: a carboxyl fragment containing the carbonyl carbon from the parent molecule and a carbonyl fragment containing the $\alpha$-carbon from the parent molecule. These carbonyl compounds—either ketones or aldehydes—are themselves susceptible to oxidative scission, which opens the door to sequential reactions that often form redundant products (e.g., acetic acid is produced by secondary scission of acetone). In addition, under typical reaction conditions, linear methyl ketones can form 2,3-diones, which undergo a separate manifold of scission reactions that may also lead to redundant products.\(^{23}\) Finally, combustion pathways are evident from carbon oxides typically observed in the product mixture. To minimize these artifacts, we selected 3-methyl-2-butane (3M2B) as a probe molecule. It is attractive for...
various reasons. First, methyl substitution at the internally positioned $\alpha$-carbon (C$_3$) prevents the formation of a 2,3-dione, which reduces the number of oxidative fragmentation pathways. Secondly, its asymmetric carbon chain ensures that C$_1$-C$_2$ scission and C$_2$-C$_3$ scission form unique products that are easily resolved by gas chromatography. We further note that its dominant scission products—acetic acid and acetone—are relatively stable under typical reaction conditions, minimizing secondary decomposition pathways. Next, its tertiary $\alpha$-carbon is particularly susceptible to oxidative scission, whereas its primary $\alpha$-carbon is not. This ensures a high degree of selectivity to a single oxidative scission pathway, i.e., scission of the C$_2$-C$_3$ bond to form acetic acid and acetone. Importantly, its inherent susceptibility to oxidative scission allows us to study the reaction at low temperatures, which suppresses parallel scission of the C$_1$-C$_2$ bond, secondary scission reactions, and combustion. That said, the oxidative scission of 3-methyl-2-butanone still produces a complex product distribution that does not immediately reconcile with the intuitive macroscopic reactions displayed in Scheme 4.2. To gain further insight, we examined selectivity trends for a range of fractional conversions during the oxidative scission of 3-methyl-2-butanone over VO$_x$/$\gamma$-Al$_2$O$_3$ at 453K (Figure 4.2).

**Figure 4.2.** Molar selectivity during the oxidation of 3-methyl-2-butan as a function of conversion on VO$_x$/$\gamma$-Al$_2$O$_3$. b) and c) highlight data for CO$_2$ and isobutyric acid. Conditions: $T = 453$ K, $P_{3MB} = 11$ Torr, $P_{O_2} = 133$ Torr, and helium balance.
In this conversion range, we observed four products: acetone, acetic acid, carbon dioxide, and isobutyric acid. At the zero conversion limit (Figure 4.2a), acetone and acetic acid exhibited equal, non-zero selectivities (49.2%). This is consistent with the C₂-C₃ scission pathway illustrated in Scheme 4.2, indicating that acetone and acetic acid are produced in equimolar quantities through direct consumption of 3-methyl-2-butanone. We observed that acetone selectivity was invariant with reactant fractional conversion, whereas acetic acid selectivity decreased slightly (≈46% selectivity) as a function of fractional conversion. This indicates that acetone is a stable product, whereas a portion of acetic acid is consumed by sequential reactions. Isobutyric acid (Figure 4.2c) had a positive y-intercept at 0.8% selectivity, indicating that it is a primary oxidative scission product, which aligns with Scheme 4.2. If isobutyric acid forms through a pathway analogous to the acetone/acetic acid pair (Scheme 4.2), one expects the generation of an equimolar quantity of formaldehyde, which is not reflected in our data. Instead, we observed the equimolar production of CO₂ at the zero-conversion limit, with a y-intercept of 0.8 +/- 0.2%. This indicates that CO₂ and isobutyric acid are co-products formed through primary oxidative scission of the methyl α-carbon in 3-methyl-2-butanone (i.e., scission of the C₁-C₂ bond). We attribute the observed presence of CO₂ instead of formaldehyde to the rapid decomposition of formaldehyde under oxidizing conditions, either on the surface or homogeneously, which gives CO₂ the appearance of a primary scission product.²⁴⁻²⁵

As conversion increased, isobutyric acid selectivity declined from 0.7% to 0.3%. Like acetic acid, isobutyric acid is consumed by secondary reactions. Over the same conversion range, selectivity toward CO₂ increased from 0.8% to 3.8%, which is roughly four times as large as the measure of isobutyric acid selectivity at the zero conversion limit (0.8%). Clearly, CO₂ formation is not limited to formaldehyde decomposition; it must also be formed through secondary
combustion reactions. Declines in selectivity toward isobutyric and acetic acid mirror the increase in CO₂ selectivity, suggesting that both are consumed by combustion. Furthermore, because overall selectivity toward C₂-C₃ scission was roughly 99%, we assume high bulk and surface concentrations of acetic acid/acetate and conclude that acetic acid combustion is likely the primary source of CO₂ in this system. Finally, at conversion rates below 2%, oxidative scission of 3-methyl-2-butanone was > 97% selective to the primary, C₂-C₃ bond scission pathway, and we observed minimal interference from competing parallel or sequential reactions. For this reason, rates of acetic acid and acetone formation measured at the zero-conversion limit provide a reasonable estimate of the intrinsic kinetics necessary for oxidative scission of the C₂-C₃ bond in 3-methyl-2-butanone. To ensure simplicity, we report the average formation rate for acetic acid and acetone hereafter, and we refer to this quantity as the rate of “oxidative scission.” It is important to note that oxidative scission rates vary dramatically with the degree of substitution at the α-carbon, so these data are only strictly representative for the oxidative scission of a tertiary α-carbon. We next discuss apparent reaction orders in 3-methyl-2-butanone, oxygen, and vanadium.

![Graph](image)

**Figure 4.3.** Oxidative scission rates as a function of vanadium loading (P₃M₂B = 11 Torr, P₀₂ = 130 Torr, T = 473 K.)
We first present oxidative scission rates as a function of vanadium loading (Figure 4.3) measured over VOₓ/Al₂O₃ catalysts prepared at 0.4–4.0 VOₓ/nm² (1.2–11 wt%). As anticipated, oxidative scission rates increased with VOₓ loading; however, the vanadium order was slightly higher than unity (1.27). Typically, a non-unity order in a Koros-Nowak-type analysis is interpreted as a sign of transport control;²⁶ however, it is necessary to vary active site density without changing active site structure in order to provide rigorous data supporting this conclusion. Unfortunately, the structure of dispersed vanadium oxides is a strong function of vanadium loading, so a strict Koros-Nowak analysis was difficult to conduct. In this set of catalysts, Raman spectra (Figure S4.10), XRD spectra (Figure S4.11), and DR-UV-Vis edge energies (Table S4.3) indicate a clear shift from highly dispersed vanadium oxides to oligomeric and bulk vanadium oxides as vanadium loadings increase. For this reason, the nonlinear relationship between oxidative scission rates and vanadium loading may also indicate a structure-sensitive reaction; unfortunately, proving this theory requires that we first demonstrate kinetic control. Because we could not change the vanadium loading without also changing the vanadium structure, we employed a theoretical analysis (supporting information) to demonstrate kinetic control. Using conservative estimates for rates of heat and mass transfer and considering the most demanding regimes for kinetic control (high exothermicity, high temperatures, and high reaction rates), we found that the threshold criteria for both inter- and intra-particle heat and mass transfer limitations were satisfied by at least one order-of-magnitude. We therefore conclude that the data in Figure 4.3 are kinetically controlled and that oxidative ketone scission is a structural sensitive reaction on vanadium oxides. A greater-than-unity vanadium order indicates that reaction rates were enhanced at higher vanadium loadings. Considering that UV-Vis edge energies indicate that increased vanadium loadings lead to increasingly oligomeric species, this observation
suggests that polyvanadates are more active than monovanadates. It is clear that oxidative ketone scission produces two fragments and ultimately requires the insertion of two oxygen atoms into the parent ketone, so it is reasonable to expect that oxidation rates may change as a function of the proximity of vanadium cations and labile lattice oxygens.

Figure 4.4. Orders of reaction observed during 3M2B oxidative scission reaction: oxygen order (P_{3M2B} = 11 Torr, 4 V VO_x/γ-Al_2O_3) and 3M2B order (P_{O_2} = 130 Torr, 4 V VO_x/γ-Al_2O_3). Conditions: T = 473 K, and helium balance.

As illustrated in Figure 4.4, oxidative ketone scission had a fractional, positive order dependence on 3-methyl-2-butane (0.60 ± 0.03). This is consistent with the positive hydrocarbon orders observed during the oxidation of propylene to acrolein,^27 ethane to ethylene and acetaldehyde,^28 and alcohol to aldehyde^29-30 over supported vanadates. Positive orders are attributed to sparse hydrocarbon coverage, which is logical at the elevated temperatures required for oxidation. Figure 4.4 also displays a positive, fractional order in dioxygen (0.37 ± 0.02); however, this runs counter to expectations. Oxidation rates over vanadium oxides are typically invariant with oxygen pressure.\(^31\) This has been attributed to rate control by reduction of the lattice cation. Vanadium-catalyzed oxidations typically proceed through Mars-van-Krevelen redox cycles, wherein the transfer of lattice oxygen to bound substrates is coupled to V-O bond scission.\(^32\) This creates a partially reduced vanadium cation and a corresponding oxygen vacancy; subsequent dissociation of molecular oxygen regenerates the V\(^{5+}\) cation and heals the defect. Typically, the
rate of a Mars-van-Krevelen cycle is controlled by V-O bond scission.\textsuperscript{33-34} Theoretically, rate control by V-O scission can result in a positive O\textsubscript{2} order if the surface is rich in oxygen vacancies, which seems implausible. Slow V-O bond scission implies relatively rapid O\textsubscript{2} dissociation. Furthermore, the formation of V\textsuperscript{5+} is thermodynamically favorable in the presence of dioxygen (e.g., for V\textsubscript{2}O\textsubscript{3} (s) + O\textsubscript{2} (g) \rightarrow V\textsubscript{2}O\textsubscript{5} (s), \( G^\circ = -220 \text{ kJ mol}^{-1} \) at 298K). Under conditions that enable rapid and effectively irreversible vanadium oxidation, few oxygen vacancies will exist; on a surface with no oxygen vacancies, rate control by V-O scission manifests as a zero-order dependence on molecular oxygen. The fact that we observed a positive oxygen order suggests either that something other than V-O bond scission controls the rate of oxidation or that there is an alternate mechanism for oxygen insertion during ketone oxidative scission. For example, mechanisms reliant on the formation of C-O bonds between surface adsorbates and chemisorbed oxygen (Langmuir-Hinshelwood)\textsuperscript{34-35} or surface adsorbates and gas-phase oxygen (Eley-Rideal)\textsuperscript{36} have precedence in the literature, and either can be plausibly consistent with a positive oxygen order.

To aid in resolving the roles of gas-phase and lattice oxygen, we considered trends observed during temperature-programmed surface reactions (TPSR) of 3-methyl-2-butanone over SiO\textsubscript{2}, γ-Al\textsubscript{2}O\textsubscript{3} and VO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} under anaerobic (He) and aerobic (15% O\textsubscript{2}/He) conditions (Figures 4.5 and 4.6). In all systems, we tracked effluent concentrations of 3-methyl-2-butanone, acetic acid, acetone, CO, CO\textsubscript{2}, and H\textsubscript{2}O. Here, we highlight 3-methyl-2-butanone, acetone, and acetic acid as they are all involved in the primary oxidative scission reaction. Profiles for combustion products are included in the supporting information (Figure S4.12).

Under anaerobic conditions (Figure 4.5), we observed only trace desorption of unreacted 3-methyl-2-butanone from SiO\textsubscript{2}. Ketones bind at oxide surfaces through acid-base interactions,\textsuperscript{37}
so one expects minimal adsorption on SiO$_2$. Furthermore, SiO$_2$ is non-reducible, so one expects no substrate oxidation under anaerobic conditions. Over γ-Al$_2$O$_3$, we saw that significant quantities of 3-methyl-2-butane desorbed in an intact state. The desorption of 3-methyl-2-butane occurs from 353–473K, and we can generally deconvolute this profile into two broad peaks (387K and 416K). Significant ketone uptake is consistent with the Lewis-acidic nature of γ-Al$_2$O$_3$, which gives it a tendency to bind ketones more strongly than SiO$_2$. Despite appreciable coverage of 3-methyl-2-butane on γ-Al$_2$O$_3$, we observed neither oxidative scission nor combustion under He, which is consistent with expectations for a non-reducible solid oxide. Finally, we considered the TPSR of 3-methyl-2-butane over a fully oxidized (i.e., pre-calcined) VO$_3$/γ-Al$_2$O$_3$ sample under anaerobic conditions. In order to isolate the role of lattice oxygen, the calcined catalyst was purged with UHP helium (400 mL min$^{-1}$) for 40 mins at 573K to remove chemisorbed, non-lattice oxygen prior to dosing the surface with 3-methyl-2-
butanone. In contrast with the TPSR profiles for non-reducible SiO$_2$ and γ-Al$_2$O$_3$, the majority of surface-bound 3-methyl-2-butanone was converted over VO$_x$/Al$_2$O$_3$ to form acetone and trace acetic acid (375–575K). This clearly indicates that oxidative scission of the C$_2$-C$_3$ bond in 3-methyl-2-butanone occurs over VO$_x$/Al$_2$O$_3$ under an He atmosphere. Because the lattice is the only oxygen source in this experiment, this establishes the existence of a Mars-van-Krevelen pathway for oxidative ketone scission. As illustrated in Figure S4.12, we observed the onset of combustion pathways starting at roughly 473K, indicating that lattice reduction can also facilitate the combustion of adsorbed species. However, because this occurs only in high-temperature regimes, this appears to be a higher-barrier process than oxidative scission.

![Figure 4.6](image-url)  
**Figure 4.6.** Temperature programmed surface reaction obtained from 3M2B dosed samples under 15% O$_2$/1% Ar/helium balance.

