Pathways, mechanisms, and kinetics of propylene oxidation on reducible metal oxide catalysts

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Abstract

We report the pathways, mechanism, and kinetics for the formation of side products during propylene oxidation to acrolein on two metal oxide catalysts: Bi$_2$Mo$_3$O$_{12}$ and a molybdenum-based mixed metal oxide doped with nickel and cobalt. This work showcases the utility of combining kinetic measurements, product rank and stability analysis, co-feed experiments, isotopic tracer studies, and kinetic modeling in the investigation of complex reaction networks during oxidation reactions on reducible metal oxide formulations.

The trends of the yields of all C$_1$ – C$_3$ products of propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K as a function of conversion show that acrolein, acetaldehyde, acetone, and acetic acid are direct oxidation products of propylene while acrylic acid and ethylene are secondary products. Co-processing acetaldehyde, acetone, acrylic acid, and acetic acid, separately, with propylene, oxygen, and water revealed (i) the existence of over-oxidation reactions of acrolein to acrylic acid and ethylene and oxidation pathways from acetone to acetaldehyde and acetic acid, (ii) the promotional effects of water on the synthesis rates of acetaldehyde from acrolein, acetone from propylene, acetic acid from acetaldehyde and acrylic acid, and (iii) the inhibitory effects of water on the decomposition of acetic acid to CO$_x$ and acrylic acid to acetaldehyde and ethylene.

We employ isotopic tracer experiments with allyl alcohol$_{^13}$C$_3$ and acrylic acid$_{^13}$C$_3$ to show that the carbon backbone of propylene is preserved in the sequential oxidation of propylene to allyl alcohol, acrolein, and acrylic acid during propylene oxidation at 623 K on a molybdenum-based mixed metal oxide catalyst promoted with cobalt and nickel used in the commercial production of acrolein. Transient kinetic measurements in conjunction
with co-feed experiments of C\textsubscript{2} and C\textsubscript{3} aldehydes and carboxylic acids show that
decarbonylation and decarboxylation reactions, reactions of organic compounds with
surface-adsorbed oxygen species, and total combustion reactions are the three mechanisms
for C-C bond cleavage. C-C bond formation reactions that result in C\textsubscript{4} – C\textsubscript{6} byproducts
occur via: (i) the addition reaction of a propylene-derived surface allyl (C\textsubscript{3}H\textsubscript{5}) species with
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products, or (ii) the addition reaction of an acrolein (acrylic acid)-derived surface ethenyl
(C\textsubscript{2}H\textsubscript{3}) intermediate with propylene to form pentadiene and with acrolein to form C\textsubscript{5} cyclic
oxygenates.

We develop a kinetic model to quantitatively capture the kinetic behavior of all C\textsubscript{1}-
C\textsubscript{3} products during propylene oxidation on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} using pseudo-first-order rate
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rates affected by water. We expand this model to include all C\textsubscript{1} – C\textsubscript{6} byproducts and surface
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containing intermediates in propylene oxidation to acrolein at 623 K on a molybdenum-
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The molecular level understanding of the mechanistic pathways and intrinsic active sites for byproduct formation during the partial oxidation of propylene will provide a fundamental assessment of catalysts for industrial acrolein production and guide future development of metal oxide catalysts.
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Chapter 1. Introduction

1.1. Motivation

The selective partial oxidation of hydrocarbons plays an essential role in the upgrading of oil- and natural gas-based platform chemicals to oxygenate-based bulk chemicals (Table 1.1). It is estimated that selective oxidation processes contribute, directly and indirectly, up to 60% of bulk chemicals and intermediates with a total global market up to $40 billion [1]. Even though many oxidation reactions in industrial processes can achieve single-pass conversion and selectivity exceeding 90% (Table 1.1), due to the high volume of production a one, or less, point percentage increase in the yield of the desired product can result in significant increases in profit.

Table 1.1. Catalytic oxidation processes for the manufacturing of bulk chemicals

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Conversion</th>
<th>Selectivity</th>
<th>Catalyst/Promoters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1,2-Dichloroethane</td>
<td>&gt;99 % [5]</td>
<td>98 % [5]</td>
<td>Cu-Al-O/Mg</td>
</tr>
<tr>
<td>Propylene</td>
<td>Acetonitrile</td>
<td>99 % [8]</td>
<td>82 % [8]</td>
<td>Mo-V-O/Bi, Ce, W, K, Ti, Cr</td>
</tr>
<tr>
<td>Butane</td>
<td>Maleic anhydride</td>
<td>86 % [9]</td>
<td>66 % [9]</td>
<td>V-P-O/Mo, Zn, Mg, Sc, Cr</td>
</tr>
</tbody>
</table>
Given the high single-pass conversion and selectivity of existing oxidation processes, the formation of byproducts becomes the limiting factor in increasing the yield of the desired compound. Furthermore, the side products, even at ppm level concentrations, adversely affect the production and downstream processing of the target compound. As an example, the partial oxidation of propylene to acrolein on multicomponent molybdenum-based oxide catalysts generates C$_2$ and C$_3$ acidic components as side products which can initiate irregular polymerization of acrolein and its downstream product acrylic acid [14,15]. The C$_{4+}$ side products in the same process cause fouling in the reactor system and deactivate the catalyst [16]. The systematic study of (i) the pathways constituting the overall reactions that leads to the formation of the byproducts, (ii) the reaction mechanisms comprising of elementary-step transformations from the reactants to the products in these pathways and the identity of the intermediates, and (iii) the kinetics of these pathways involving the functional forms and the estimated kinetic parameters of the rate expressions that describe the evolution of the product spectrum as the reaction progresses becomes a promising, albeit under-utilized, approach in improving the production of oxygenate chemicals.

The complexity of the structure and functionality of the heterogeneous catalysts employed in partial oxidation reactions represents the first major challenge in the study of byproduct formation in this chemistry. Most partial oxidation processes listed in Table 1.1 take place over reducible metal oxide catalysts with gas-phase oxygen as the oxidant. Mixed metal oxide catalyst formulations employed in industrial practice comprise almost without exception multiple metal components, e.g., the molybdenum-based formulations for the oxidation of propylene to acrolein are often promoted simultaneously with bismuth,
nickel, cobalt, iron, and alkaline, together with trace amounts of tin, zinc, tungsten, chromium, manganese, magnesium, antimony and titanium \[16–20\]. The number of mixed metal phases increases rapidly with the number of metal components; introducing Fe into the Bi-Mo oxide system for the partial oxidation of propylene to acrolein results in the formation of single phases Fe$_2$O$_3$ and Fe$_3$O$_4$, binary phases Fe$_2$(MoO$_4$)$_3$, FeMoO$_4$, and BiFeO$_3$, and tertiary phases BiFeMoO$_6$ and Bi$_3$(FeO$_4$)(MoO$_4$)$_2$ \[21,22\]. A multitude of catalytic centers – lattice oxygen, vacancy sites, surface hydroxyl groups, and low coordinated metal centers – which can participate in formation of side products during oxidation reactions are proposed to exist on the surface of reducible metal oxides; a detailed discussion on the types of oxygen species on reducible metal oxide is presented in section 1.3. Oxygen species on the surface of reducible metal oxides. Furthermore, atomic force microscopy revealed the large-scale reconstruction of MoO$_3$ (010) surface under hydrogen or methanol atmosphere resulting from crystallographic shear plane formation caused by a high coverage of vacancy site \[23,24\], illustrating the ability of reducible metal oxides to reconstruct under reaction conditions that exposes different undercoordinated metal sites and changes the adsorption properties of the surface.