We next considered the impact of introducing molecular O$_2$ (15% in He) into the system (Figure 4.6). We observed no major differences between TPSR over SiO$_2$ and TPSR under anaerobic
conditions. It is clear that there was no appreciable uptake of 3-methyl-2-butanone from SiO₂, and we again observed no evidence of oxidative scission or combustion; both results are consistent with a non-acidic, non-reducible oxide. TPSR profiles over γ-Al₂O₃, on the other hand, changed significantly upon the introduction of molecular O₂. Under anaerobic conditions, we observed only desorption of unconverted 3-methyl-2-butanone. In contrast, under 15% O₂, most of the 3-methyl-2-butanone reacted via oxidative scission of its C₂-C₃ bond to form acetone and trace acetic acid. It is noteworthy that this occurred despite the presence of a non-reducible lattice, which establishes that oxidative ketone scission can occur without lattice reduction, i.e., the reaction does not necessarily occur through a lattice-facilitated Mars-van-Krevelen cycle. Instead, acid-base interactions between γ-Al₂O₃ and 3-methyl-2-butanone are sufficient to induce oxidative cleavage in the presence of molecular O₂. Consistent with the observation of a positive oxygen order, this suggests either a Langmuir-Hinshelwood or Eley-Rideal mechanism. At temperatures ranging from 373–723K, we observe the onset of combustion.

Finally, we considered the TPSR of 3-methyl-2-butanone on VOₓ/Al₂O₃ under 15% O₂ in He. In this case, the substrate was fully reacted, and the quantities of desorbed acetone and acetic acid increased relative to the quantities observed for both VOₓ/Al₂O₃ under anaerobic conditions (Figure 4.5) and γ-Al₂O₃ under aerobic conditions (Figure 4.6). Interestingly, oxidative scission over γ-Al₂O₃ and VOₓ/γ-Al₂O₃ occurred in a similar temperature range in the presence of O₂ (358–473K). Furthermore, that temperature range was significantly lower than the temperature range for oxidative scission facilitated by lattice reduction alone on VOₓ/Al₂O₃ (Figure 4.5, 375–568K). Although anaerobic TPSR experiments over VOₓ/γ-Al₂O₃ demonstrate that oxidative scission can occur through lattice reduction, the pathway mediated by molecular O₂ exists at relatively low temperatures, suggesting that oxidative scission via lattice reduction is the higher-
barrier process of the two. Finally, we observed that combustion has a slightly lower onset temperature over VO₃/γ-Al₂O₃ in the presence of O₂ (356-686K) than under anaerobic conditions.

![Image](image.png)

**Figure 4.7.** Initial transient period of 3M2B oxidative scission over a) 8.0 V VO₃/γ-Al₂O₃ and b) γ-Al₂O₃. Conditions: T= 453 K, P₃M2B = 11 Torr, P₀₂ = 130 Torr, and helium balance.

Though TPSR experiments are informative regarding the extent to which lattice-mediated and O₂-mediated pathways contribute to oxidative scission, they raise additional questions. For example, steady-state selectivity data (Figure 4.2) establish the expectation that oxidative scission of 3-methyl-2-butanone will produce equimolar quantities of acetone and acetic acid, yet we consistently observed sub-stoichiometric production of acetic acid during TPSR. In addition, while we observed oxidative scission over γ-Al₂O₃ during TPSR under 15% O₂, γ-Al₂O₃ was inert at comparable temperatures and oxygen pressures in a packed bed. These discrepancies probably arose because steady-state packed bed data reflect the behavior of a surface after reaching its “working” state, whereas TPSR reflects the transient behavior of a surface pre-
saturated with 3-methyl-2-butanone and subjected to a temperature ramp. We attempted to reconcile these observations by characterizing the approach to a steady state under 15% O\(_2\) in He, at 453K, and over γ-Al\(_2\)O\(_3\) and VOx/γ-Al\(_2\)O\(_3\) (Figure 4.7).

Upon initial exposure of γ-Al\(_2\)O\(_3\) to 3-methyl-2-butanone (Figure 4.7a), we observed increasing formation rates for acetone and CO\(_2\), whereas CO and acetic acid were observed in trace quantities. Production rates for all the aforementioned products then decayed as a function of time on stream. Unconverted 3-methyl-2-butanone was clearly the dominant species observed over γ-Al\(_2\)O\(_3\). This was true for all conditions, but especially as the system approached steady state. Consistent with observations in TPSR experiments, the data obtained from short spells on stream indicate that γ-Al\(_2\)O\(_3\) is active for oxidative scission, as evidenced by acetone formation. However, scission rates decreased by nearly one order of magnitude over approximately 60 minutes on stream. Despite its intrinsic ability to facilitate oxidative scission, γ-Al\(_2\)O\(_3\) becomes inactive as its surface approaches steady state coverage. Furthermore, we observed only trace quantities of acetic acid in the system, despite the stoichiometric requirement that it must form in equimolar quantities with acetone. This suggests that acetic acid, or precursors thereof, remains bound to the catalyst surface under reaction conditions, which may implicate carboxylate adsorption as the primary mode of deactivation.

The approach to a steady state over VOx/γ-Al\(_2\)O\(_3\) differs significantly from the process described above (Figure 4.7b). We observed that the conversion of 3-methyl-2-butanone was complete for the duration of the experiment. Flowrates of acetone and acetic acid increased monotonically, ultimately reaching steady state values of 0.78 and 0.74 µmol s\(^{-1}\) g\(^{-1}\) within about 60 minutes on stream. Carbon monoxide and CO\(_2\) formation rates increased during the initial 8 mins on stream, reaching a maximum of 0.11 and 0.52 µmol s\(^{-1}\) g\(^{-1}\). Thereafter, formation rates for CO and CO\(_2\)
decreased to 0.05 and 0.25 $\mu\text{mol s}^{-1}\text{g}^{-1}$. After roughly 60 minutes on stream, the overall product distribution was consistent with that observed under steady state conditions in a packed bed (Figure 4.2). Finally, although acetone and acetic acid approached the same steady state production rate, there was a clear difference in their trajectories. Specifically, acetic acid formation lagged acetone formation during approximately the first 30 minutes on stream, after which point their production rates converged as anticipated for the steady state system. Acetone and acetic acid clearly formed on different time scales, which calls into question the concerted formation of acetone and acetic acid in a C$_2$-C$_3$ scission step. It is more likely that the C$_2$-C$_3$ scission step produces distinct surface fragments – acetone and acetic acid precursors – that undergo independent oxidation and/or desorption steps, each with distinct intrinsic kinetics. We attribute the difference in steady state selectivities for acetone and acetic acid to the combustion of acetic acid, as observed in packed bed experiments.

To provide insight into the nature of surface species and regimes during their formation, we analyzed FTIR spectra. First, we examined spectra obtained during the saturation of VO$_x$/γ-Al$_2$O$_3$ with 3-methyl-2-butanone under anaerobic conditions at 313K (Figure 4.8c and 4.8d). We observed multiple bands that are consistent with gas-phase 3-methyl-2-butanone, and we attribute these to vibrational modes in surface species that are unperturbed by adsorption. We are confident that these modes can be assigned to surface species because 3-methyl-2-butanone partial pressures were maintained at 0.2 Torr, which is sufficiently low to avoid the detection of gas-phase species. Furthermore, we did not observe the prominent carbonyl band of gas-phase 3-methyl-2-butanone at 1734 cm$^{-1}$ (Figure S4.1).$^{39}$

We focus subsequent discussion on bands that are distinct from those observed in gas-phase 3-methyl-2-butanone. As surface species accumulated, we observed a band at 1683 cm$^{-1}$, which we
attribute to the carbonyl group in 3-methyl-2-butanone coordinated to a Lewis-acidic cation through oxygen lone pairs. This assignment is consistent with the prior analysis of ketone adsorption on Lewis-acidic solid oxides;\textsuperscript{37, 40} furthermore, we observed a similar band (1690 cm\textsuperscript{-1}) upon exposing γ-Al\textsubscript{2}O\textsubscript{3} to 3-methyl-2-butanone under identical conditions (Figure S4.6). We also observed a band at 1655 cm\textsuperscript{-1}, which we attribute to a second type of interaction between electrophilic sites on VO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} and the carbonyl oxygen of 3-methyl-2-butanone. Specifically, carbonyl bands in this region have previously been attributed to partial proton transfer from an acidic surface hydroxyl to the ketone carbonyl.\textsuperscript{40} The FTIR spectra of pyridine adsorbed on our VO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3} samples indicate that they generally have Bronsted character (Figure S4.5), making this a plausible conclusion. As the system approached a steady state, we observed bands at 1570 cm\textsuperscript{-1}, 1450 cm\textsuperscript{-1}, and 1417 cm\textsuperscript{-1}, which are assigned to carboxylates.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.8.png}
\caption{FTIR spectra of anaerobic 3-methyl-2-butanone oxidative scission over 8.0V VO\textsubscript{x}/γ-Al\textsubscript{2}O\textsubscript{3}. a) and b) steady state at each labeled temperature, c) and d) transient period at 313K. Conditions: P 3-methyl-2-butanone= 0.2 Torr, helium balanced.}
\end{figure}
We attribute these bands to bidentate carboxylates wherein both oxygen atoms are coordinated to lattice cations (Figure 4.9). Along with the growth in carboxylate features during surface saturation at 313K, we observed the appearance of a band at 1130 cm\(^{-1}\). We assign this feature to a C-O stretching mode in a surface alkoxide. The dominant, macroscopic products observed during the oxidative scission of 3-methyl-2-butanone are acetic acid and acetone (Scheme 4.2). We propose that surface carboxylates precede acetic acid formation and those surface alkoxides precede acetone formation. Accordingly, we assign bands at 1570 cm\(^{-1}\), 1450 cm\(^{-1}\), and 1417 cm\(^{-1}\) to an acetate fragment and the band at 1130 cm\(^{-1}\) to an isopropoxide (1130 cm\(^{-1}\)) fragment.

We acknowledge the use of ionic terminology (carboxylates, alkoxides, etc.). This is consistent with the prior analysis of hydrocarbon and oxygenate adsorption on solid oxides, and it tacitly assumes heterolytic bond scission steps. Vanadium oxides catalyze both homolytic and heterolytic pathways, and it is worth noting that all of our subsequent analysis extends to homolytic processes without impacting our overall conclusions. We restrict ourselves to heterolytic terminology in the interest of clarity.

The formation of acetate and isopropoxide fragments (Scheme 4.3) necessitates scission of the bond between the carbonyl carbon in 3-methyl-2-butanone (C\(_2\)) and its methyl-substituted \(\alpha\)-carbon (C\(_3\)). It also requires the formation of new C-O bonds at both the carbonyl carbon (C\(_2\)) and the cleaved \(\alpha\)-carbon (C\(_3\)). Under anaerobic conditions, these new C-O bonds necessarily
involve the coordination of carbon atoms (C\(_{d+}\)) to lattice oxygen (O\(_{2}^{-}\)). Without specifying the order in which C-C scission and C-O bond formation occur, it is helpful to think of the acetate fragment as an acylium ion wherein the carbonyl oxygen is coordinated to a lattice cation (M\(_{\delta^{+}}\)) and the carbonyl carbon (C\(_{\delta^{+}}\)) is coordinated to lattice oxygen (O\(_{2}^{-}\)) (Scheme 4.4), producing a bidentate carboxylate structure as observed in FTIR. Similarly, one may view surface isopropoxide as an isopropanium ion (C\(_{\delta^{+}}\)) coordinated to lattice oxygen (O\(_{2}^{-}\)). Importantly, neither the carboxylate nor the alkoxide can desorb without further transformation. The carboxylate (RCOO-) must be protonated to form a carboxylic acid, and the alkoxide must deprotonate to form a carbonyl, with stoichiometry necessitating hydrogen transfer between the two fragments. Furthermore, because both surface species are effectively incorporated into the vanadium oxide lattice, neither can desorb without generating an oxygen vacancy and reducing lattice cations.

As the system temperature increased to 413K and beyond, the isopropoxide band (1130 cm\(^{-1}\)) decreased in size. In the same temperature range, DR-UV-Vis spectra indicate a substantial increase in d-d transitions (Figure S4.8.). This indicates the reduction of vanadium cations and
implies V-O scission; therefore, we attribute the decrease in the size of the alkoxide band to its oxidation to form acetone. That said, we did not observe acetone signatures in this experiment. We attribute their absence to the relatively weak binding interactions between ketones and the vanadium oxide surface, which should result in sparse coverages at the temperatures required for lattice reduction (413K). This conclusion is supported by the FTIR spectra of VO$_x$/Al$_2$O$_3$ obtained under 0.2 Torr acetone at 413K (Figure S4.4), which exhibit no appreciable coverage of acetone despite significant gas phase pressure. As the isopropoxide band diminished, we observed the appearance of a band at 1353 cm$^{-1}$, which we attribute to chemisorbed acetic acid.$^{42-44}$ This species is distinct from the bidentate carboxylates discussed previously in that it is a stable, protonated, closed-shell species that can desorb from the surface without protonation or further reduction of the lattice. Acetic acid formation is thus consistent with the oxidation of isopropoxide (loss of H), and reduction of the lattice (increased d-d transitions). It is noteworthy that C-C scission and C-O bond formation occurred almost immediately at 313K under anaerobic conditions, yet no further oxidation occurred until approximately 413K, commensurate with lattice reduction. This points to M-O bond scission as the rate controlling step under anaerobic conditions, which is consistent with the traditional view of Mars-van-Krevelen oxidations. As a final note, the VO$_x$/γ-Al$_2$O$_3$ surface was dominated by bidentate carboxylate features at all temperatures, whereas acetic acid, 3-methyl-2-butanone, and acetone coverage were sparse. This probably reflects a higher binding energy in bidentate carboxylates than in all other species.

Next, we considered the spectra of VO$_x$/γ-Al$_2$O$_3$ in the presence of O$_2$ (Figure 4.10). The bands observed during saturation are consistent with those observed under anaerobic conditions, and we draw similar conclusions about both. Ketone coordination occurred primarily through the carbonyl oxygen at lattice cations, and we observed carboxylate formation, which indicates C-C
scission and C-O bond formation. That said, there are significant differences. First, during saturation at 313K, the isopropoxide band (1130 cm\(^{-1}\)) diminished under O\(_2\). This occurred despite the existence of prominent carboxylate bands, which indicate that C-C scission occurred. Normalized spectra focused on specific features observed during surface saturation provide further insight (Figure 4.11). Immediately after dosing at 313K, we observed a band at 1248 cm\(^{-1}\), which we attribute to a C-C stretching mode in chemisorbed acetone (Figure S4.4).\(^{51}\) This band briefly increased in intensity, and it then decayed as carboxylates accumulated on the surface. In contrast, we observed no direct evidence of acetone formation under anaerobic conditions at 313K; we only observed the formation of a putative acetone precursor (isopropoxide) that persisted until the point of lattice reduction (413K). During saturation, we also observed the accumulation of acetic acid, evidenced by the appearance of a band at 1353 cm\(^{-1}\) (Figure 4.10). This band is noteworthy because it represents a stable carboxylic acid that can desorb without

![Figure 4.10. FTIR spectra of aerobic 3-methyl-2-butane oxidative scission over 8.0V VO\(_x\)/γ-Al\(_2\)O\(_3\), a) and b) steady state at each labeled temperature, c) and d) transient period at 313K. Conditions: P\(_3\)-methyl-2-butane\(=\) 0.2 Torr, P\(_{O_2}\)= 130 Torr, He balanced.](image-url)
further reduction of the lattice. Importantly, the analogous band was not observed under anaerobic conditions until 413K, at which point significant lattice reduction also occurred. The appearance of both primary oxidative scission products (acetone and acetic acid) at 313K suggests that, in the presence of O₂, oxidation steps occur without lattice reduction. As temperatures increased, we observed signatures of acetic acid (1353 cm⁻¹) without corresponding signatures of the alkyl fragment (alkoxide, acetone), which we attribute to weak binding (and thus reduced coverage) of ketone. At elevated temperatures, carboxylate bands dominated the surface. However, we observed that, in the presence of O₂, carboxylate signatures diminished significantly above 533K, which was not true under anaerobic conditions. This decrease in carboxylate coverage coincides with the onset of combustion reactions observed during TPSR. This suggests that dioxygen also facilitates combustion pathways, which is consistent with the loss in selectivity to acetic acid observed as a function of conversion in Figure 4.2.

To provide additional insight into the nature of vanadium reduction, we considered FTIR spectra focused on the vanadyl band at 1015 cm⁻¹. Under aerobic environments (Figure 4.12a), we observed no significant perturbation in the vanadyl band, suggesting that any vanadium
reduction occurs primarily through the scission of bonds between vanadium cations and lattice oxygen, which is consistent with the typical view of MvK pathways. Under anaerobic environments, we observed a substantial decrease in vanadyl intensity as temperatures rose above 533K. Based on FTIR spectra (Figure 4.7) that reveal no desorption of acetate at temperatures below 653K and TPSR spectra (Figure 4.5 and Figure S4.12) demonstrating that acetate species primarily desorb as combustion products, we propose that this decrease in vanadyl intensity is a signature of deep vanadium reduction (e.g., to a V3+ cation). This only occurs at temperatures at which combustion is kinetically accessible, so we primarily observed combustion products once we saw this deep reduction of vanadium atoms.

Figure 4.12. FTIR spectra of 3M2B oxidative scission over 8.0 V VO_x/γ-Al2O3: focus on the V=O stretching region at 1015 cm⁻¹ with temperatures from 313 to 653K with a) 130 Torr O2(g) and b) no O2(g). Conditions: P_3M2B = 0.2 Torr, and He balance.
4.4 Conclusion

We have demonstrated two primary pathways for the oxidative scission of 3-methyl-2-butanoic acid. The dominant (> 99%) alkyl scission pathway produces acetone and acetic acid, and the methyl scission pathway produces isobutyric acid and formaldehyde. The structure of supported vanadium oxide changes with the vanadium loading of the catalyst. The vanadium oxide order (1.27) associated with kinetic controlled reactivity data indicates the structural sensitivity of oxidative scission over vanadium oxide. In contrast with typical oxidation over supported vanadium oxide (Mars van Krevelen mechanism), in which case the reaction rate is kinetically independent in oxygen partial pressure, we observe a positive oxygen order for the oxidative scission of 3-methyl-2-butanoic acid, suggesting that the reaction proceeds via the Langmuir Hinshelwood or Eley-Rideal mechanism. Furthermore, both gas phase dioxygen and lattice oxygen are proven to initiate oxidative scission and produce acetone, but gas phase dioxygen enables the oxidative scission to proceed at a lower temperature than the temperature of the lattice oxygen. This is further demonstrated by the variations observed in surface chemical structures. Under anaerobic conditions, we observe the C-O vibration (1130 cm\(^{-1}\)) associated with surface alkoxide at 313K and the CH\(_3\) deformation (1353 cm\(^{-1}\)) in adsorbed acetic acid at 413K. This is evidence of oxidative scission initiated by lattice oxygen, and it demonstrates the reducibility of the lattice oxygen. The aerobic FTIR spectra reinforce the enhancement of gas phase dioxygen in oxidative scission. The positive order of gas phase dioxygen and V-O scission (d-d transition) indicate that both gas phase oxygen and lattice oxygen contribute to aerobic oxidative scission. With the V=O bond unaffected during aerobic oxidative scission, we propose that the V-O-M bond bridge contributes its lattice oxygen to the oxidative scission process. However, the mechanism, which involves gas phase oxygen and lattice oxygen insertions, is still
unclear. We observe the adsorption of 3-methyl-2-butanone onto a Lewis and Bronsted acid site, but the function of these acid sites in oxidative scission also remains unclear.
4.5 Support Information

4.5.1 Mass and heat transfer limitations

In this study, the rates were measured over supported vanadium oxide catalysts with various vanadium oxide loadings. Because the dispersion of supported vanadium oxides on our catalysts was highly correlated with both the catalyst synthesis method and the vanadium oxide loading, the structural sensitivity made it difficult to apply a Madon-Boudart type test\textsuperscript{53} in this system. To exclude the possibility that the measured rates were transport limiting, theoretical criteria for mass and heat transport limitations were estimated.

Table S4.1. Parameters used in calculating criteria for estimating the extent of transport control during the oxidative scission of 3-methyl-2-butane

<table>
<thead>
<tr>
<th>Physical Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst particle diameter</td>
<td>( r_p )</td>
<td>( 4.5 \times 10^{-5} )</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Porosity of the catalyst</td>
<td>( \Phi_p )</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst density</td>
<td>( \rho_c )</td>
<td>( 2.4 \times 10^6 )</td>
<td>g m(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Catalyst thermal conductivity</td>
<td>( \Lambda )</td>
<td>23</td>
<td>W m(^{-1}) K(^{-1})</td>
<td></td>
</tr>
<tr>
<td>3-methyl-2-butane concentration</td>
<td>( C_b )</td>
<td>0.39</td>
<td>mol m(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Rate</td>
<td>( r''' )</td>
<td>5.2</td>
<td>mol s(^{-1}) m(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Density of gas mixture</td>
<td>( \rho )</td>
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<td>kg m(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Viscosity of gas mixture</td>
<td>( \mu )</td>
<td>( 2.8 \times 10^{-5} )</td>
<td>Pa s</td>
<td></td>
</tr>
<tr>
<td>Diffusivity of gas mixture</td>
<td>( D_m )</td>
<td>( 1.5 \times 10^{-4} )</td>
<td>m(^2) s(^{-1})</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Specific heat of gas mixture (453 K)</td>
<td>( C_p )</td>
<td>4.5</td>
<td>kJ kg(^{-1}) K(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity of gas mixture</td>
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<td>W m(^{-1}) K(^{-1})</td>
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<tr>
<td>Mass transfer coefficient</td>
<td>( k_c )</td>
<td>0.96</td>
<td>m s(^{-1})</td>
<td>\textsuperscript{56}</td>
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<tr>
<td>Heat transfer coefficient</td>
<td>( H )</td>
<td>370</td>
<td>W m(^{-2}) K(^{-1})</td>
<td>\textsuperscript{57}</td>
</tr>
<tr>
<td>Knudsen Diffusivity</td>
<td>( D_{Knu} )</td>
<td>( 7.9 \times 10^{-7} )</td>
<td>m(^2) s(^{-1})</td>
<td>\textsuperscript{58}</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>( \delta )</td>
<td>( 1.6 \times 10^{-2} )</td>
<td>m s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Reynold number</td>
<td>( Re )</td>
<td>( 2.1 \times 10.2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prandtl number</td>
<td>( Pr )</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction enthalpy (Combustion)</td>
<td>( \Delta H_C )</td>
<td>-2900</td>
<td>kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Apparent ( E_A ) (Combustion)</td>
<td>( E_A^{AC} )</td>
<td>100</td>
<td>kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Reaction enthalpy (Oxidative scission)</td>
<td>( \Delta H_{OS} )</td>
<td>-390</td>
<td>kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Apparent ( E_A ) (Oxidative scission)</td>
<td>( E_A^{OS} )</td>
<td>70</td>
<td>kJ mol(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>
The threshold criteria were calculated at the maximum rate observed in this study (R_{internal oxidative scission} = 130 \text{ mmol g}^{-1} \text{ min}^{-1}, T = 453 \text{K}, P_{\text{system}} = 776 \text{ torr}, P_{3\text{-methyl-2-butanone}} = 11 \text{ torr}, P_{O_{2}} = 130 \text{ torr}, \text{over } 4.00 \text{ V VO}_{x}/\gamma\text{-Al}_{2}\text{O}_{3}). Table S4.1 summarizes the data used in calculating the mass and heat transfer coefficients. Although combustion always converts a minor portion of 3-methyl-2-butanone (< 15%), we used the enthalpy and apparent activation barrier of the strongly exothermic combustion to estimate the highest possible energy release in this system. The transport criteria under these relatively conservative values represent the extremes for maintaining kinetic control.

The mass and heat transfer threshold criteria were estimated using Equation S4.1–Equation S4.4,\textsuperscript{53} and the results are summarized in Table S2.

Weisz-Prater Criterion\textsuperscript{59} for the intraparticle diffusion limitations of a second order\textsuperscript{60} reaction:

\[
\frac{r^m \cdot r_p^2}{C_s \cdot D_e} < 0.3 \quad \text{(Equation S4.1)}
\]

Criterion\textsuperscript{61} for interphase mass transfer limitations:

\[
\frac{r^m r_p}{C_b k_c} < 0.15 \quad \text{(Equation S4.2)}
\]

Criterion\textsuperscript{62} for intraparticle heat transfer limitations:

\[
\frac{\Delta H_{\text{run}} |r^m r_p^2| E_A}{\lambda T_s} < 0.75 \quad \text{(Equation S4.3)}
\]

Criterion\textsuperscript{63} for interphase heat transfer limitations:

\[
\frac{\Delta H_{\text{run}} |r^m r_p| E_A}{h T_b} < 0.15 \quad \text{(Equation S4.4)}
\]
Table S4.2. Summary of threshold criteria for 3-methyl-2-butane internal oxidative cleavage reactions over VO$_x$/γ-Al$_2$O$_3$ at the highest measured rates.

<table>
<thead>
<tr>
<th>Threshold Criteria:</th>
<th>Estimated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intraparticle diffusion (W-P):</td>
<td>0.3</td>
</tr>
<tr>
<td>Interphase mass transfer:</td>
<td>0.15</td>
</tr>
<tr>
<td>Intraparticle heat transfer (combustion):</td>
<td>0.75</td>
</tr>
<tr>
<td>Interphase heat transfer (combustion):</td>
<td>0.15</td>
</tr>
<tr>
<td>Intraparticle heat transfer (oxidative scission):</td>
<td>0.75</td>
</tr>
<tr>
<td>Interphase heat transfer (oxidative scission):</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The interphase heat transfer criterion for combustion did approach the threshold value, but the one for the governing oxidative scission was at least one magnitude smaller than the threshold value. According to the estimation, the threshold criteria are met even under the most constraining conditions.

4.5.2 In situ FTIR spectra

Figure S4.1 shows the FTIR spectrum for the gas phase 3-methyl-2-butane. Conditions: $P_{3\text{-methyl-2-butane}}=2\text{ Torr}, P_{O_2}=130\text{ Torr}$ and helium balance.

Figure S4.1 shows the FTIR spectrum for the gas phase 3-methyl-2-butane. The peak at 1734 cm$^{-1}$ is assigned to its C=O stretching. Figure S4.2 and S4.3 show the full scale FTIR spectra for 8.0 V VO$_x$/γ-Al$_2$O$_3$ exposed to 0.2 Torr 3-methyl-2-butane under aerobic and anaerobic
conditions. Accordingly, the absence of the peak at 1734 cm\(^{-1}\) indicates that none of the observed peaks in these two spectra were due to gas phase 3-methyl-2-butanone.

**Figure S4.2.** FTIR spectra of 3-methyl-2-butanone over 8.0 V VO\(_x\)/\(\text{Al}_2\text{O}_3\) at various reaction temperatures. Conditions: \(P\text{3-methyl-2-butanone} = 0.2\) Torr, \(P\text{O}_2 = 130\) Torr and helium balance.

**Figure S4.3.** FTIR spectra of 3-methyl-2-butanone over 8.0 V VO\(_x\)/\(\text{Al}_2\text{O}_3\) at various reaction temperatures. Conditions: \(P\text{3-methyl-2-butanone} = 0.2\) Torr, \(P\text{O}_2 = 0\) Torr and helium balance.
Figure S4.4 shows the full scale FTIR spectra for 8.0 V VO$_x$/γ-Al$_2$O$_3$ exposed to 0.2 Torr acetone at 313K under 130 Torr O$_2$. The peak at 1248 cm$^{-1}$ is attributed to the C-C stretching mode in adsorbed acetone.

The adsorption of pyridine onto the 8.0 V VO$_x$/γ-Al$_2$O$_3$ catalyst is shown in Figure S 4.5. The peak at 1540 cm$^{-1}$ represents pyridine adsorbed on the Bronsted acid site, and the peak at 1450 cm$^{-1}$ represents pyridine adsorbed on the Lewis acid site.$^{64}$
4.5.3 The oxidative scission of 3-methyl-2-butanoic acid over \(\gamma\)-Al\(_2\)O\(_3\)

We examined spectra obtained during the saturation of the \(\gamma\)-Al\(_2\)O\(_3\) surface under 0.2 Torr 3-methyl-2-butanoic acid in He at 313K (Figure S4.6). Figure S4.6a highlights the regions dominated by carbonyl (1600–1800 cm\(^{-1}\)) and carboxyl (1350–1550 cm\(^{-1}\)) features, while Figure S4.6b focuses on the vibrational modes associated with C-H, C-O, and C-C bonds (1050–1400 cm\(^{-1}\)).