The complexity of the reaction pathways and the chemistry involved present another challenge for the systematic study of byproduct formation during oxidation of organic compounds on metal oxide surfaces. As an example, during the partial oxidation of propylene to acrolein on a multicomponent molybdenum-based metal oxide catalyst, over 30 products were observed with carbon numbers ranging from one to seven, demonstrating the existence of pathways that directly contract or elongate the carbon backbone of the reactant \[25\]. These pathways are in sharp contrast to the desired pathways
in Table 1.1 most of which retain the carbon backbone of the reactant. Furthermore, a variety of functional groups appear in the product spectrum of propylene oxidation to acrolein: hydrocarbon (ethylene), alcohol (allyl alcohol), aldehyde (acetaldehyde), carboxylic acid (acetic acid), aliphatic (ethane), aromatic (benzene) [25], demonstrating the participation of a wide range of chemistry on the catalyst surface with different chemo- (allyl alcohol, acrolein, acrylic acid) and regio- (propanal, acetone) selectivity.

Given the multiple layers of complexity in the study of oxidation reactions of organic compounds on reducible metal oxide surfaces, we endeavor in this work to (i) present experimental methods that have proven effective for assessing pathways and mechanisms in complex reaction network, (ii) demonstrate the recurring pathways and mechanisms for the transformation of organic functional groups and the formation and cleavage of C-C bonds on reducible metal oxide catalysts, and (iii) describe the functional form for the synthesis rate and identify major formation pathways of side product via construction of kinetic models. We employ the oxidation of propylene to acrolein on molybdenum-based catalysts as a case study to showcase the application of our methods. The rest of chapter 1 provides two short surveys on (i) the types of experimental tools employed in this work including analysis of product rank and stability, co-feed experiments of products and probe molecules, and isotopic tracer experiments, and (ii) the type of active sites demonstrated on reducible metal oxide surfaces which we envision to participate directly in the formation pathways of byproducts including lattice oxygen, vacancy sites, and surface hydroxyl groups. Chapter 2 examines the reaction pathways for the formation of C3 and smaller products during propylene oxidation on Bi2Mo3O12 formulation utilizing analysis of product rank and stability and co-feed experiments of products and probe
molecules. Chapter 3 presents our study of propylene oxidation on a multicomponent molybdenum-based metal oxide formulation employed in the industrial manufacturing of acrolein, expands the network in chapter 2 to include C₄ – C₆ products, and identifies the mechanisms for the formation and cleavage of C-C bonds in this system via isotopic tracer experiments. Chapter 4 codifies the qualitative information in the previous two chapters into numerical kinetic parameters and quantitative mechanistic descriptors via the developments of two kinetic models with rate expressions derived from both pseudo-first-order rate law and the reaction mechanisms. Chapter 5 showcases the utility of our method in a different system: the hydrogenation of butanal to butanol on a supported Cu/ZnO formulation.

1.2. Useful experimental tools to understand complex reaction network and mechanism

The oxidation of organic compounds on reducible metal oxides often results in a large number of products, albeit at low selectivities, with different carbon chain length (products containing one to seven carbons were observed during propylene oxidation on a multicomponent bismuth-molybdenum-based oxide catalyst [25]) and a wide range of functional groups including but not limited to hydrocarbons, alcohols, aldehydes, carboxylic acids, aliphatic, aromatic compounds. The formation of these products follows a wide range of reaction mechanisms on a multitude of active sites, as discussed in depth in the next chapters. Given the multiple layers of complexity, the study of pathways, mechanisms, and kinetics of reactions in this chemistry requires a systematic approach with appropriate tools. We have identified three experimental techniques as useful for
explicating the pathways in the reaction networks and aspects of specific mechanisms. The first technique, the product rank and stability analysis, requires yields of the products to be analyzed at a variety of reactant conversions, while the other two techniques, product co-feed experiments with products and probe molecules, and isotope labeling experiments, involve co-processing additional species with the reaction mixture.

The product rank and stability analysis, initially proposed by Wojciechowski and coworkers [26,27], is a powerful tool for establishing the involvement and sequence of pathways in series-parallel reaction networks. In this technique, the initial value and trend of the selectivity of a product as a function of the conversion of the organic reactant reveal the rank and stability of that product in the reaction network, respectively. Kube et al. [28] observed a decreasing selectivity of ethylene from an initial non-zero value as a function of ethane conversion during ethane oxidation on three formulations: MoVTeNb oxide, vanadium oxide supported on meso-structured silica, and vanadium-free carbon nanotubes, thus identifying ethylene as a primary unstable product which is formed directly from ethane and is consumed to form other products as the reaction progresses. Utilizing the same method, the authors identified acetic acid as a primary and secondary unstable product, and CO and CO$_2$ as primary and secondary stable products and constructed the reaction network for ethane oxidation on all three formulations. The selectivity plots further reveal propylene as a primary unstable product, acrylic acid and acetic acid as secondary unstable products, and CO and CO$_2$ as secondary stable products, allowing the authors to propose the same reaction network for propane oxidation on these three formulations.

Co-feed experiments in which a product is co-processed with the reactants at concentrations comparable to the observed level in the normal conditions evince the
stability and consumption pathways of that product under reaction conditions. In their study of catalytic partial oxidation of ethane to acetic acid over Mo1V0.25Nb0.12Pd0.0005Ox, Linke et al. [29] observed that co-processing 300 kPa acetic acid to a feed comprising of 600 kPa ethane and 120 kPa oxygen increased the selectivity of CO2 from 20% to 28% at 3% ethane conversion, demonstrating the conversion of acetic acid to CO2. The same co-feed experiment also revealed the formation pathways of methanol, acetone, and ethyl acetate from acetic acid, as well as the insensitivity of acetaldehyde formation rate and ethane consumption rate on the co-fed acetic acid. Further co-feed experiments with ethylene and water revealed the oxidation of ethylene to acetic acid and a water-promoted pathway for the direct oxidation of ethane to acetic acid. Naumann d'Alnoncourt et al. [30] studied propane oxidation to acrylic acid on MoVTeNb oxide catalysts and observed the formation of propylene at ~90% selectivity at propane conversions below 3%; propylene selectivity decreased with increasing propane conversions. Co-processing propylene to the feed comprising of propane, oxygen, and water increased acrylic acid formation rate exclusively without lowering the propane consumption rate, reinforcing the proposal of consecutive oxidation of propane to propylene and eventually acrylic acid.

Isotopic tracer experiments elicit mechanisms of pathways in the reaction networks with the identity of intermediates involved. Miller et al. [31] studied acrolein oxidation to acrylic acid on a multicomponent vanadium-molybdenum-based catalyst and co-processed acrylic acid-13C3 with a feed initially comprising of acrolein, oxygen, and water in a recirculating batch reactor. The authors observed the formation of only unlabeled (13C0) and fully labeled (13C2) isotopologues of ethylene, acetaldehyde, and acetic acid with comparable fractions of 13C2 labels, suggesting that these products were formed from a
common C$_2$ intermediate. Since the distributions of all three C$_2$ products extrapolated to zero acrolein conversion contained an unlabeled $^{13}$C$_0$ isotopologue, the common C$_2$ intermediate originates from both acrolein and acrylic acid. The authors also observed the isotopologue distributions of $^{13}$C$_2$-labeled C$_5$ products furfural, 3-furaldehyde, 4-cyclopentene-1,3-dione, and 3-cyclopentene-1,2-dione at near or above 10% in the same co-feed experiments with acrylic acid-$^{13}$C$_3$, demonstrating the participation of the C$_2$ intermediate in the formation of C$_5$ products, presumably via additional reactions with a C$_3$ compound in the system. Kube et al. [32] studied the oxidation of propane on vanadium-based oxide catalysts and performed oxidation of $^{13}$C-2-propane. The authors observed the value of 0.66 for the ratio $^{12}$CO$_2$/($^{12}$CO+$^{12}$CO$_2$) during $^{13}$C-2-propane oxidation on MoVTeNb oxide catalyst, indicating preferred oxidation of the methyl carbon in propane to CO$_2$ on MoVTeNb oxide. On silica-supported vanadium oxide, the authors observed the value of 0.63 for the ratio of $^{12}$CO/($^{12}$CO+$^{12}$CO$_2$), indicating a preferred formation of CO from the methyl carbon of propane. These data support the proposition that on MoVTeNb oxide propane undergoes sequential oxidation to acrolein and then acrylic acid which decomposes via decarboxylation to form CO$_2$, while on silica-supported vanadium oxide decarbonylation of acrolein to form CO is preferred over oxidation to acrylic acid.