Considering the higher wavenumber first, we observed a relatively well-defined band in the carbonyl region (1690 cm\(^{-1}\)). It was characteristic of a C=O bond coordinated to a Lewis-acidic Al\(^{3+}\) through its oxygen lone pairs.\(^3\) As the carbonyl species accumulated, we observed a faint band in the carboxyl region (1599 cm\(^{-1}\)). Prior spectroscopic analyses of acetone adsorbed on \(\gamma\)-Al\(_2\)O\(_3\) assigned this band to a C=C stretching mode associated with the formation of enols or enol-like surface intermediates.\(^3\) Enol formation implies the deprotonation of the \(\alpha\)-carbon,
which should convert basic lattice O\(^2^-\) sites into hydroxyls. The remaining features observed on γ-Al\(_2\)O\(_3\) are attributed to unperturbed C-C and C-H bonds in the adsorbed 3-methyl-2-butanone. The positions of these bands were nearly identical to those observed for gas phase 3-methyl-2-butanone (Figure S4.1); however, we are confident that these bands are attributable to the surface species. The bands, therefore, reflect vibrational modes in surface-bound 3-methyl-2-butanone that largely retain their gas-phase character upon adsorption. Taken together, we conclude that, on γ-Al\(_2\)O\(_3\) at 313K, 3-methyl-2-butanone binds to γ-Al\(_2\)O\(_3\) primarily through interactions between the carbonyl oxygen and a coordinatively unsaturated aluminum cation. There is also some evidence for the deprotonation of an α-hydrogen to form an enol-like surface species; however, we did not observe evidence of C-C scission or any subsequent oxidation steps.

As the temperatures increased, the bands associated with chemisorbed 3-methyl-2-butanone were replaced by broad bands at 1567 cm\(^{-1}\) and 1460 cm\(^{-1}\), which we attributed to adsorbed carboxylate.\(^{41}\) Interestingly, despite clear evidence of C-C scission and C-O bond formation, we observed no acetic acid signatures, which should have a methyl vibration at 1330–1355 cm\(^{-1}\) based upon reference experiments. As the carboxylate bands increased in intensity, we observed a band at 1307 cm\(^{-1}\). This band cannot be attributed to a carboxylate; however, its appearance alongside carboxylate features suggests it is a product of C-C scission. Carboxylate formation necessitates the co-production of an alkyl fragment; accordingly, we attributed this band to CH\(_3\) deformation in a reduced (\(\delta-\)) alkyl fragment that is likely to be coordinated to an Al cation.\(^{47,65-66}\) This is supported by the Al-C vibrational modes reported by Tysoe.\(^{67-68}\) One can also rationalize this assignment indirectly: if the alkyl fragment was oxidized (\(\delta+\)), it would coordinate to lattice oxygen, forming either an alkoxide (1120–1170 cm\(^{-1}\)) or chemisorbed acetone (1248 cm\(^{-1}\)), yet we observed no such features. The spectra clearly show that C-C
scission and carboxylate formation can occur without lattice reduction; however, further oxidation to stable products (i.e., products that can desorb) is not possible without lattice reduction. For this reason, on $\gamma$-Al$_2$O$_3$ in the absence of O$_2$, carboxylate and alkyl fragments remain reduced and surface-bound, dominating IR spectra under all conditions where C-C scission is kinetically accessible. In this case, the features associated with carboxylate and alkyl fragments persisted until 653K, which is consistent with the fact that we did not observe oxidation products below 653K during TPSR of 3-methyl-2-butanone on $\gamma$-Al$_2$O$_3$ under He. Importantly, these observations indicated that C-C scission could occur without oxidation.

Next, we considered analogous spectra obtained during the surface saturation of $\gamma$-Al$_2$O$_3$ under 0.2 Torr 3-methyl-2-butanone and 15% O$_2$ in He at 313K (Figure S4.7). Introducing O$_2$ during surface saturation caused no significant changes compared to the anaerobic case at 313K; the bands remained consistent with molecularly adsorbed 3-methyl-2-butanone, and we saw some
evidence of enol formation. Increasing the temperature again induced the formation of carboxylates. Arguably, they were observed at lower temperatures and were more pronounced than in analogous experiments under a He atmosphere. The previously discussed band at 1307 cm\(^{-1}\), which we assigned to a reduced alkyl fragment, was diminished under O\(_2\), suggesting oxidation to acetone as discussed in the context of alkoxide oxidation on VO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\). As in the vanadium case, we observed no appreciable carbonyl or acetone signatures, which we again attributed to unfavorable adsorption thermodynamics for the ketone at temperatures where C-C scission is kinetically accessible. Our main evidence for the completion of the oxidative scission cycle was the appearance of a band at 1328 cm\(^{-1}\), which we attributed to chemisorbed acetic acid.\(^6^9\) Again, this was distinct from the carboxylate species observed in the anaerobic system, where the carboxylates never fully converted to acetic acid and were most likely to have been associated with the formation of a bond between the carbonyl carbon and non-labile oxygen atoms in the alumina lattice. Our observation of a fully oxidized acetic acid here suggests that the oxidative scission step directly produces the carboxylic acid without the requirement of lattice reduction, consistent with our observation that \(\gamma\)-Al\(_2\)O\(_3\) inherently catalyzes oxidative ketone scission under aerobic conditions. Carboxylate features dominated the surface of \(\gamma\)-Al\(_2\)O\(_3\) at all temperatures where C-C scission was indicated, suggesting high carboxylate coverages under most reaction conditions.

4.5.4 Diffuse reflectance UV-Vis Spectra

To probe the oxidation state of the vanadium cation during ketone oxidative scission, we considered temperature-resolved steady state DR UV-Vis spectra obtained under various gas compositions (Figure S4.8). The prominent band at ~4.5ev is associated with ligand-to-metal charge-transfer bands for V-O bonds; in general, they are consistent with vanadium in a +5
The inset focuses on the region from 1.5 to 3 eV range, where d-d transitions were observed. On a fresh catalyst (i.e., prior to exposure to 3-methyl-2-butanone and under 15% O₂ in He), we observed no intensity in the d-d transition region, which is again consistent with a fully oxidized vanadium center (V⁵⁺) since it has no d-electrons. Upon exposure to 3-methyl-2-butanone, we observed a small increase in d-d transitions, which indicates a partial reduction of vanadium cations. This is consistent with our observation that C-C scission and the formation of an acetone precursor from the alkyl side chain of 3-methyl-2-butanone occurred almost immediately upon adsorption. Consistent with the FTIR spectra that showed the evolution of an acetone-like CH₃ band at temperatures above 313K, we observed an additional increase in d-d transitions, which is consistent with a further reduction of V; based on IR spectra, we
attributed this to the onset of acetone formation, which requires vanadium reduction. We observed a more significant increase in d-d transitions as the temperatures exceeded 423K. A significant rise was observed when the temperature increased from 373K to 423K; from FTIR spectra and steady state reactivity data, we observed acetic acid formation in this temperature range. This increase in d-d transitions is most likely to have been associated with an increase in the percentage of reduced vanadium atoms upon the surface; it can be reasonably attributed to the onset of acetic acid desorption (e.g., monodentate acetic acid, the small increase in oxygen vacancies as acetate starts desorbing, etc.). Cycle at 423K; thus, raising the reaction temperature to 473K only increases the population of reduced vanadium oxides rather than the extent of the reduction of vanadium cation.

4.5.4 Vanadium oxide dispersion on VOx/γ-Al2O3 catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Edge Energy (eV)</th>
<th>UV-Vis VOx speciation</th>
<th>Raman Spectra VOx speciation</th>
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<td>n=2</td>
<td></td>
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<td>Na3VO4</td>
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<td>Poly</td>
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<tr>
<td>V2O5</td>
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<td>Crys</td>
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<tr>
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<td>3.17</td>
<td>Poly</td>
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<td>Poly</td>
</tr>
<tr>
<td>0.80 V*</td>
<td>3.08</td>
<td>2.64</td>
<td>Poly</td>
</tr>
<tr>
<td>4.00 V*</td>
<td>2.70</td>
<td>2.35</td>
<td>Poly</td>
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<tr>
<td>8.00 V*</td>
<td>2.35</td>
<td>2.17</td>
<td>Crys</td>
</tr>
<tr>
<td>12.0 V*</td>
<td>2.36</td>
<td>2.13</td>
<td>Crys</td>
</tr>
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</table>

This study considered the order of support vanadium oxide for 3-methyl-2-butane oxidative scission reactions. To estimate the vanadium oxide order, the logarithm of rates measured over supported vanadium oxide catalysts with different vanadium loadings was plotted as a function...
of the logarithms of their vanadium oxide concentrations. In this case, we used the vanadium oxide weight percentage as the vanadium oxide concentration for each catalyst with one assumption: all the supported vanadium oxides were well dispersed on the catalyst surface; that is, only negligible crystal vanadium oxide (V₂O₅) existed on the catalyst surface. We used Raman and DR-UV-Vis spectroscopy to examine this assumption.

From many studies conducted on supported vanadium oxides, the decrease in the edge energies of the samples correlates well with the increase in the domain size of the surface vanadium oxide (the extent of oligomerization of monovanadates or polyvanadates). As shown in Figure S4.5, the edge energy of each sample was obtained as the intersection between the y-axis and the tangent line in the low energy rise of the function \([F(R_\infty)hu]^{1/n}\). In this function, \(F(R_\infty)\) is the Kubelka-Munk function calculated from the absolute reflectance \((R_\infty)\); \(n = 1/2\) and 2 were reported for supported vanadium oxide catalysts and represent directly and indirectly allowed transitions, respectively. As shown in Table S3, the edge energies of sodium orthovanadate (Na₃VO₄, monovanadate), sodium metavanadate (NaVO₃, polyvanadate), and vanadium pentoxide (V₂O₅,
crystal) were used as references for the identification of supported vanadium oxide speciation. Accordingly, catalysts with 0.40 V and 0.80 V loading had edge energies lower than NaVO₃; hence, we claim that there are no crystal vanadium oxides on their surface. The edge energies of 1.60 and 4.00 V are higher than NaVO₃ but lower than V₂O₅, and their vanadium oxide dispersion needs further investigation.

Figure S4.6 shows Raman spectra for catalysts synthesized with different γ-Al₂O₃ support (Strem Chemicals, 95%). According to our previous analysis in Chapter 2, the peak at 997 cm⁻¹ was attributed to the vanadyl bond (V=O) in crystal V₂O₅, the peak at 1037 cm⁻¹ was due to the same bond in polyvanadates, and the peak at 1024 cm⁻¹ was assigned to V=O in monovanadate. From our Raman spectra, only polyvanadates were observed on the 4.00 V* catalyst, which had lower edge energy (2.70 for n = 1/2, 2.35 for n = 2) than NaVO₃. One could argue that the Raman spectroscopy may have less of a detection limit than the UV-Vis spectroscopy. Still, the peak at 1037 cm⁻¹ of 4.00 V* indicated that polyvanadates dominated the surface, and most of the supported vanadium oxides were well dispersed. Nevertheless, the edge energies of the catalysts

![XRD patterns for catalysts, supports and V₂O₅ crystal. The V₂O₅ structure was only observed on the 8.0 V catalyst.](image)

**Figure S4.11.** XRD patterns for catalysts, supports and V₂O₅ crystal. The V₂O₅ structure was only observed on the 8.0 V catalyst.
(8.00 V* and 12.0 V*) were relatively stable once well-defined crystal vanadium oxides formed upon their surface. Because the edge energy of 4.00 V is smaller than 4.00 V*, we suggest a slightly higher vanadium oxide dispersion for 4.00 V. Therefore, we expect that the most loaded vanadium oxides are well dispersed on the catalysts (0.4–4.0 V) employed in this study.

4.5.5 Temperature programmed surface reaction combustion products

Figure S4.7 demonstrates the desorption rates of combustion products from 3-methyl-2-butanone dosed 8.0 V VO$_x$/γ-Al$_2$O$_3$ TPSR as a function of the reactor temperature. For γ-Al$_2$O$_3$ support under anaerobic conditions, only a small amount of CO (373–513K) and water (473–723K) was observed. The addition of oxygen significantly increased the level of combustion in the system. The combustion started at
361K, reached its maximum at 656K, and continued until 723K. Switching the γ-Al₂O₃ support to the 8.0 V VOₓ/γ-Al₂O₃ catalyst showed similar combustion features for the corresponding oxygen atmospheres. Still, very little combustion was observed when there was no gas-phase oxygen in the reactor. Under the aerobic conditions, the combustion reached its maximum (555K) and finished (673K) more rapidly than the support. Only a negligible amount of combustion products was detected over SiO₂. The combustion over 2.30 V VOₓ/SiO₂ began at 358K, featured two strong peaks at 384K and 435K, and a weak peak at 560K. Compared with the SiO₂ support, similar to the oxidative scission, the observed combustion over the SiO₂ catalyst was solely from the species adsorbed on the surface vanadium oxides. Therefore, we suggest the combustion observed at higher than 560K was mostly from the species adsorbed on γ-Al₂O₃ support.
4.6 References


CHAPTER 5

Kinetics of the Oxidative Scission of Methyl Ketones Over VO_{x/\gamma-Al_2O_3}: the role of Acid
and Redox Sites and the Finalized Elementary Steps
5.1 Introduction

In the previously chapter, we have proposed a heterogenous mechanism for the oxidative scission of methyl ketones over supported vanadium oxide catalyst. The oxidative scission of 3-methyl-2-butaneone produces an acyl fragment and an alkyl fragment. In the homogenous mechanism, these two fragments react with gas phase dioxygen, producing either a dioxetane\(^1,^2\) or peroxide\(^3\) structures that further cleave into ketone(or aldehyde) and carboxylic acid.\(^4\) Counter to the homogenous mechanism, the observed kinetics dependence of both gas phase dioxygen and supported vanadium oxide suggests that lattice oxygen participates in the oxidative scission, indicating a possible combination of Eley-Rideal and Mars van Krevelen mechanism. In addition, significant interactions between surface acid sites and the carbonyl group in 3-methyl-2-butaneone were observed by FTIR spectroscopy, suggesting Lewis and Bronsted acid site are additional possible active sites. Aiming to establish the role of acid, base, and redox sites, and accordingly resolving the corresponding active site and elementary steps for the oxidative scission reaction, the employed catalyst bed was poisoned or modified with probe molecules at the steady state of 3-methyl-2-butaneone oxidative scission. In this study, pyridine was used to block both Lewis and Bronsted acid site;\(^5,^6\) 2,6-di-tert-butylpyridine (2,6-DTBP) was used to block Bronsted acid site;\(^7,^8\) ammonia was employed to poison acid sites and the V=O bond;\(^9,^{10}\) and finally, water was introduced to generate excess hydroxide and proton on the catalyst surface.\(^11\) Kinetics analysis was supported by surface structural insights observed in the mimic experiments monitored with the transmissive FTIR spectroscopy. At last, a rate-determine step was highlighted according to the isotropic exchange experiment.
5.2 Materials and Methods

5.2.1 Reagents

The oxidative scission rates of 3-methyl-2-butanone (Acros, 98%), 2-butanone (Acros 99%) and 2-butanone-1,1,1,3,3-d5 (Sigma, 98 atom%) were quantified. Pyridine (Acros, 99+%), 2,6-di-tert-butylpyridine (Acros, 97%), H2O, and ammonia (Airgas, 1% ammonia, 1% Ar in He) were separately introduced to poison the 8.0V VOx/γ-Al2O3. The catalyst was synthesized through incipient wetness method12-13 involving γ-Al2O3 (Advanced Materials, 97%), ammonia metavanadate (Sigma, 99.5%), and oxalic acid (Acros, 99%). A sequential purifier (Spectrapure) purified water to a resistivity >18.2 MΩ·cm. Instruments calibration were performed with acetone (Fisher, Optima), acetic acid (Acros, 98%), acetaldehyde (Sigma, 99.5+%), acetonitrile (Acros, 99.9%), and CO2 (Airgas, 20%, 1% Ar, He balance). O2 (Airgas, UHP) and He (Airgas, UHP) were used as the carrier gas in the reactor setup. Chemical blends, including O2 (Airgas, 15%, He balance), Ar (Airgas, 1%, He balance), and ammonia (Airgas, 1%, 1% Ar, He balance) were used in ammonia co-feeding, FTIR spectroscopy and temperature programmed desorption.

5.2.2 Reactivity measurement

Reactivities of the oxidative scission in different conditions were obtained at steady state in a tubular packed bed reactor. The details of the reactor setup were demonstrated in Chapter 2. For the packed bed reactor, 20-30 mg of 8.0V VOx/γ-Al2O3 diluted with 80-120 mg quartz powder in the same size (45-90 μm radius) was loaded into an up-flow half-inch stainless steel reactor and packed with two pieces of quartz wool. Quartz chips supported the catalyst bed in the upstream, and a type K thermocouple (Omega) was placed directly to the downstream of the catalyst bed to monitor the reaction temperature. The effluent from the reactor was analyzed by an online gas
chromatography (HP 5890) equipped with one flame ionized detector connected with an HP-INNOWax column for hydrocarbons, and one thermal conductivity detector connected with a Restek ShinCarbon ST Micropacked column for carbon oxides. Reaction products were identified by comparing the mass spectrum observed from the GC-MS (Agilent 7890 and 5975 C mass spectrometer detector) to NIST libraries. Before each experiment, the catalyst bed was calcined at 723K for 4hrs in a gas mixture consisting of 16.7% O$_2$ in a He balance.$^{14}$ The catalyst bed was cooled to a desired reaction temperature and then exposed to the reactant. The packed bed reactor reached steady state of oxidative scission in approximately 15-20 hours. The steady state rate of oxidative scission was recorded, and the system was subsequently switched to new conditions. The rate of each following steady state was obtained to represent the reactivity of the catalyst at corresponding conditions.

Methyl ketones cleaves through two different pathways.$^{15-16}$ The methyl scission breaks the C-C bond between the methyl group and the carbonyl group, and the alkyl scission cuts the carbonyl group out from the C3 carbon. The oxidative scission is only referred to the alkyl scission (selectivity $\geq 99\%$) in this paper. The oxidative scission of methyl ketones generates an acyl fragment and an alkyl fragment, which subsequently produces equimolar of carboxylic acid and ketone (or aldehyde). The catalyst mass normalized production rate of each molecule from the oxidative scission was showed to trace their behaviors in different conditions. However, the average production rates of the two corresponding molecules were estimated, discussed and compare as the oxidative scission rate. Equation 5.1-5.2 summarized method to estimate the mass normalized production rate of one molecule and the oxidative scission rate:

$$PR_i = \frac{F_i}{M_{\text{catalyst}}}$$  \hspace{1cm} (5.1)
In Equation 5.1 and 5.2, $PR_i$ stands for the production rate of chemical i, $F_i$ stands for the molar flowrate of chemical i, $M_{catalyst}$ is the mass of catalyst used in the packed bed reactor, and R stands for the oxidative scission rate.

5.2.3 Acid property of the catalyst

The acidity profile of $8.0 \text{ V VO}_x/\gamma-\text{Al}_2\text{O}_3$ was determined by ammonia, and pyridine temperature programmed desorption (TPD) in this experiment.\textsuperscript{17-18} Generally, 200-300 mg of sample were prepared in a 1/2-inch quartz tube between two quartz wool (Technical Glass Products) end plugs. The whole tube was further situated in a temperature-programmed furnace (Omega Engineering). The temperature of the furnace was regulated by a PID controller (Love, series 16A) and monitored by a type K thermocouple (Omega). Before analysis, all samples were calcined in situ at 723K for 4 hours under 60 sccm air flow (Airgas, Ultra Zero). Subsequently, the cell was cooled to 423K and purged under 100 sccm of He flow dried over molecular sieves for more than 90 minutes. After pretreatment, catalysts were dosed with ammonia (1% ammonia and 1% argon, Airgas) or pyridine (6.86 torr). The point of surface saturation in ammonia and pyridine were determined by tracking signals of ammonia ($m/z = 16$) and pyridine ($m/z = 79$) in the effluent with a mass-selective residual gas detector (Stanford Instruments RGA 100), respectively. After the saturation of probe molecule on the catalyst surface, the cell was purged under 400 sccm of He for 1h to remove physically adsorbed probe molecule and further ramped to 723K at 10 K min$^{-1}$ under He with 1.0 mol% Ar as an internal standard to remove chemisorbed probe molecule.
5.2.4 FTIR spectroscopy

Pressed thin, coherent, self-supported wafer of 1.0 VO\textsubscript{x}/\textgamma-Al\textsubscript{2}O\textsubscript{3} powders were prepared and mounted inside an \textit{in situ} IR-cell equipped with KBr or ZnS windows. Greater detail of the cell stated in Chapter 3. A Nicolet 6700 FT-IR spectrometer with a DTGS detector was used for measurements in transmission mode (120 scans at 4.0 cm\textsuperscript{-1} resolution). Spectra of the empty cell under the stream of O\textsubscript{2}/He (Airgas, 15% O\textsubscript{2}) at 413 K were acquired as background for subsequent experiments. Wafer was calcined under air at 723 K (3 K min-1, 4 h hold, 100 mL min-1) and cool down to the desired temperature under O\textsubscript{2}/He. Spectra were recorded continuously during the process of posterior experiments with 5 min intervals.

For the surface poisoning, pyridine was vaporized and introduced into the gas stream with a partial pressure of 2 torr until saturating the surface of the catalyst at 413 K. The system was then purged for 30 min to remove the physisorbed pyridine and cool down to 313 K. 3-methyl-2-butanone was then vaporized into the stream at 0.15 torr to minimize IR absorbance from gas phase molecules. After reaching a steady state, the sample temperature was increased to 353 K, 413 K, and 473 K instep using a ramp rate of 3 K min\textsuperscript{-1}.

For each probe molecule co-feeding experiment, 3-methyl-2-butanol was first vaporized into the system at 453 K to mimic the packed bed reactor. After reaching a steady state, the probe molecule was then co-feed into the stream. Pyridine was vaporized with a partial pressure of 2 torr, and water was also vaporized with the partial pressure of 5, 10, 30, and 60 torr. Ammonia was co-fed with an additional flow of NH\textsubscript{3}/He (Airgas, 1% Ammonia in a He balance) to maintain partial pressure of 6.5 torr.
5.3 Results and Discussion

To probe the acid property of the 8.0 V VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3}, the temperature programmed desorption (TPD) of ammonia and pyridine were performed in separate experiments. The catalyst mass normalized desorption of ammonia and pyridine were plotted as a function of temperature (Figure 5.1). The desorption of ammonia started at 450K, featured in three distinct peaks at 479, 519, and 567K, and ended at 710K. Pyridine desorbed from the catalyst surface with similar features beginning at 465K, with three peaks at 488, 531, and 580K, and a long tail until 715K. The desorption peaks at low temperatures (479-488K) were attributed to probe molecules adsorbed from weak acid sites or physisorbed probe molecules, whereas the probe molecules associated with strong acid sites desorbed at higher temperatures.\textsuperscript{19} A slightly higher desorption temperature for pyridine compared to ammonia was also observed. This can be rationalized by the fact that the basicity of pyridine is higher than that of ammonia.\textsuperscript{20} The nitrogen in pyridine is able to donate its lone pair of electrons more easily than ammonia, resulting in the stronger adsorption of pyridine compared to ammonia. In addition, a clear gap between the quantity of desorbed ammonia and pyridine was observed. With an average pore size of 60 Å, this gap is

![Figure 5.1. Ammonia and pyridine TPD over 8.0 V VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3}.](image)
unlikely to be attributable to the diffusion difference that is induced by the difference in the molecule sizes of pyridine and ammonia. In addition to acid sites, studies of NOx reduction with ammonia and supported vanadium oxides have shown that ammonia can adsorb on supported vanadium oxides by forming N-O bonds with the lattice oxygen in the V=O vanadyl bond.21 The larger quantity of desorbed ammonia that we observed compared to that of pyridine may consequently have been attributable to the ammonia bound to vanadium oxides.

We next considered the influence of acid sites in the oxidative scission of 3-methyl-2-butanone over supported vanadium oxides. Pyridine was introduced to the system while the oxidative scission of 3-methyl-2-butanone was at steady state over an 8.0V VOx/γ-Al2O3 catalyst (Figure 5.2). Despite pyridine co-feeding and adsorption, no new chemical was observed with a carbon balance higher than 98%, indicating a negligible direct reaction between pyridine and 3-methyl-2-butanone. The production of acetic acid and acetone remained equimolar throughout the experiment, indicating that neither the alkyl fragment nor the acyl fragment reacted with the surface or gas-phase pyridine.
Before pyridine co-feeding, the oxidative scission of 3-methyl-2-butane reached the first steady state at approximately 15 hours. The oxidative scission of 3-methyl-2-butane produced an equimolar quantity of acetic acid and acetone with a steady state scission rate of 2.11 μmol s⁻¹ g⁻¹. At approximately 20 hours, 2 Torr of pyridine was mixed into the gas mixture that entered the reactor. A step change was observed immediately after the addition of pyridine. The oxidative scission rate was initially halved (0.967 μmol s⁻¹ g⁻¹) and slowly decreased to the second steady state (0.741 μmol s⁻¹ g⁻¹) with an additional 0.226 μmol s⁻¹ g⁻¹ rate loss. According to pyridine TPD result, adsorbed pyridine would not desorb from the catalyst surface below 465K; therefore, we expected that while the system was reaching the second steady state through pyridine co-feeding, all the acid sites would be bound with pyridine. Thereafter, the reactor was switched back to the reference conditions by discontinuing pyridine supply, and all the gas-phase and physiosorbed pyridine was purged from the reactor while approaching the new steady state with the reference conditions. The system reached a final steady state at 28 hours on stream with a rate of 1.61 μmol s⁻¹ g⁻¹. Compared with the first steady state, a rate loss of 0.496 μmol s⁻¹ g⁻¹ was observed in the final steady state.

The addition of pyridine into the system significantly impacted upon the rate of oxidative scission. Because most of pyridine in the system interacted with the acid sites on the catalyst surface, at least one type of acid site was involved in the oxidative scission reaction. In addition, the existence of scission products during the second steady state showed that pyridine co-feeding did not completely impede the oxidative scission of 3-methyl-2-butane. This indicates that acid sites may not be the only available sites for the oxidative scission reaction on VOₓ/γ-Al₂O₃ catalyst. Another alternative interpretation is that 3-methyl-2-butane or other reaction intermediates substitute for the weakly adsorbed pyridine and progress the oxidative scission.
During the period when pyridine was introduced into and purged from the reactor, both reversible and non-reversible declines in the oxidative scission rate of 3-methyl-2-butanone were observed. In this case, we attributed the 0.496 μmol s⁻¹ g⁻¹ non-reversible decrease to adsorbed pyridine on relatively strong acid sites that always remained on the catalyst surface. Adsorbed pyridine would occupy surface space and create repulsion to nearby adsorbents. Thus, it can sterically decrease the surface coverage of adsorbed 3-methyl-2-butanone, which affects the oxidative scission rate. These were summarized as the pyridine surface poisoning consisting of both site blocking effect and steric effect.

Counter to the non-reversible decrease, two plausible interpretations exist for the reversible impact of pyridine co-feeding. The physiosorbed pyridine through van der Waals interactions with the catalyst surface could decrease the local concentration of 3-methyl-2-butanone just a few Å above the active site and induce a decline in the surface coverage of adsorbed 3-methyl-2-butanone. Alternatively, the gas-phase pyridine could compete with 3-methyl-2-butanone in terms of adsorption onto acid sites; it forms a relatively weak bond and can be replaced by 3-methyl-2-butanone. We summarized the combination of the two possible factors as the solvent effect of pyridine.