The employment of a recirculating batch reactor offers many advantages in the application of all three experimental techniques listed above. A batch reactor allows for observing the selectivity of all products as a function of conversion in a single experiment, trivializing the application of Wojciechowski’s criteria. The effects of the co-fed products and probe molecules are assessed continuously as the reaction progresses, allowing for confirmation of the effects. Most notably, the batch reactor allows a broad permeation of a
small amount of isotopic tracer atoms in the reaction network as a function of conversion, probing the mechanisms of pathways that do not directly involve the co-fed isotopic compound at a reduced cost of experiment. A recirculating batch reactor also enables low single-pass conversions (<1%) across the catalyst bed, eliminating intra-particle and inter-phase mass and energy transport limitations, as well as transport limitations within the catalyst bed which are prevalent in highly exothermic oxidation reaction systems.

1.3. Oxygen species on the surface of reducible metal oxides

In striving to understand and rationalize the mechanisms for the chemistry of side product formation over reducible oxide catalysts, we simplify our consideration of catalyst surface reactivity by considering only three types of catalyst surface sites, apart from adsorbed carbon-containing surface intermediates. We consider lattice oxygen (O\(_L\)) and vacancy (V) sites as first explicated by Mars and van Krevelen [33], where O\(_L\) may either abstract H from or become inserted into molecules through C-O bond formation, leaving V when consumed. We also account for hydroxyl (OH) sites generated either via H abstraction from a reactant by O\(_L\) or surface equilibration with water, as has been established for a variety of catalytic reactions over reducible oxides [34–38]; these sites are responsible for H insertion into molecules and intermediates. Although the properties and subcategorization of these sites (e.g., specific O\(_L\) sites attributed to oxygen insertion, C-C bond scission, hydrogen abstraction, or inactivity) are areas of active study on specific catalysts, broad definitions of site functionalities are sufficient for describing partial oxidation mechanisms as we illustrate in this thesis.
Acrolein\textsuperscript{16}O was the exclusive product when propylene was oxidized with \textsuperscript{18}O\textsubscript{2} over β-bismuth molybdate in an isotopic tracer experiment performed by Keulks [39] at 698 K, demonstrating the participation of lattice oxygen in acrolein synthesis. Furthermore, the comparison between the total amount of \textsuperscript{16}O in the products from the same experiment and the density of oxygen atoms on the catalyst surface, based on BET surface measurements, estimated that oxygen atoms from 500 atomic layers of the catalyst, virtually the entire bismuth molybdate particle, could participate in the oxidation reaction. Keulks [39] did not observe oxygen exchange between \textsuperscript{16}O\textsubscript{2} and \textsuperscript{18}O\textsubscript{2} on β-bismuth molybdate between 523 K and 773 K and thus concluded that \textsuperscript{16}O on the catalyst surface did not incorporate into acrolein via gas phase scrambling to produce \textsuperscript{16}O\textsuperscript{18}O. Wragg et al. [40] provided further evidence for the insertion of lattice oxygen into the carbon backbone when they observed the formation of acrolein enriched with \textsuperscript{18}O during propylene oxidation using \textsuperscript{16}O\textsubscript{2} on an α–bismuth molybdate, the oxygen of which was labeled with \textsuperscript{18}O. Peacock et al. [41] reported that acrolein could be synthesized on α-bismuth molybdate at 773 K using only propylene as the reactant (in the absence of gas phase oxygen), demonstrating the oxidative potential of lattice oxygen atoms. The amount of oxygen absorbed by α-bismuth molybdate after the reaction with pure propylene at 773 K, determined via dosing known amounts of oxygen to the catalyst, was equal to the total amount of oxygen removed as acrolein, water, CO, and CO\textsubscript{2} [41], confirming the role of gas phase oxygen in re-oxidizing the catalyst surface. Grasselli and coworkers [42] proposed a reaction mechanism for propylene oxidation on α-bismuth molybdate consistent with the formation of the allyl species and the role of lattice oxygen (Figure 1.1). Studies of different catalytic systems such as oxidative dehydrogenation of butene on bismuth molybdate and selective oxidation
of xylenes on vanadium oxide showed that the facile reactivity of lattice oxygen is a characteristic of selective oxidation reactions [43]. The participation of lattice oxide ions in oxidation reaction was termed the MvK mechanism following Mars and van Krevelen’s kinetic study of selective oxidation of aromatic compounds on vanadium oxide [33].

The adsorption of oxygen on molybdenum oxide (MoO$_3$) at temperatures up to 423K [44] yielded an electron paramagnetic resonance (EPR) signal between $g=2.016$ and $g=2.018$ [45–48], indicating the formation of a surface adsorbed oxygen species. Ben Taarit and Lunsford [47] experimentally confirmed the peroxy O$_2$ nature of this oxygen species when they observed a splitting of this EPR signal into two sets of six equally spaced lines when $^{17}$O$_2$ with nuclear spin I=5/2 was used in the adsorption. This splitting pattern resulted
from the electronic-nuclear spin interaction that generated 2I+1 lines for each nucleus. Kolosov et al. [49] also reported the splitting of O_2^- EPR signal into six lines when ^{95}\text{MoO}_3 with nuclear spin I=5/2 was utilized for the adsorption and concluded that the O_2^- species binds to a molybdenum center. This adsorbed oxygen species was also observed on α- and γ-bismuth molybdate via EPR spectroscopy [50]. The dissociative adsorption of nitrous oxide (N_2O) on MoO_3 yielded two EPR signals with g_1=2.020 and g_2=2.006 [45], demonstrating the formation of an adsorbed oxygen species different from O_2^-.

Independent adsorption of N_2^{17}O on MoO_3 [51] and N_2O on ^{95}\text{MoO} [49] resulted in sextet splitting patterns of both signals, leading the investigators to conclude that the adsorbed species contained a single oxygen atom bonded to a Mo center.

The stoichiometric reaction between propylene and O_2^- adsorbed on V_2O_5 at 473 K performed by Yoshida et al. [52], in which the total amount of oxygen in the products was confirmed to be equal to the amount of adsorbed oxygen, yielded a mixture of oxygenated products including acetaldehyde, propylene oxide, propionaldehyde, acetone, acrolein, CO, and CO_2, demonstrating the ability of O_2^- to oxidize alkenes. The authors proposed an epoxide intermediate which decomposed to aldehyde products besides acrolein based on the formation of propylene oxide, as shown in Figure 1.2. Similarly, acetaldehyde and methanol, as well as carbonate, formate, and acetate ions were the main products of the stoichiometric reaction between propylene and adsorbed O_2^- on MgO at 448 K [53]. Thermal decomposition of propylene oxide on the same MgO catalyst yielded acetaldehyde and methanol as the main products [53], further supporting the claim that an epoxide intermediate, such as propylene oxide, is a precursor for acetaldehyde formation from propylene oxidation with surface O_2^-.