We observed that adsorbed residues, mostly consisting of species with a carboxylate group, were formed on the catalyst surface during the oxidative scission reaction and remained on the surface until 593K in previous in situ FTIR spectra (Chapter 3 and 4). The residues that remained on the catalyst surface during pyridine poisoning analysis may have prevented the adsorption of pyridine onto acid sites and produced the limited influence of the acid site poisoning. This hypothesis was further tested using in situ transmission FTIR spectroscopy, which also provided
insights into the adsorption of pyridine, as well as the nature of acid sites and other surface species upon exposing 8.0V VO$_x$/$\gamma$-Al$_2$O$_3$ to 3-methyl-2-butanone and pyridine.

A mimic pyridine poisoning experiment was performed with the in situ transmission FTIR spectroscopy, and the steady state FTIR spectra at each labeled condition were summarized (Figure 5.3). The region between 1150 and 1850 cm$^{-1}$ was highlighted to focus our discussion upon surface carboxylate groups and the nitrogen bonds formed by the adsorption of pyridine onto Bronsted and Lewis acid sites. For the steady state of 3-methyl-2-butanone oxidative scission at 473K (red line), seven peaks were observed from the deconvolution (Figure S5.1). Five of the peaks at 1342, 1401, 1459, 1564, and 1616 cm$^{-1}$ were attributed to surface adsorbed carboxylate groups.$^{22-23}$ The three peaks at 1342, 1401, and 1459 cm$^{-1}$ were due to the symmetric O-C-O stretching, whereas the three at 1564 and 1616 cm$^{-1}$ were assigned to the asymmetric O-C-O stretching.$^{24-25}$ These peak assignments indicate at least two coordination types of surface acetate.$^{26}$ Finally, the peak at 1353 cm$^{-1}$ was assigned to the methyl group$^{27-28}$ deforming in
adsorbed acetic acid and the peak at 1656 cm\(^{-1}\) was assigned to carbonyl group adsorbed on Bronsted acid site.\(^{29}\)

Transitioning to the steady state of 3-methyl-2-butane oxidative scission with the co-feeding of pyridine (blue line), several new peaks appeared due to the adsorption of pyridine onto the catalyst surface. Within those new peaks, the one at 1450 cm\(^{-1}\) was attributed to the N-M bond which was formed through the adsorption of pyridine onto the Lewis acid site, while the one at 1540 cm\(^{-1}\) was assigned to the N-H bond that was generated from the adsorption of pyridine onto the Bronsted acid site.\(^{5,30}\) The ratio (0.586) of Bronsted to Lewis acid sites was estimated according to the Beer Lambert Law.\(^{31}\) The existence of adsorbed pyridine directly removed the aforementioned concern about insufficient acid site blocking due to the surface acetate. The co-feeding of pyridine eliminated the peaks of carbonyl groups adsorbed on Bronsted acid site (1656 cm\(^{-1}\)) and adsorbed acetate at 1342, 1401, and 1616 cm\(^{-1}\).\(^{32,33}\) The co-fed gas-phase pyridine competes with 3-methyl-2-butane for adoption onto acid sites and induces a relatively low 3-methyl-2-butane surface coverage, which, in turn, decreases the surface coverage of the reaction intermediate. Because acid sites are required for the formation of adsorbed acetate, adsorbed pyridine occupies the corresponding acid sites and prevents the formation of adsorbed acetate and acetic acid. These observations were consistent with the prior analysis of the influence of 3-methyl-2-butane oxidative scission by pyridine co-feeding in the steady state rate.

At the new steady state after discontinuing pyridine supply (green line), the decrease in the area of the peak at 1450 cm\(^{-1}\) and the increase in the intensity of peaks at 1460 and 1564 cm\(^{-1}\) reflected the same corresponding trends in the surface coverage of pyridine adsorbed on Lewis site and bidentate adsorbed acetate. These observations suggest that 3-methyl-2-butane or the
acyl fragments from the oxidative scission replaced pyridine on the Lewis site and formed more bidentate adsorbed acetate. However, no variation was observed in the peak of pyridine adsorbed on the Bronsted acid site, which suggests that the Bronsted acid site is not the sole hydrogen donor. The existence of the peaks of pyridine adsorbed on the Bronsted and Lewis acid sites suggest both of the acid sites may contribute to the non-reversible 0.496 μmol s⁻¹ g⁻¹ rate loss of the oxidative scission. In addition, instead of monodentate adsorbed acetate, we observed a new peak at 1690 cm⁻¹ which was attributed to a carbonyl group adsorbed on Lewis acid site on γ-Al₂O₃.²⁴

![Figure 5.4](image)

**Figure 5.4.** Steady state FTIR spectra exposing a pyridine titrated catalyst surface to 3-methyl-2-butanone at each labeled temperature. The red dots show the integration method for peak area estimation. Conditions: P₃-methyl-2-butanone = 0.2 Torr, P_O₂ = 130 Torr in a He balance.

We next considered the adsorption and reaction of 3-methyl-2-butanone onto a pyridine titrated catalyst surface and the steady state FTIR spectra were collected at each labeled condition (Figure 5.4). Before being exposed to 3-methyl-2-butanone, the catalyst was saturated with
pyridine and purged at 423K (black line). The adsorption of pyridine rises prominent peaks discussed above. The peak at 1450 cm\(^{-1}\) was due to pyridine adsorbed onto the Lewis acid site and the peak at 1540 cm\(^{-1}\) was attributed to the adsorbed pyridine on the Bronsted acid site.\(^5\) A Bronsted to Lewis acid site ratio of 2.796 was observed. This indicated that the calcined catalyst surface had more accessible protons than metal cations. The temperature of the system was cooled to 313K under 15% O\(_2\) in He, and the catalyst was then exposed to 0.2 Torr of 3-methyl-2-butanone at 313K (red line). Several new peaks appeared at 1690, 1570, and 1450 cm\(^{-1}\). These peaks were all previously observed when 3-methyl-2-butanone was introduced to the calcined catalyst and support. The peak at 1690 cm\(^{-1}\) was due to the 3-methyl-2-butanone adsorbed on the Lewis acid site on \(\gamma\)-Al\(_2\)O\(_3\);\(^{34}\) the peaks at 1570\(^{-1}\) and 1450 cm\(^{-1}\) were assigned to the bidentate adsorbed carboxylate group in acetate produced from the oxidative scission of 3-methyl-2-butanone.\(^{26}\) We did not observe a peak at 1353 cm\(^{-1}\), indicating no chemisorbed acetic acid on the catalyst surface. As discussed in Chapter 3, this further suggests that all the adsorbed acetate has at least one oxygen atom that is part of the catalyst lattice.

After exposing the catalyst to 3-methyl-2-butanone, the area of the peak of pyridine adsorbed on the Lewis acid site decreased from 1.67 to 1.35, whereas the peak of pyridine bound to the Bronsted acid site remained the same. This was consistent with the observation that only 3-methyl-2-butanone bound to the Lewis acid site on \(\gamma\)-Al\(_2\)O\(_3\) was observed. However, a previous study of the adsorption of 3-methyl-2-butanone on \(\gamma\)-Al\(_2\)O\(_3\) in aerobic conditions showed no obvious carboxylate groups at 313K (Figure S5.5). Accordingly, because pyridine adsorbed on the Bronsted acid site was not influenced, the observed acetate at 313K must be generated by 3-methyl-2-butanone adsorbed on the Lewis acid site. Consequently, we attribute the observed carboxylate groups to the acetate produced by the oxidative scission of 3-methyl-2-butanone.
adsorbed on the Lewis acid site \((V^{5+})\) in vanadium oxide. Above 313K, the peak at 1690 cm\(^{-1}\) diminished as the desorption of 3-methyl-2-butanone is promoted by the increase in temperature and becomes more rapid than its adsorption. The carboxylate peaks increased with the decrease in the peaks of pyridine adsorbed on both the Bronsted and Lewis acid sites. If the acetate that produced from the oxidative scission reaction adsorbed on a Bronsted acid site, a bonding would be generated between a carboxylate oxygen in acetate and the proton on the lattice oxygen. Depending on the strength of the bonding between the proton and two oxygen atoms, two coordination types of adsorbed acetic acid were observed.\(^{35}\) However, regardless of which coordination dominates the catalyst surface, a peak at 1353 cm\(^{-1}\) that represents the CH\(_3\) deformation in adsorbed acetic acid is expected. Within all the conditions in which pyridine existed on the catalyst surface, the lack of the CH\(_3\) deformation indicates that the decrease in the intensity of the peak related to the Bronsted acid site is not associated with the oxidative scission of 3-methyl-2-butanone. This may suggest that the Bronsted acid site is not participating in the oxidative scission of 3-methyl-2-butanone. To clarify the role of the Bronsted acid site, 2,6-di-tert-butylpyridine co-feeding, which only occupies Bronsted acid sites, was carried out with the oxidative scission of 3-methyl-2-butanone.

To aid in resolving the role of the Bronsted acid site in the oxidative scission of 3-methyl-2-butanone, we next examined the effects of 2,6 di-tert-butylpyridine (2,6-DTBP), which only adsorbed on the Bronsted acid site, through its co-feeding and adsorption on the catalyst surface. The trends observed during 2,6-DTBP saturation and purging were largely consistent with those observed during pyridine co-feeding and purging, hence, we were able to draw similar conclusions. The oxidative scission of 3-methyl-2-butanone reached steady state at 15 hours on
stream with a mass normalized rate of 2.19 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \). An initial 1.22 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \) rate loss was observed following the transition to 2,6-DTBP co-feeding at 19 hours on stream, and we attributed this decrease to the solvent effect of 2,6-DTBP. The 2,6-DTBP surface poisoning resulted in another 0.452 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \) decline in the rate of the oxidative scission, which recovered to 1.60 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \) after the 2,6-DTBP supply was discontinued. In this case, we observed a final 0.597 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \) non-reversible rate loss. The final rate loss by adsorbed 2,6-DTBP was slightly higher than that of the adsorbed pyridine (0.496 \( \mu \text{mol s}^{-1} \text{ g}^{-1} \)). Accordingly, this observation indicates most of the rate loss that was observed with the adsorbed pyridine was attributable to its poisoning of the Bronsted acid site. Because 2,6-DTBP has two extra tert-butyl groups, which occupy more space than pyridine when adsorbed onto the catalyst surface and result in a relatively large steric effect, we attributed the higher rate loss through the 2,6-DTBP surface poisoning to the larger steric effect through the adsorption of 2,6-DTBP. All the observations from pyridine and 2,6-DTBP co-feeding and the corresponding FTIR spectra.
suggest both Bronsted and Lewis acid sites participate in the oxidative scission of 3-methyl-2-butanoate.

**Figure 5.6.** The steady state rate of oxidative scission of 3-methyl-2-butanoate with ammonia poisoning. Reference conditions: $P_{3\text{-methyl-2-butanoate}} = 12$ Torr, $P_{O_2} = 130$ Torr, He balanced, $T = 453$K.

We next considered trends in the reactivity of the oxidative scission obtained during analogous ammonia co-feeding (Figure 5.6). In this study, the catalyst bed used in pyridine co-feeding was regenerated and a similar steady state rate ($2.13 \mu$mol s$^{-1}$ g$^{-1}$) was observed. The oxidative scission of 3-methyl-2-butanoate produced equimolar amounts of acetone and acetic acid while approaching the steady state. At 20.5 hours on stream, the helium supply was switched to an ammonia/helium blend and 6 Torr of ammonia were mixed with 130 Torr of O$_2$ and 12 Torr of 3-methyl-2-butanoate in a helium balance. Compared with the rapid half-fold initial decline observed in the case of pyridine co-feeding, extrapolating the acetone flowrate during the co-feeding of ammonia period to the starting point (20.5 hours) approached the first steady state, indicating a negligible initial rate drop and, consequently, the nonsignificant solvent effect of ammonia. However, the flowrate of the acetic acid ($0.207 \mu$mol s$^{-1}$ g$^{-1}$) was decreased by an order of magnitude and had entirely vanished at 21 hours on stream. Instead of acetic acid, an
equimolar quantity of acetonitrile was produced accompanied by acetone from the oxidative scission of 3-methyl-2-butanone. The system reached a new quasi-steady state at 27 hours on stream. Thereafter, the rate of oxidative scission continued to decrease but with an indistinct decrease rate and approached 0.274 μmol s⁻¹ g⁻¹ at the transition point back to the reference conditions. Interestingly, an initial drop in the rate of oxidative scission was observed as the system switched to the reference conditions. Discontinuing the ammonia supply almost eliminated the oxidative scission of 3-methyl-2-butanone within the reference conditions. An initial scission rate of 0.033 μmol s⁻¹ g⁻¹ was observed with equimolar amounts of acetone and acetonitrile. The production rate of acetonitrile continued to decrease and ceased at 30 hours on stream. In contrast to the transition to ammonia co-feeding where the production of acetonitrile and the disappearance of acetic acid occurred simultaneously, the production of acetic acid was not observed until 31 hours on stream. The equimolar production of acetone and acetic acid was observed at 36 hours on stream with a scission rate of 0.112 μmol s⁻¹ g⁻¹. The rate of oxidative scission then slowly recovered and reached 0.170 μmol s⁻¹ g⁻¹ at 40 hours on stream.