The facile reaction of adsorbed O_2^- with the carbon
double bond, an electron-rich center, demonstrated its electrophilic nature. Volodin and Cherkashin [54] investigated reactions of adsorbed O⁻ species on ZnO with gas phase methane at 90 K and reported the disappearance of O⁻ EPR signals and the appearance of a new EPR signal attributed to a surface-bound CH₃ radical, indicating that the adsorbed O⁻ ions caused facile dehydrogenation of methane. Similarly, fragmentation of alkanes and alkenes by O⁻ was observed on MgO at room temperature [55,56], illustrating the high electrophilicity of this oxygen species.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CHO} + \text{CO} & \rightarrow \text{CH}_2\text{CH}_2\text{COOH} \\
\text{CH}_2\text{CH}_2\text{CHO} + \text{O}_2 & \rightarrow \text{CH}_2\text{CH}_2\text{O}\text{O}_2
\end{align*}
\]

Figure 1.2. Schematic illustration of proposed mechanism for propylene oxidation with adsorbed O₂⁻ on V₂O₅ surface supported on SiO₂. Reprinted from S. Yoshida et al., Bull. Chem. Soc. Jpn. 47 (1974) 1564–1567.

Hydroxyl groups are prominent species on metal oxide surfaces and thus are expected to play a role in the surface reactions with organic molecules [57,58]. The presence of surface hydroxyl groups on Al₂O₃ was identified by a broad infra-red (IR) adsorption band between 3600 and 3700 cm⁻¹ characteristic of O-H vibrations [59]. Desorption of water upon heating various metal oxides in vacuo confirmed the formation of surface hydroxyl groups from dissociative adsorption of water on coordinately unsaturated metal sites [60,61]. Similarly, adsorption of alcohols on MoO₃ yielded IR bands at 1000-1100, 1440, and 2825-2850 cm⁻¹ which are characteristic of C-O bond
stretches, C-H bond deformation and C-H bond stretching [62,63], respectively, indicating the formation of surface alkoxy groups. An IR adsorption band at 1425-1450 cm\(^{-1}\) was observed on ammonia-exposed MoO\(_3\) [63], indicating the generation of ammonium ions, NH\(_4^+\), on the surface Brønsted acid sites. When water was pre-adsorbed on MoO\(_3\), the intensity of this IR band increased significantly and persisted upon degassing at room temperature [64], illustrating the formation of strong Brønsted acidic hydroxyl groups on the MoO\(_3\) surface in the presence of water. Formation of the IR band at 1545 cm\(^{-1}\) characteristic of a surface-bound pyridinium ion upon pyridine adsorption on MoO\(_3\) was only observed when the catalyst was pretreated with water [65,66], further proving the role of water in determining the surface Brønsted acidity and concentration of hydroxyl groups on MoO\(_3\).

Acetone with a 6.7% \(^{18}\)O enrichment was synthesized from the oxidation of propylene over a SnO\(_2\)/MoO\(_3\) mixed oxide in an isotopic labeling experiment with 8.6% \(^{18}\)O water employed as a co-reactant by Moro-Oka et al. [67]. Takita et al. [68] observed a linear relationship between the rate of acetone formation and the concentration of surface Brønsted acidic sites on SnO\(_2\)/MoO\(_3\) mixed oxides, as measured via n-butylamine titration. Oxidation of 1-butene and 1-pentene on the same catalyst produced the corresponding methyl ethyl ketone and methyl propyl ketone, respectively, while the reaction of isobutene gave tert-butyl alcohol as the main product [67]. These observations led Ozaki and coworkers [67,68] to propose

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![Figure 1.3. Schematic illustration of proposed mechanism for acetone formation with hydroxyl group on the surface of SnO\(_2\)/MoO\(_3\). Adapted from Y. Moro-Oka, Y. Takita, A. Ozaki, J. Catal. 27 (1972) 177–184.](image-url)
a reaction mechanism involving the addition of a surface hydroxyl group to an alkene molecule to give a surface alkoxy species which subsequently undergoes dehydrogenation yielding the corresponding ketone, as shown in Figure 1.3.

While the participation of surface lattice oxygen, adsorbed oxygen species, and hydroxyl groups in oxidation reactions of organic compounds on reducible metal oxides has been established, we demonstrate in this thesis the concurrent existence and tandem role of all three oxygen species in the mechanisms for the formation of side products during propylene oxidation on molybdenum-based multicomponent metal oxide formulations. The employment of these three surface oxygen species and their inherent chemistries described above, together with the identification of carbon-containing surface intermediate, is adequate to describe all experimental observations that we present in the following chapters.
Chapter 2. Mechanistic Origins of Unselective Oxidation

Products in the Conversion of Propylene to Acrolein on

\[ Bi_2Mo_3O_{12} \]

* Reported from L. Bui, R. Chakrabarti, A. Bhan, ACS Catal. 6 (2016) 6567–6580. © 2016 American Chemical Society

2.1. Introduction

The selective oxidation of propylene to acrolein is the first step for the industrial production of many acrylate-based polymers and high value chemicals. The minor production of undesired products, including aldehydic, ketonic, and acidic derivatives of propylene and ethylene, poses significant challenges for the downstream processing of acrolein and acrylic acid [69–71]. The acidic side products initiate irregular polymerization of acrolein and acrylic acid, while the aldehydes and ketones cause reactor fouling [14,15]. The observed byproducts include CO\textsubscript{x} [39,41,42,72–81], acetaldehyde [42,81–84], and ethylene [81] on bismuth molybdates but extend to include acetone [85–87], acetic acid [85], and acrylic acid [85,87,88] on complex mixed metal oxide formulations. The detailed mechanisms and kinetics for the formation of carbonyl and acidic byproducts on bismuth molybdates and other catalysts for the selective oxidation of propylene to acrolein, however, remain ambiguous or unknown.

Industrial catalysts for this process are complex metal oxides containing molybdenum and bismuth as essential components and many other element additives [18,89]. Previous investigations have demonstrated the participation of lattice oxygen in
the oxidation of propylene to acrolein: Peacock et al. [41] observed acrolein synthesis on Bi₂Mo₃O₁₂ at 773 K using propylene as the only reactant; independently, Wragg et al. [40] reported the formation of acrolein₁⁸O on ¹⁸O-labelled Bi₂Mo₃O₁₂ from propylene oxidation using ¹⁶O₂ as the oxidizing agent. Grasselli and coworkers [42,79,90,91] performed extensive studies of the oxidation of allylic iodine, azopropene, and a series of allyl alcohol isotopologues deuterated at various positions on bismuth molybdates; the facile oxidation of these probe molecules to acrolein and the isotopic content of the products demonstrated that surface allyl species are reaction intermediates in the oxidation of propylene to acrolein. The accepted route for acrolein synthesis on bismuth molybdates is a Mars-van-Krevelen-like mechanism: propylene activation through abstraction of a methyl hydrogen, lattice oxygen incorporation in the surface propylene-derived allyl precursor, and catalyst surface regeneration with gas-phase oxygen [22,42,78,80,81,92–95].

Propylene oxidation on Bi-Mo-based formulations results in a variety of C₃ and smaller byproducts as mentioned above, the transformations of these byproducts on metal oxides in turn involve numerous catalytic functions including H-abstraction, hydroxylation, decarbonylation, and decarboxylation. Zhai et al. [81] concluded that acetaldehyde was formed in a parallel pathway to acrolein synthesis on Bi₂Mo₃O₁₂ and Bi-V-Mo mixed oxides based on the observed formation of acetaldehyde at less than 1% propylene conversion. Moro-Oka et al. [67] noted that propylene was oxidized to acetaldehyde on SnO₂-MoO₃ mixed oxides without interaction with adsorbed water or surface hydroxyl groups due to a lack of ¹⁸O incorporation in acetaldehyde in isotopic tracer experiments with H₂¹⁸O co-feeds during propylene oxidation. Takita et al. [68]
demonstrated that acetone formation on SnO₂-MoO₃ mixed oxides, however, does involve surface hydroxyl groups as evidenced by the linear relationship between acetone formation rate with the number of Brønsted acidic sites measured from ex-situ n-butylamine titration. The authors proposed a mechanism for acetone formation involving the addition of propylene to a surface acidic hydroxyl group to form an isopropoxy intermediate which undergoes dehydrogenation [96]. Serwicka et al. [97] studied acrolein adsorption and oxidation to acrylic acid on Mo heteropoly acid (K₃PMo₁₂O₄₀) at 423 K and noted the appearance of an electron-spin-resonance (ESR) signal that was attributed to a reduced catalyst with oxygen-deficient unit cells. IR spectra of the same acrolein-exposed catalyst revealed C=O bonds of the adsorbed organic species [97]. The authors postulated a mechanism for acrylic acid formation that starts with dissociative chemisorption of acrolein to the oxide surface forming a surface acrylate ion. This acrylate intermediate desorbs with a surface hydrogen adatom to produce acrylic acid and an oxygen vacancy site on the surface. Tichy proposed a similar mechanism for acrolein oxidation to acrylic acid on Mo-V oxide [98].

In this work, we report formation rates of all C₁ – C₃ products during propylene oxidation in the presence of different co-fed probe molecules to develop an extensive reaction network describing the formation and consumption of these products on Bi₂Mo₃O₁₂ at 623 K. The reaction rates were assessed under conditions that permit strict kinetic control and precise measurement at high propylene chemical conversions (0 – 25%) in a gradient-less recirculating batch reactor. We postulate a set of elementary steps detailing the molecular transformations for all C₁ – C₃ eluents and the relevant type of active site and surface intermediate for each reaction. Rank and stability analysis of the
products reveals that acrolein, acetaldehyde, acetic acid, and acetone are primary unstable products, acrylic acid and ethylene are secondary products, and CO and CO$_2$ are both primary and secondary products. The oxidation reactions of propylene to acetone, acrolein to acetaldehyde, and acetaldehyde to acetic acid are shown to be promoted by water, while the decomposition pathways of acetic acid to CO$_x$ and acrylic acid to ethylene and acetaldehyde are inhibited by water. CO$_x$ is produced mainly from the fragmentation of C$_3$ species (propylene, acrolein, acrylic acid, acetone) to C$_2$ products (acetaldehyde, acetic acid) and from the total oxidation of C$_2$ compounds. Nucleophilic lattice oxygen, surface hydroxyl groups, and surface active sites for acid decarboxylation are proposed as catalytic centers for reactions that are independent of, promoted by, and inhibited by water, respectively.

2.2. Materials and methods

2.2.1 Catalyst preparation and characterization

Bismuth molybdate Bi$_2$Mo$_3$O$_{12}$ was prepared by a complexation method using citric acid as described by Zhai et al. [81]. Briefly, 2.64 g ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O) (15 mmol Mo, 99.98%, Sigma-Aldrich) and 2.92 g citric acid (15 mmol, 99.5%, Sigma-Aldrich) were dissolved in 30 cm$^3$ de-ionized water. A separate solution was prepared by dissolving 4.86 g bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$.5H$_2$O) (10 mmol, 99.9%, Sigma-Aldrich) and 1.92 g citric acid in 50 cm$^3$ 1 N HNO$_3$. The molybdenum-containing solution was added to the bismuth-containing solution at ambient temperature and the resulting clear solution was heated at 343 K for 12 h in a static oven. The resulting thick yellow gel was dried at 393 K for 2 h in a static oven. The
resulting brown solid was heated in dry air (1.67 cm$^3$ s$^{-1}$ at NTP conditions, Ind. Grade, Matheson Trigas) from ambient temperature to 873 K with a rate of 0.083 K s$^{-1}$ and held for 6 h. Powder X-ray diffraction (XRD) patterns (collected on a Bruker D8 diffractometer using Cu K $\alpha$ radiation (40 kV, 40 mA)) confirmed the Bi$_2$Mo$_3$O$_{12}$ phase-purity of the synthesized sample (Figure 2.1). An external surface area of ~0.4 m$^2$ g$^{-1}$ for the resulting Bi$_2$Mo$_3$O$_{12}$ formulation was determined from a t-plot calculation from nitrogen adsorption/desorption isotherms measured at liquid nitrogen temperature on a Micromeritics ASAP 2020 porosity and surface area analyzer after degassing under vacuum for 3 h at 473 K. X-ray photoelectron spectroscopy (XPS) analysis of the catalyst (collected on a Surface Science SSX-100 spectrometer at 298 K) confirmed the surface Bi:Mo:O composition of 2:3:10 (Figure 2.2) and electron binding energies for Bi 4f7, Bi 4f5, Mo 3d5, Mo 3d3, and O 1s of 159.6, 164.9, 232.7, 235.8, and 530.7 eV (Figure 2.3), respectively, in agreement with the reported XPS data for Bi$_2$Mo$_3$O$_{12}$ [99]. XPS measurements were performed with a monochromated aluminum source (1486.6 eV) with electron binding energy corrected via referencing to the C 1s binding electron (285 eV).

Figure 2.1. X-ray diffractogram of the Bi$_2$Mo$_3$O$_{12}$ catalyst used in this study, also included for reference is a diffractogram for Bi$_2$Mo$_3$O$_{12}$ (JCPDS PDF # 00-021-0103).
Figure 2.2. X-ray photoelectron spectrum of the Bi$_2$Mo$_3$O$_{12}$ catalyst.

Figure 2.3. XPS spectra of Bi 4f (top left), Mo 3d (top right), O 1s (bottom left), and C 1s (bottom right) with decompositions for Bi$_2$Mo$_3$O$_{12}$. 
2.2.2 Kinetic measurements of propylene oxidation on Bi$_2$Mo$_3$O$_{12}$

Catalytic reactions were performed in a recirculating batch reactor (Figures Figure 6.1 and Figure 6.2) on a packed catalyst bed in a quartz tube (0.4 cm inner diameter, 0.32 cm$^3$ catalyst bed volume) equipped with a K-type thermocouple penetrating the axial and radial centers of the catalyst bed. Isothermal reaction conditions were maintained using two cartridge heaters (Omega Engineering Inc., CIR-2100, 600 W) inserted inside two split-tube aluminum sleeves regulated by a Watlow temperature controller (96 Series). Intra-particle and inter-phase mass and energy transport limitations, as well as transport limitations within the catalyst bed, were negligible as assessed by criteria originally proposed by Mears [100], Anderson [101], and Weisz-Prater [102] (Section 6.2. Heat and mass transfer calculations). The total volume of the reactor was 535 cm$^3$. All transfer lines in the recirculating system were maintained at 433 K to prevent condensation of the reactants and products.

Catalyst particles with sizes between 180 and 425 μm (80–40 mesh) were obtained by pressing and sieving the as-synthesized Bi$_2$Mo$_3$O$_{12}$ powder. The catalyst bed was heated to 623 K from ambient conditions with a rate of 0.083 K s$^{-1}$ in dry air (0.83 cm$^3$ s$^{-1}$ at NTP conditions) and held for 12 h prior to kinetic measurements. The catalytic oxidation of propylene was performed at 623 K with 0.4 g Bi$_2$Mo$_3$O$_{12}$ with an initial feed composition of 6 kPa propylene (99.99%, Matheson TriGas), 34 kPa air (21% oxygen and 79% nitrogen, Ultra Zero Certified grade, Matheson TriGas), 7 kPa water (de-ionized), and 69 kPa helium (grade 4.7, Minneapolis Oxygen Company). For co-feed experiments, 0.5 – 2.5 M solutions of the following compounds were prepared in de-ionized water: acetaldehyde (99.5%,
Sigma-Aldrich), acetone (99.7%, Sigma-Aldrich), acrylic acid (99.7%, Sigma-Aldrich), acetic acid (99.5%, Sigma-Aldrich), and propylene oxide (99.5%, Sigma-Aldrich).