Ammonia co-feeding behaved completely differently to the pyridine co-feeding. The production of acetonitrile indicates that the co-fed ammonia was involved in the oxidative scission of 3-methyl-2-butanone. The absence of isopropylamine or acetone imine with an average carbon balance higher than 99% indicates that the oxidative scission was still initiated by gas phase oxygen. Indeed, it also suggests that the contact between the produced acetone and the catalyst surface is negligible, otherwise the adsorbed ammonia would react with the adsorbed acetone through an ammonia nucleophilic addition.³⁶
To aid in mechanistic insights into the production of acetic acid, we next determined the pathway from an acyl fragment to acetonitrile. According to the selective reduction of NO$_x$ to N$_2$ by ammonia in a similar system, a complete conversion to N$_2$ was not observed until 523 to 573K.$^{37}$ Consequently, we proposed that if acetonitrile is produced by the analogous reduction of adsorbed acetic acid with ammonia, we would not observe the complete conversion of acetic acid at 453K. In addition, an analysis of the impurity in the 3-methyl-2-butanone supply showed 0.4 mol. % of acetic acid, which is equivalent to a mass normalized flowrate of 0.084 µmol s$^{-1}$ g$^{-1}$ in our reactor. This quantity of acetic acid was subtracted for data analysis in this study; however, the ammonia co-feeding lowered the mass normalized flowrate of the acetic acid impurity, resulting in a flowrate of 0.033 µmol s$^{-1}$ g$^{-1}$ at 28 hours on stream. The loss in the amount of acetic acid impurity explains the slightly higher production rate of acetonitrile to acetone while approaching the new quasi-steady state. This also demonstrates the reduction ability of ammonia, which can convert acetic acid to acetonitrile. More importantly, the remaining acetic acid impurity supports our hypothesis given that the reduction of acetic acid to acetonitrile in our reactor was not 100%. Therefore, instead of a sequential reaction pathway from 3-methyl-2-butanone to the acyl fragment, adsorbed acetic acid and, finally, acetonitrile, the observed acetonitrile was directly produced by a reaction between the adsorbed ammonia and the acyl fragment. One can envisage that the adsorbed ammonia reacts with the acyl radical or acylium, further reduces the carbonyl oxygen to a water molecule and forms acetonitrile, which subsequently desorbs from the catalyst surface. The pathway of acetonitrile strengthens our previous conclusion that acetic acid and acetone are not produced simultaneously from the cleavage of a dioxetane structure that is generated by inserting a dioxygen into the C=C double bond in the enol form of 3-methyl-2-butanone.
In transitioning to the first switching point, in contrast with the dramatic impact of pyridine’s solvent effect, the solvent effect of ammonia is minor. Bearing in mind that ammonia has less basicity and a smaller size than pyridine,\textsuperscript{20} its marginal solvent effect is acknowledged. Nonetheless, the relatively weak interactions between ammonia and acid sites cannot explain the severe surface ammonia poisoning during the ammonia co-feeding period and the additional decrease, which nearly halted the oxidative scission following the transition back to the reference conditions. These observations indicate that ammonia not only reacts with acyl radical or acylium but also poisons a unique site, which contributes to the production of acetic acid. It is noteworthy that ammonia can bind to sites other than acid sites on the surface of supported vanadium oxide catalyst. In addition to acid sites, it has been proposed that ammonia adsorbs on the vanadyl group in vanadium oxide and reduces two adjacent V=O bonds to V-OH and V-O-NH$_2$.\textsuperscript{9} However, we have demonstrated that the V=O bond does not engage in the oxidative scission of 3-methyl-2-butanone under either aerobic or anaerobic conditions in Chapter 4. In addition, the V-O vibrations in V-OH and V-O-NH$_2$ were observed in FTIR spectra (Figure S5.6) with peaks at 966 and 930 cm$^{-1}$.\textsuperscript{38} These peaks disappeared quickly after switching back to the reference conditions. Thus, the poisoning of V=O should not significantly influence the oxidative scission and could not have contributed to the final non-reversible rate loss observed at 40 hours on stream.

Next, we considered the V-OH-Al bond bridge. We have previously proposed the V-O-Al bond bridge as the provider of the lattice oxygen that produces acetic acid but the 2,6-DTBP co-feeding experiment suggests that the V-OH-Al bond bridge is more likely to be the active site that produces acetic acid. Although one could argue that the incomplete decrease in the rate of the oxidative scission with 2,6-DTBP co-feeding is associated with the existence of a weak
Bronsted acid site, we suggest that there is a possible second OH donor on the catalyst surface that is not influenced by 2,6-DTBP. At the steady state of 3-methyl-2-butanone oxidative scission, we propose that there are two possible types of V-OH-Al bonds on the surface of our catalyst. The first is the Bronsted acid site and the second is formed by the adsorption of the hydrogen atom (H), which is produced from the enolization of 3-methyl-2-butanone onto the V-O-Al bond bridge. Consequently, the pyridine and 2,6-DTBP poisoning on the Bronsted acid site did not halt the oxidative scission reaction, and this suggests that ammonia poisons both types of V-OH-Al bond bridges differently from its adsorption on a Bronsted acid site. If the production of acetic acid follows the Mars van Krevelen mechanism, once it is reduced, the oxygen vacancy in V-O-Al will be re-oxidized with the gas phase dioxygen. Here, we propose that ammonia also has the ability to re-oxidize the surface vacancy that is generated by the consumption of the lattice oxygen. During the ammonia co-feeding period, in addition to the gas phase dioxygen, adsorbed ammonia oxidizes the surface vacancy on the catalyst surface and forms a V-NH-Al bond bridge. Compared with the oxygen atom, the nitrogen atom has a relatively weak electronegativity, and thus its ability to break the V-N or N-Al bonding is weaker than the corresponding oxygen atom. Thus, once the V-NH-Al is formed, it cannot participate in the oxidative scission of 3-methyl-2-butanone and produces corresponding nitrile or amide. In the conversion of furfural to 2-methylfuran, Mironenko and Vlachos demonstrated that the oxygen vacancy on a RuO₂ catalyst can be oxidized with furfuryl alcohol through a reverse Mars van Krevelen mechanism to cleave the C-O bond and generate 2-methylfuran.³⁹ This shows that the surface vacancy is not dedicated to gas phase dioxygen, and supports our hypothesis that ammonia can also oxidize a similar type of oxygen vacancy.
To summarize the observations and trends in the ammonia co-feeding experiment, ammonia binds to the surface vacancy that is generated by producing an acetic acid and oxidizes the vacancy to a V-NH-Al bond bridge, when it is first introduced to the system at steady state with the oxidative scission of 3-methyl-2-butanone. This V-NH-Al bond bridge prevents the regeneration of the active site to produce acetic acid and causes a dramatic decrease in the production of acetic acid from 20.5 to 21 hours on stream. Simultaneously, ammonia adsorbs on acid sites and on the V=O bond to generate the corresponding minor solvent effect. Thereafter, a 3-methyl-2-butanone replaces the ammonia that is adsorbed on the weak Lewis acid site. Adsorbed 3-methyl-2-butanone undergoes enolization and generates an adsorbed enolate, which, in turn, reacts with gas phase oxygen and produces acetone and an acyl fragment (e.g., acyl radical or acylium). One possible pathway for this adsorbed acyl fragment is to react with the V-NH-Al and form an acetamide (Figure 5.7a) that cannot desorb from the catalyst surface by breaking both the V-N and N-Al bond bridge through hydrogenation. This coordinate type of acetamide occupies an accessible Lewis acid site of 3-methyl-2-butanone and contributes to the surface ammonia poisoning observed from 20.5 to 27 hours on stream and the final non-reversible rate loss. Alternatively, the adsorbed acyl fragment reacts with adsorbed ammonia on either the acid sites or V=O bond to produce adsorbed acetamide (Figure 5.7b) with a coordinate type that differs from the previous one in the V-NH-M bond bridge. This acetamide is further
reduced to acetonitrile and desorbed from the surface. After transitioning back to the reference conditions, the partial pressure of ammonia decreases to zero, resulting in the disappearance of surface adsorbed accessible ammonia. Consequently, the production of acetonitrile decreases to zero and the acetamide bound to the V-NH-Al bond bridge dominates the catalyst surface, resulting in the almost dissipated oxidative scission of 3-methyl-2-butanone. Meanwhile, the adsorbed ammonia that induces the solvent effect is slowly removed from the catalyst, and the rate of oxidative scission slowly recovers from 27 to 40 hours on stream.

![Figure 5.8. Oxidative scission rates as a function of water partial pressure over 8.0V VOₓ/γ-Al₂O₃. The dot line represents steady state oxidative scission rate of 3-methyl-2-butanone with no water co-feeding. Conditions: P₃-methyl-2-butanone = 12 Torr, P_O₂ = 130 Torr, T = 453 K.](image)

The role of reducible hydroxyl groups on the catalyst surface seems to be important for the oxidative scission of 3-methyl-2-butanone. Many research teams have demonstrated that the hydration of support vanadium oxide breaks a V-O-M bond bridge and forms a V-OH and M-OH bond pair.¹¹,⁴⁰ Next, we discuss the impact of water co-feeding, or hydration of the catalyst surface, on the reactivity of the oxidative scission reaction.
The oxidative scission rates of 3-methyl-2-butane were examined as a function of water partial pressure and presented on logarithmic axes (Figure 5.8). Before the water was introduced into the reactor, the oxidative scission of 3-methyl-2-butane was allowed to reach a steady state, maintaining a rate of 2.17 μmol s⁻¹ g⁻¹. The rate of oxidative scission increased with water partial pressure; however, the rates at high water partial pressure levels were excessive, resulting in high conversions (>10%) that made the reactor non-differential. Therefore, we do not attempt to discuss the kinetics of the water co-feeding system. We noticed that the addition of 5 Torr of water into the packed bed reactor only increased the oxidative scission rate to 2.34 μmol s⁻¹ g⁻¹.

In contrast, subsequent increases in water partial pressure caused a significant increase in oxidative scission rates. This observation suggests that there is a water partial pressure threshold for effective promotion of oxidative scission.

Figure 5.9. Steady state FTIR spectra of oxidative scission of 3-methyl-2-butane with water co-feeding. The dot line separates the figure into two parts: the right side is not normalized; the left side is normalized according to absorbance at 1200 and 1800 cm⁻¹. Conditions: P3-methyl-2-butane = 0.2 Torr, P02 = 120 Torr, He balanced; T = 453K. R.C. reference conditions
We next considered the in situ FTIR spectra obtained during the mimic water co-feeding experiment, with the aim of examining the influence of water co-feeding on the nature of the catalyst surface and the corresponding adsorbents (Figure 5.9). The FTIR spectra in the 1200 to 1800 cm\(^{-1}\) range were normalized, whereas the original spectra in the 800 to 1200 cm\(^{-1}\) wavenumber range were presented for quantitative analysis. The spectrum observed under reference conditions is identical to the spectrum obtained in the pyridine co-feeding experiment. Furthermore, a peak at 1015 cm\(^{-1}\) was assigned to the V=O vanadyl bond in dispersed vanadium oxides.\(^{41}\) This peak was not impacted by variations in water partial pressure in the system. This observation is consistent with previous studies in which the V-O-M bond bridge is solely hydrated to V-OH and M-OH bonds. In contrast with the V=O peak at 1015 cm\(^{-1}\), the peaks at 1353, 1401, and 1616 cm\(^{-1}\) were erased, and the addition of water decreased the intensity of the peaks at 1459 and 1564 cm\(^{-1}\). These occurrences indicate the absence of monodentate adsorbed acetate and a decrease in the surface coverage of bidentate adsorbed acetate on the hydrated catalyst surface.\(^{26}\)

It is noteworthy that the addition of 5 Torr of water did not significantly affect the rate of oxidative scission in the packed bed reactor; however, a clear shift was observed in the corresponding FTIR spectrum. We attribute this observation to the systematic difference between the packed bed reactor and the in situ reactor in the transmissive FTIR spectroscopy. In the in situ reactor, the catalyst powder was pressed into a pellet that fits into the sample holder, resulting in a dramatic decrease in the macroporous catalyst's surface area. The decrease in the surface area of the catalyst pellet, together with an insignificant level of 3-methyl-2-butanone partial pressure, resulted in a relatively small quantity of adsorbed acetate, which can be removed relatively easily, as compared with removal from a packed bed reactor. A further increase in
water partial pressure to 10 Torr and above did not significantly reduce the intensity of carboxylate peaks (1459 and 1564 cm\(^{-1}\)) in the in situ reactor; however, the corresponding increase in a packed bed reactor significantly intensified the rate of oxidative scission, suggesting that the role of water is not constrained to surface cleaning, which produces new accessible sites.

Due to the acid-base characteristics of VO\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\), the adsorption of water dissociates the water molecule into a proton and a hydroxide. The proton then reacts with the V-O-M bond bridge, generating active sites that produce adsorbed acetic acid. The oxygen ion in hydroxide is more electronegative than the oxygen, which bound to a Lewis acid site, in adsorbed acetic acid. Therefore, the hydroxide substitutes the monodentate adsorbed acetic acid through nucleophilic substitution, forming a gas phase acetic acid and an accessible hydroxyl group, which can further react with an acyl fragment produced via oxidative scission of 3-methyl-2-butanone. As discussed above, the addition of water can directly upgrade the V-O-M bond bridge to a pair of M-OH and V-OH bonds,\(^{40}\) increasing the quantity of V-OH bonds that participate in the production of adsorbed acetic acid. Consequently, the addition of water not only promotes the desorption of adsorbed acetic acid, or acetate, but also increases the surface coverage of available hydroxyl for the reduction of the acyl fragment.
1) Adsorption of 3-methyl-2-butanone on Lewis acid sites in VO₅(Al)

2) Enolization of adsorbed 3-methyl-2-butanone

3) Oxidation of enolate to an adsorbed 3-methyl-2-butanone radical

4) Addition of gas phase dioxygen

5) Homolytic O-O scission

6) Production of acetone.