The initial reactant mixture with and without co-feeds was recirculated at 3 cm$^3$ s$^{-1}$ in the reactor for 30 minutes using a micro-recirculating pump (Metal Bellows, MB-21) before introduction to the catalyst bed. The contents of the reacting gas mixture were sampled at 35-minute intervals and separated using an Agilent 6890 gas chromatograph (GC) equipped with an HP-Plot/Q column (30.0 m x 320 μm x 0.20 μm) for all organic products in series with a MolSieve-5A column (30.0 m x 320 μm x 0.20 μm) for nitrogen, oxygen, and CO. The separated compounds were identified using mass spectrometry and quantified using a flame ionization detector (FID) for all organic compounds and a thermal conductivity detector (TCD) for water, nitrogen, oxygen, CO, and CO$_2$.

The net synthesis rate of a species was estimated by fitting a sextic polynomial to the molar quantity of that species as a function of time and calculating the first order derivative. The net synthesis rate of a species was extrapolated to zero propylene conversion to calculate the initial synthesis rate of that product.

2.3. Results and discussion

2.3.1. Product rank and stability analysis

The products of propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ (623 K, <25% conversion, 6 kPa C$_3$H$_6$, 7 kPa O$_2$, 7 kPa H$_2$O) included acrolein, acetaldehyde, acetone, acrylic acid, acetic acid, ethylene, butadiene, benzene, CO, and CO$_2$. Trace amounts of crotonaldehyde and methyl vinyl ketone were detected at propylene conversions exceeding 10%; the subject of this report, however, is the kinetic and mechanistic interpretation of C$_1$ – C$_3$
product formation pathways during propylene oxidation. The rank and stability of a product can be qualitatively assessed by following its yield as a function of conversion of the main reactant as originally proposed by Wojciechowski and coworkers [26,27]. Figure 2.4 shows yield versus conversion plots for those species exceeding 0.1 % carbon selectivity, while Table 2.1 summaries the stability and order within the reaction network of each product.

Figure 2.4. Yields (on a carbon basis) of the propylene oxidation products on Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> with respect to propylene conversion as assessed in a gradient-less recirculating batch reactor. Reaction parameters: 400 mg Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, 623 K, initial reaction mixture comprised of 6 kPa propylene, 7 kPa oxygen, and 7 kPa water.
Acrolein, acetone, acetaldehyde, and acetic acid are categorized as primary unstable products based on the observed decrease in selectivity of each product with conversion from an initial non-zero value. Co-processing acetic acid with propylene/oxygen/water mixtures revealed pathways leading to CO\textsubscript{x} (Section 2.3.2.5. Consumption pathway of acetic acid.) demonstrating that acetic acid is also an unstable product formed in the partial oxidation of propylene on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}. The selectivities of both CO and CO\textsubscript{2} increased from initial non-zero values, indicating that CO and CO\textsubscript{2} are both primary and secondary products. The yields of acrylic acid, ethylene, butadiene, and benzene showed zero slopes at low conversions on the yield-conversion plots; therefore, these species are classified as secondary products that are not formed directly from propylene. Given the qualitative assessment of the Wojciechowski’s criterion, the secondary classification of products does not exclude kinetically minor formation pathways of these products from propylene. The application of Wojciechowski’s criterion establishes the qualitative product rank but does

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**Table 2.1. Product orders and stabilities in propylene oxidation on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} at 623 K up to 25% propylene conversion.**

<table>
<thead>
<tr>
<th>Product</th>
<th>Product order and stability</th>
<th>Carbon selectivity (/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial\textsuperscript{a}</td>
</tr>
<tr>
<td>Acrolein</td>
<td>Primary unstable</td>
<td>74</td>
</tr>
<tr>
<td>CO</td>
<td>Primary and secondary</td>
<td>2.0</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>Primary and secondary</td>
<td>4.0</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>Secondary</td>
<td>1.4</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>Primary unstable</td>
<td>8.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>Primary unstable</td>
<td>6.9</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>Primary unstable</td>
<td>3.0</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Secondary</td>
<td>0.11</td>
</tr>
<tr>
<td>Butadiene</td>
<td>Secondary</td>
<td>0.07</td>
</tr>
<tr>
<td>Benzene</td>
<td>Secondary</td>
<td>0.08</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: Extrapolated values to zero propylene conversion.
not provide the interconnectivity between the products nor the associated kinetics of these pathways. Subsequently, we performed a series of independent co-feed experiments to elucidate the reaction network and to develop a kinetic model describing the formation and consumption of every C$_1$ – C$_3$ product.

2.3.2. Reaction network of propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ as inferred from co-feed experiments

All C$_1$ – C$_3$ product formation rates were noted to be independent of initial oxygen partial pressure (7 – 13 kPa) for propylene conversions below 25%. The zero-order dependency of acrolein synthesis rate on oxygen partial pressure is consistent with previously reported steady-state kinetic measurements for propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ (3 – 16 kPa C$_3$H$_6$ and O$_2$, 573 – 723 K) [77,81]. The insensitivity of the formation rates of byproducts of propylene oxidation on oxygen partial pressure suggests that these species are formed either on active sites where oxygen-derived intermediates are predominantly prevalent or through kinetically relevant steps that do not involve oxygen or oxygen-derived species.

2.3.2.1. Consumption pathways of propylene.

Acrolein, acetaldehyde, acetone, and acetic acid are formed via direct oxidation of propylene as evinced by their primary product rank assignment via Wojciechowski’s criterion. The initial acetone formation rate increased from 0.08, 0.12, to 0.16 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ with 2, 4, and 7 kPa water pressures (Figure 2.5a), respectively, reflecting a promotional effect of water on acetone formation from propylene. The observed initial synthesis rates of acrolein, acetaldehyde (Figure 2.5b), and acetic acid (Figure 2.5c) were
invariant with different initial water pressures, demonstrating the kinetic irrelevancy of water partial pressure on the oxidation of propylene to these products. The oxidation of propylene to acetaldehyde and acetic acid necessitates the formation of a C_1 byproduct which is postulated to be CO_x since C_1 compounds besides CO_x were not observed.

Figure 2.5. Initial formation rates of acetone (a), acetaldehyde (b), acetic acid (c), ethylene (d), and CO_x (e) on 400 mg Bi_2Mo_3O_12 at 623 K in the presence of different identities and amounts of probe molecules co-processed with the initial reaction gas mixture comprising of 6 kPa propylene, 7 kPa oxygen, and different amounts of water.
Analogous experiments with acetaldehyde, acetone, acrylic acid, and acetic acid independently co-processed with 6 kPa propylene, 7 kPa oxygen, and varying amounts of water were performed to further probe the formation and consumption pathways of oxygenate products and their kinetic dependence on water partial pressure. The products were introduced in small amounts (<0.3 kPa) compared to propylene to avoid changes in surface coverage with identity and amount of co-feed. Acrolein co-feed experiments were not performed due to its acute toxicity. The formation and consumption pathways of propylene and seven products formed in carbon selectivities exceeding 0.1 % based on the product stability analysis and on the results of the various co-feed experiments are summarized in Figure 2.6.

2.3.2.2. Formation and consumption pathways of acetaldehyde.

We identified four precursors of acetaldehyde: propylene, acetone, acrylic acid, and acrolein (Figure 2.6). Figure 2.5b shows the effects of co-processing different amounts of acetone and acrylic acid on initial acetaldehyde formation rate. The initial formation rate of acetaldehyde increased from 0.30, 0.35, 0.39, to 0.47 μmol min⁻¹ (m² cat)⁻¹ with 0, 0.04, 0.07, and 0.14 kPa acetone, respectively, demonstrating that acetone is converted to acetaldehyde on Bi₂Mo₃O₁₂ under our reaction conditions. Variation in the initial amount of water with constant initial acetone partial pressure at 0.14 kPa did not affect the initial formation rate of acetaldehyde, reflecting the insensitivity of acetone conversion to acetaldehyde with water pressure. The initial formation rate of acetaldehyde also increased from 0.30, 0.48, 0.58, to 0.69 μmol min⁻¹ (m² cat)⁻¹ in the presence of 0, 0.09, 0.15, and
0.25 kPa acrylic acid co-fed to the reaction gas mixture, respectively. Increasing the initial amount of water from 1.3 to 6.7 kPa in the presence of 0.09 kPa acrylic acid decreased the initial formation rate of acetaldehyde from 0.75 to 0.48 μmol min⁻¹ (m² cat)⁻¹, showing the inhibitory effect of water on the synthesis of acetaldehyde from acrylic acid.

Initial formation rates of both acetic acid and COx increased with co-processing acetaldehyde (Figure 2.5c and Figure 2.5e), illustrating the direct oxidation of acetaldehyde in parallel reactions to these species (Figure 2.6). The initial formation rate of acetic acid in the presence of 0.1 kPa co-fed acetaldehyde increased from 0.10, 0.12, to 0.20 μmol min⁻¹ (m² cat)⁻¹ with 1.6, 3.0, and 8.1 kPa initial water partial pressures, demonstrating a positive water partial pressure dependence of acetic acid formation rate from acetaldehyde. The initial formation rate of COx, however, was not affected by variation in water partial pressure in the presence of 0.1 kPa co-fed acetaldehyde.
Varying the initial partial pressure of water from 2 to 7 kPa in the absence of any co-feed increased acetaldehyde formation rate at propylene conversions exceeding 5% (Figure 2.7), indicating that either acetaldehyde formation from a secondary pathway is promoted by water or acetaldehyde decomposition is inhibited by water. Based on the dependency of acetaldehyde decomposition rates to CO$_x$ and acetic acid on water partial pressure discussed above, together with the inhibitory effect of water on acetaldehyde formation from acrylic acid and the independence of acetaldehyde formation rate from acetone on water pressure, we postulate that the formation of acetaldehyde from acrolein is promoted by water.

![Figure 2.7. Acetaldehyde molar amounts with respect to time and propylene conversion during propylene oxidation in a gradient-less recirculating batch reactor. Reaction parameters: 400 mg Bi$_2$Mo$_3$O$_{12}$, reaction temperature 623 K, initial reaction mixture in individual experiments comprised of 6 kPa propylene, 7 kPa oxygen, (●) 7 kPa, (◆) 4 kPa, and (□) 2 kPa water. The inset shows the net synthesis rate of acetaldehyde (in μmol min$^{-1}$ (m$^2$ cat)$^{-1}$) with respect to time (bottom axis in min) and propylene chemical conversion (top axis in mol%) in the same experiments.](image)
2.3.2.3. Formation and consumption pathways of acrylic acid.

The secondary product rank assignment of acrylic acid, the analogous oxidation of acetaldehyde to acetic acid, and the absence of C$_1$ products such as formaldehyde and formic acid that rules out carbon-chain-growth reactions from acetaldehyde and acetic acid to acrylic acid leads us to propose a formation pathway of acrylic acid from acrolein (Figure 2.6). Decreasing the initial water pressure from 7 to 2 kPa induced a minor drop in the molar amount of acrylic acid which can be explained by the inhibitory effect of water on the consumption rate of acrylic acid to acetaldehyde (as discussed in Section 2.3.2.2. Formation and consumption pathways of acetaldehyde.); therefore, we postulate that acrylic acid formation rate from acrolein is independent of water pressure.

Figure 2.5c and Figure 2.5d show the effect of co-processing different amounts of acrylic acid on the initial formation rates of ethylene and acetic acid. The initial synthesis rate of ethylene increased from 0.0035, 0.028, 0.036, to 0.045 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ with 0, 0.09, 0.15, and 0.25 kPa acrylic acid. The initial formation rate of acetic acid also increased from 0.08, 0.20, 0.22, to 0.27 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ in the same experiments, reflecting conversion pathways from acrylic acid to ethylene and acetic acid (Figure 2.6). Increasing the initial amount of water from 1.3 to 6.7 kPa in the presence of 0.09 kPa acrylic acid decreased the initial formation rate of ethylene from 0.063 to 0.028 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$. Conversely, the initial acetic acid formation rate increased from 0.08 to 0.20 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ in the same experiments, demonstrating the promotional effect of water on the formation of acetic acid from acrylic acid in contrast to the inhibitory effects of water on acrylic acid decomposition pathways to acetaldehyde and ethylene.
2.3.2.4. Consumption pathways of acetone.

We identified three products of acetone decomposition: acetaldehyde, acetic acid, and CO\textsubscript{x} (Figure 2.6) by co-processing different amounts of acetone with the initial reaction gas mixture. The initial formation rate of acetic acid increased from 0.08, 0.17, 0.28, to 0.48 μmol min\textsuperscript{-1} (m\textsuperscript{2} cat)\textsuperscript{-1} with 0, 0.04, 0.07, and 0.14 kPa acetone, respectively (Figure 2.5c). The initial formation rate of CO\textsubscript{x} also increased from 0.44, 0.64, 0.86 to 1.17 μmol min\textsuperscript{-1} (m\textsuperscript{2} cat)\textsuperscript{-1} in the same experiments, showing that acetone is converted to acetaldehyde and CO\textsubscript{x} in parallel reactions on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} under our reaction conditions (Figure 2.5e). Variation in the initial amount of water with a constant initial partial pressure of acetone at 0.14 kPa did not affect the formation rates of either acetic acid or CO\textsubscript{x}, demonstrating the insensitivity of acetone conversion with water pressure.

2.3.2.5. Consumption pathway of acetic acid.

We investigated the consumption of acetic acid by co-processing different amounts of acetic acid and water with the reaction mixture. The initial net synthesis rate of acetic acid decreased from 0.08, -0.21, -0.38, to -0.64 μmol min\textsuperscript{-1} (m\textsuperscript{2} cat)\textsuperscript{-1} in the presence of 0, 0.11, 0.18, and 0.30 kPa initial partial pressure of acetic acid, showing the proportional dependence of acetic acid consumption rate to its molar amount. A negative synthesis rate denotes a net consumption of the compound. Varying the initial water pressure from 7.1 kPa to 2.7 kPa with constant initial partial pressure of acetic acid at 0.11 kPa decreased the net synthesis rate of acetic acid from -0.21 to -0.47 μmol min\textsuperscript{-1} (m\textsuperscript{2} cat)\textsuperscript{-1}, reflecting the inhibitory effect of water on the consumption rate of acetic acid. The initial synthesis rates of all C\textsubscript{1} – C\textsubscript{3} products did not increase except for CO\textsubscript{x}. 
2.3.4. Proposed mechanistic pathways for propylene oxidation on Bi$_2$Mo$_3$O$_{12}$