7) Reduction of acyl radical to bidentate adsorbed acetate

8) Combustion of bidentate adsorbed acetate

9) Protonation of bidentate adsorbed acetate
In light of the mechanistic insights described above, a plausible sequence of elementary steps for 3-methyl-2-butanone oxidative scission over VO₅/γ-Al₂O₃ is presented (Scheme 5.1). We have demonstrated that the V=O bond does not participate in the oxidative scission reaction in Chapter 4, so it is not involved in any of the following steps. The gas phase 3-methyl-2-butanone adsorbs onto the Lewis acid site (V⁵⁺) of the supported vanadium oxide. It forms an enolate by reducing the vanadium cation to V⁴⁺ and donating a hydrogen atom to the nearby oxygen.⁴² The enolate oxidizes the vanadium cation back to V⁵⁺ and generates a 3-methyl-2-butanone radical centered at the internal α-carbon (C₃) of the carbonyl group.⁴ This radical is attacked by gas phase dioxygen, forming a peroxide structure (Scheme 5.1, Step 4).⁴³⁴⁴ The presence of acetonitrile, which is produced by the reaction between adsorbed ammonia and the acyl fragment of 3-methyl-2-butanone, disproves the hypothesis that a dioxetane intermediate is generated during the oxidative scission and it cleaves into acetic acid and acetone. We derived this idea from the
mechanism of homogenous ketone scission, by which the O-O bond in peroxide breaks via homolytic scission and forms an oxygen radical.\textsuperscript{43,45} Instead of abstracting a hydrogen atom to produce a hydroxyl group, the oxygen radical spontaneously triggers oxidative scission and produces a gas phase acetone with an adsorbed acyl radical. Compared to the V-OH-M bond bridge, the V-O-M bond bridge is more nucleophilic; hence, it is more likely to attack the acyl radical. Because vanadium is more electronegative than alumina (Pauling scale), the relatively weak O-Al bond breaks and forms a bidentate chelating or bridging adsorbed acetate on the vanadium cation. These adsorbed acetates can be burnt to combustion products or be protonated to monodentate adsorbed acetic acid. Alternatively, the hydroxyl in the V-OH-Al bond bridge attacks the acyl radical and forms a bidentate chelating adsorbed acetic acid. Unlike the bidentate adsorbed acetate, the bidentate adsorbed acetic acid desorbs the surface by sequentially breaking two V-O bonds and leaves a vacancy in the supported vanadium oxides. As observed in the ammonia co-feeding experiment, this vacancy can be oxidized either by gas phase dioxygen or by ammonia through the Mars van Krevelen mechanism. Once oxidized by ammonia, the V-NH-Al bond bridge reacts with the acyl radical. It forms an acetamide which cannot desorb the catalyst surface and discontinues the oxidative scission of 3-methyl-2-butanone by poisoning its active site.

The temperature programmed surface reaction experiments with 3-methyl-2-butanone in Chapter 4 have demonstrated that the temperature associated with lattice oxygen reduction through the Mars van Krevelen mechanism is higher than the temperature associated with the utilization of a gas phase dioxygen via the Eley-Rideal mechanism. The mechanism depicted in Scheme 5.1 consists of both Eley-Rideal and Mars van Krevelen mechanisms, suggesting that the lattice oxygen reduction controls the rate of oxidative scission. In traditional Mars van Krevelen
oxidation, the lattice is reduced by breaking the M-O bond. The proposed mechanism for oxidative scission involves two V-O scissions, which consecutively break the V-OH and V-O bonds in the bidentate chelating adsorbed acetic acid. If the cleavage of the V-OH bond is the rate determining step for the oxidative scission, then a secondary kinetics isotope effect is expected during the transformation from V-OH to V-OD. To understand the kinetic significance of the V-OH or V-O scission, we next compared the rates of oxidative scission for 2-butane and perdeuterated 2-butane (Figure 5.10). An evident decrease was observed following the transition to a deuterated catalyst surface; the oxidative scission rate associated with 2-butane was 1.14 times the rate associated with deuterated 2-butane. This secondary kinetics isotope effect clearly indicates that the rate-determining step involves atoms that are adjacent to a hydrogen or deuterium atom, suggesting that the V-OH scission (Scheme 5.1, Step 10) that produces a monodentate adsorbed acetic acid is the rate determine step for the oxidative scission of methyl ketones.
5.4 Conclusion

The function of different surface sites during oxidative scission of ketone on supported vanadium oxide was investigated thoroughly by employing pyridine, water, ammonia, and 2,6-DTBP cofeeding and pyridine poisoning experiments. Pyridine cofeeding and poisoning experiment revealed that ketone and its carbonyl fragments produced from scission bond to Lewis acid sites, and Bronsted acid sites are not the sole proton/hydrogen source for the production of acetic acid. 2,6-DTBP cofeeding insinuated that Bronsted acid site is involved in the oxidative scission and strong acid sites restrained the desorption of acetic acid, which does not contribute to oxidative scission at the steady state. The presence of ammonia drives the reaction into an alternate route with the production of acetone and acetonitrile. The transition from the ammonia co-feeding back to reference conditions nearly vanished the oxidative scission rate, suggesting that ammonia is capable of poisoning vacancy sites generated from the consumption of lattice hydroxyl in the V-OH-M bond bridge and forming the V-NH-M bond bridge. Reversible adsorption of ammonia on vanadyl structure was antithetical to the irreversible reaction rate drop from the addition of ammonia, suggests that vanadyl bond does not participate in the reaction. Water can drastically promote the reaction rate by dissociation into proton and hydroxide, which generates extra sites characterized as accessible hydrogen sources and facilitates the desorption of acetic acid. In contrast, bidentate adsorbed acetate was not cleaned by water, reinforced the fact that carboxylate bound on strong acid sites can only desorb through combustion. A kinetic isotopic effect experiment using perdeuterated 2-butanone yielded a secondary kinetics isotope effect, which manifests V-OH scission as rate determining step. We eventually have successfully developed a set of comprehensive elementary steps for the oxidative session of ketone on supported vanadium oxide.
5.5 Supporting Information

In Figure S5.1, the steady state FTIR spectrum of 3-methyl-2-butanone oxidative scission were empirically deconvoluted into seven Gaussian peaks at 1342, 1353, 1401, 1459, 1564, 1616, and 1656 cm\(^{-1}\).

Figure S5.1. Peak deconvolution of steady state FTIR spectra of 3-methyl-2-butanone oxidative scission. The FTIR spectrum of catalyst was subtracted. Conditions: \(P_{\text{pyridine}} = 2\) Torr (when co-feeding), \(P_{3\text{-methyl-2-butanone}} = 0.2\) Torr, \(P_{O_2} = 130\) Torr, He balanced, \(T = 453\) K.

Figure S5.2. Steady state FTIR spectra of oxidative scission of 3-methyl-2-butanone with pyridine poisoning. Conditions: \(P_{\text{pyridine}} = 2\) Torr (when co-feeding), \(P_{3\text{-methyl-2-butanone}} = 0.2\) Torr, \(P_{O_2} = 130\) Torr, He balanced. Full size version.
Figure S5.3. Steady state FTIR spectra exposing a pyridine titrated catalyst surface to 3-methyl-2-butanone at each labeled temperature. Conditions: P3-methyl-2-butanone = 0.2 Torr, PO2 = 130 Torr, He balanced. Full size version.

Figure S5.4. Steady state FTIR spectra of oxidative scission of 3-methyl-2-butanone with water co-feeding. Conditions: P3-methyl-2-butanone = 0.2 Torr, PO2 = 130 Torr, He balanced; T = 453K. R.C. stands for reference conditions. Full size version.
**Figure S5.5.** FTIR spectra of 3-methyl-2-butanone adsorbed onto γ-Al2O3 support. Conditions: \( P_{3\text{-methyl-2-butanone}} = 0.2 \text{ Torr}, P_{\text{O}_2} = 130 \text{ Torr} \) in a He balance, \( T=313 \text{K} \).

**Figure S5.6.** FTIR spectra of oxidative scission of 3-methyl-2-butanone with ammonia poisoning. The bottom dark spectrum shows the steady state of 3-methyl-2-butanone oxidative scission prior to ammonia co-feeding, the top dark spectrum shows the steady state of 3-methyl-2-butanone oxidative scission after ammonia supply is discontinued. The peaks at 966 and 930 cm\(^{-1}\) appeared and increased during ammonia co-feeding. However, they all disappeared after gas phase ammonia was purged from the reactor. Conditions: \( P_{\text{ammonia}} = 6 \text{ Torr} \) (when co-feeding), \( P_{3\text{-methyl-2-butanone}} = 0.2 \text{ Torr}, P_{\text{O}_2} = 130 \text{ Torr} \), He balanced.
5.6 References


CHAPTER 6

Future Works
6.1 Microkinetic analysis

With the elementary steps established in Chapter 5, it is pertinent to use this kinetic framework as a reference point to derive a rate expression for the oxidative scission of 3-methyl-2-butanone over supported vanadium oxide. All the information discussed in Chapters 4 and 5 provides a rigorous chemical foundation for a detailed microkinetic analysis. With the regressed elementary interaction energies and kinetic parameters, the analysis of the microkinetics of the oxidative scission is able to provide a fundamental description of the reactivity in the supported vanadium oxide catalyzed oxidative scission of methyl ketones. This is particularly applicable to the target reaction of this project, the oxidative scission of levulinic acid (LA) to maleic anhydride (MA). Compared with the oxidative scission of 3-methyl-2-butanone, the production of MA is most likely to be carried out in a similar system if it is to be commercialized. Therefore, a fundamental understanding of the kinetics and thermodynamics of the oxidative scission over supported vanadium oxide is significant for the additional upgrading of the catalyst performance. To accomplish this, macrokinetic data, including the apparent reaction order of oxygen, ketones, and aldehyde, and reaction barriers were collected (Table 6.1). The uncertainties represent a 95% confidence interval.
Table 6.1 Macrokinetics data for the methyl ketones oxidative scission over supported vanadium oxide. Conditions if not listed as a variable: \( P_{\text{hydrocarbons}} = 12 \) Torr, \( P_{\text{O}_2} = 130 \) Torr, in a He balance, \( T = 466 \)K.

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<th>Oxygen Order</th>
<th>Reactant Order</th>
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<td>0.60 ± 0.03</td>
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</table>

*: \( \gamma \)-Al2O3 (Strem, 95%); **: \( \gamma \)-Al2O3 (Advanced Materials, 97%)

* T= 453K for the order study of 3-methyl-2-butane.
6.2 Steady-state isotopic transient kinetic analysis (SSITKA)

In Chapter 4, we demonstrated that a weak Lewis acid site, a weak Bronsted acid site, and a hydrogen atom bound to lattice oxygen participate in the oxidative scission of 3-methyl-2-butanone over supported vanadium oxide catalysts. The combination of different active sites makes the normalization of the rate, which estimates the intrinsic reactivity of the catalyst, extremely difficult. Consequently, it is challenging to rigorously compare the reactivity of catalysts with different structures and to analyze the corresponding structure-function relationship. In addition, the quantification of the accessible active sites associated with the catalyst at a steady state of a reaction is difficult. As a result of deactivation, the surface of the catalyst at the steady state of a reaction is unnecessarily equivalent to the fresh catalyst that is mostly used to quantify the active sites. The SSITKA experiment is the essential method to estimate the intrinsic reactivity, or turnover frequency (TOF), of the catalyst without the quantities of the corresponding active sites.\textsuperscript{2-3} In fact, the observed TOF, together with the catalyst mass normalized rate, can be used to estimate the quantity of active sites at the steady state of a reaction.\textsuperscript{2}

The design for an SSITKA reactor setup is shown in Figure 6.1. The upper part of the reactor includes two controlled flow systems, in which a set of a syringe and a pump controls the influent liquid phase chemical and the mass flow controller controls the influent gas. A 4-port valve is employed to smooth and shorten the transition period between the two flow systems. The two back-pressure regulators are used to minimize any perturbations while switching the 4-port valve.\textsuperscript{4} The two 2-way valves create a bypass to the reactor. In addition, we can pressurize the reactor by switching the bottom
2-way valve to the bypass and the top 2-way valve to the inlet of the reactor. The 34-port valve collects the effluent from the reactor, and the samples in the 34-port valve are analyzed by the online gas chromatography (GC). Depending upon the interactions between the chemicals involved in the reaction and the stationary phase in the GC column, the analysis of one injection with gas chromatography can take up to 20 mins. This limits the number of data points observed in a short time. With the 34-port valve, we have the flexibility to store 16 samples of the effluent at any desired time on stream. The employed reduced gas analyzer (RGA) traces mass to charge ratios as a mass spectrometry rather than separating chemicals from each other. Thus, it cannot distinguish chemicals that have similar major mass to charge ratios, such as acetaldehyde and acetic acid. In conjunction with its relatively poor detection limitation, the RGA is
only employed to provide a rough online reference of the reactor and helps to determine when to store a sample for GC analysis.

For a transient kinetic experiment, the reaction is initially allowed to reach a steady state (System 1). An inert chemical tracer, which has negligible surface residence time on the catalyst, is fed into System 1 to correct for the gas phase holdup in the reactor. Then the reactor is switched to a new flow system (System 2), which has the same settings as System 1 but a different reactant. The reactant in System 2 must have a nearly identical structure and reactivity to the reactant in System 1 to maintain the similar kinetic and thermodynamic features of the system during the transition from the steady state of System 1 to the new steady state of System 2. The corresponding transient response of the system is observed after System 2 reaches the new steady state.

![Figure 6.2](image)  
**Figure 6.2.** A sketch of SSITKA figure. Product 1 is produced from the first flow system, and product 2 is produced from the second flow system.

A typical normalized transient response profile is shown in Figure 6.2. Kinetic parameters can be estimated from the normalized transient response signal (RS). The area between the response of Product 1 and the inert chemical is the mean surface residence time \( \tau_1 \) (Equation 6.1) of Product 1. The inverse of the mean surface residence time is the
turnover frequency (Equation 6.2) associated with Product 1 in the corresponding conditions, and the surface coverage of accessible active sites ($\theta_a$, Equation 6.3) is estimated by the product of the catalyst mass normalized rate ($R_1$) and TOF. In Equation 6.1, $t_i$ stands for the time on stream of the transition point.

$$\tau_i = \int_{t_i}^{\infty} (RS_i - RS_i) dt$$

(6.1)

$$\text{TOF} = \tau_i^{-1}$$

(6.2)

$$\theta_a = R_1 \cdot \tau_i$$

(6.3)

With this technique, we can directly measure the intrinsic reactivity of the supported vanadium oxide catalyst with different surface vanadium oxide structures to analyze the structure-function relationship between vanadium oxide speciation and the oxidative scission of methyl ketones. In Chapter 3, we demonstrated that the influence of the main carbon chain length upon the rate of the oxidative scission of methyl ketones is negligible above the five-carbon chain. Consequently, we can use symmetric ketones, such as 3-pentanone and 4-heptanone, as the reactants for the transient kinetic experiment. The symmetric ketone has two identical scission pathways that produce a pair of aldehyde and carboxylic acid. This reduces the complexity of the product analysis compared with an asymmetric ketone, which produces two pairs of scission products. The flame ionizer detector installed in the GC cannot distinguish Ar from the reactor effluent; thus, we need to select a hydrocarbon as the inert tracer for our system. A light alkane or alkene, such as methane or ethylene, would be a good choice.
6.3 References


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