The existence of surface nucleophilic lattice oxygen which participates in the formation of the main product acrolein via a Mars-van-Krevlen-like mechanism has been confirmed by the Bell [74,81,103,104], Grasselli [42,90,91,105,106], and Keulks [39,72,76,77,80] groups via kinetic measurements, isotopic tracer experiments, and density functional theory studies. We posit it infeasible to develop mechanistic rationale for the interconnectivity in the proposed reaction network and the observed kinetic effects of different co-feeds and water on the formation and consumption of the unselective products during propylene oxidation with lattice oxygen as a unique active site on the catalyst surface. We propose the existence of three additional types of active sites that are present on Bi$_2$Mo$_3$O$_{12}$ during propylene oxidation and discuss reports from the literature that support the existence of such active sites: an active site that dissociatively adsorbs water to generate surface hydroxyl groups, an active site that adsorbs gas-phase oxygen to form electrophilic surface oxygen species, and an active site that performs decarboxylation of carboxylic acids. Figure 2.8A presents a schematic for the proposed active sites on Bi$_2$Mo$_3$O$_{12}$. Interconversion between the proposed types of active sites is possible; this notion is supported by the formation of surface hydroxyl groups in the catalytic cycle of propylene oxidation to acrolein on the nucleophilic lattice oxygen site, as proposed by Burrington and Grasselli [42] and by Zhai et al. [81]. Consequently, with gas-phase composition varying as a function of reaction time in our batch-reactor studies and varying with space time in a flow reactor, the catalyst surface could be evolving in terms of both surface coverage and the number of active sites.
We propose in Figure 2.8B a detailed reaction mechanism for the formation and consumption of all observed C1–C3 species during propylene oxidation consistent with the observed kinetic effects of co-feeds and water. We propose six types of elementary steps to occur on the four types of active sites: (i) abstraction of a hydrogen atom from an organic species by the catalyst surface; (ii) abstraction of a hydrogen adatom from the surface by an organic species, i.e. the reverse of reaction (i); (iii) incorporation of a lattice oxygen atom to an organic species; (iv) addition reaction of an organic species with a hydroxyl group; (v) addition reaction of an organic species with an electrophilic adsorbed oxygen species; and (vi) decarboxylation of a carboxylic acid. Below, we discuss evidence in support of the existence of the proposed catalytic sites and mechanistic pathways in Figure 2.8.

Grasselli et al. [92] proposed a mechanism for acrolein formation from propylene on Bi2Mo3O12 (Figure 2.8B, Box a): (i) abstraction of a methyl hydrogen forming a surface allyl intermediate, (ii) incorporation of a lattice oxygen atom forming a surface allyloxide, (iii) second hydrogen abstraction and desorption of the formed acrolein leaving behind a surface oxygen vacancy, and (iv) reoxidation of the lattice oxygen active site with gas-phase oxygen (not shown in Figure 2.8B). Bell and coworkers [74,81] recently proposed a similar reaction mechanism. Dimerization of propylene-derived allyl species on Bi2O3 generated hexadiene [107]; independently it has been noted that allyl iodide and allyl azide can be readily oxidized on MoO3 to form acrolein [42,90]. These observations suggest the
roles of Bi and Mo in the catalytic cycle: Bi centers activate propylene molecule by catalyzing allylic C-H bond cleavage, while Mo centers oxidize the allyl intermediate to acrolein [108]. This view is supported by DFT calculations by Jang and Goddard [95] showing surface Bi (V) moieties as possible active centers. Conversely, recent DFT calculations by Getsoian et al. [104] suggest that Mo-oxo moieties, assisted by nearby Bi centers, are active centers for the cleavage of the allyl C-H bond on propylene.

We postulate electrophilic adsorbed oxygen as a surface reactive species on Bi$_2$Mo$_3$O$_{12}$ to justify the direct fragmentation of propylene to acetaldehyde and acetic acid.
Previous reports by the Spiridonov, Lunsford, and Kazansky groups have confirmed the formation of adsorbed oxygen species on MoO$_3$, as either diatom or adatom oxygen, via electron paramagnetic resonance (EPR) spectroscopy [44,47,49]. Volodin and Cherkashin [54] investigated the reaction of adsorbed oxygen on a ZnO surface with gas phase methane at 90 K and reported the appearance of an EPR signal attributed to CH$_3$ radicals, indicating the facile dehydrogenation of methane by the adsorbed oxygen via homolytic C-H bond cleavage. Yoshida et al. [52] proposed two surface intermediates as the precursors to acetaldehyde during propylene oxidation on V$_2$O$_5$ with adsorbed oxygen at room temperature: (i) an epoxy-like species from addition of an oxygen adatom to the C=C double bond of propylene and (ii) a 1,2-dioxetane-like species from the reaction of propylene and an adsorbed molecular oxygen. We postulate that a similar mechanism is responsible for the fragmentation of propylene to acetaldehyde and acetic acid on Bi$_2$Mo$_3$O$_{12}$. The strained three-and four-member rings of the surface intermediates facilitate C-C bond cleavage to produce CO$_x$ and a surface acyl species which abstracts a hydrogen adatom from the surface to give acetaldehyde or is further oxidized to acetic acid. Acetaldehyde, acetic acid, and CO$_x$ initial synthesis rates increased from 0.3 to 3.0, 0.08 to 0.15, and 0.44 to 2.95 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, respectively, upon co-processing 0.031 kPa propylene oxide with the reaction gas mixture (Figure 2.5b, c, and e), illustrating the rapid conversion of propylene oxide to CO$_x$, acetaldehyde, and acetic acid in agreement with our proposed mechanism. The co-fed propylene oxide was consumed completely at less than 1% propylene conversion with a lower-bound estimated consumption rate of 2.9 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, demonstrating the unstable nature of propylene oxide and the epoxy-like
intermediate formed upon reaction of propylene with adsorbed oxygen on Bi$_2$Mo$_3$O$_{12}$ under our reaction conditions.

We propose that the dissociative adsorption of water on Bi$_2$Mo$_3$O$_{12}$ increases the surface concentration of hydroxyl groups which act as active sites for the formation of acetone from propylene, acetaldehyde from acrolein, and acetic acid from acetaldehyde. This postulate is consistent with the promotional effect of water on the rates of these reactions as evinced in Figures 2.5a, 2.5c, and 2.5e. Previous investigations [62–66] have confirmed the formation of Brønsted acidic surface hydroxyl groups on Mo- and Mo-mixed oxides via IR spectroscopy and probe molecule adsorption studies. Takita et al. [96] identified a hydration-dehydrogenation sequence between propylene and a surface-bound hydroxyl group on Sn-Mo mixed oxides as the reaction mechanism for propylene oxidation to acetone on these catalysts. We postulate that acetone formation on Bi$_2$Mo$_3$O$_{12}$ follows a similar mechanism (Figure 2.8B, Box b).

The formation of ethylene from acrolein in our reaction network suggests decarbonylation of acrolein occurs to form a surface vinyl species which abstracts a hydrogen adatom from the surface to generate ethylene. We postulate that this surface vinyl species also reacts with a neighboring hydroxyl group to form acetaldehyde. The decarbonylation reaction of acrolein is initiated by cleavage of the aldehydic C-H bond to form an acrolyl species on a lattice oxygen active site. The subsequent decarbonylation of the acyl intermediate, therefore, is proposed to occur on the same active site. Zhai et al. [81] recently proposed a similar vinyl intermediate as the precursor for acetaldehyde formation on Bi$_2$Mo$_3$O$_{12}$. 
The two mechanistic pathways for acrolein and acetone formation from propylene lead us to consider two possible mechanisms for the oxidation of aldehyde to the corresponding acid (Figure 2.8B, Box c). The insensitivity of acrylic acid amount with respect to initial water pressure suggests that acrylic acid formation occurs on the lattice oxygen active site where the aldehydic hydrogen of acrolein is cleaved to generate a surface acyl intermediate which sequentially incorporates a lattice oxygen and abstracts a surface hydrogen adatom. The promotional effect of water on the synthesis rate of acetic acid from acetaldehyde (Figure 2.5c), however, suggests an alternative pathway involving addition of the aldehyde to a hydroxyl group generating a surface acetal species which undergoes dehydrogenation to form the acid.

The similar inhibitory effects of water on the total combustion of acetic acid to CO₂ and the fragmentation of acrylic acid to acetaldehyde and ethylene suggests that acrylic acid and acetic acid decompose following similar mechanistic pathways. We postulate that both acids undergo decarboxylation on the same active site as the first step in their decomposition reactions. The inhibitory effect of water on the initial decomposition rates of acrylic acid (Figure 2.5b and d) and acetic acid (Figure 2.5c) suggests that water competitively adsorbs on the active site that performs decarboxylation of acrylic acid and acetic acid. Vohs and Barteau [109] observed decarboxylation of adsorbed acetate on ZnO surface at ~600 K to form CO₂ and surface carbon which was removed by oxidation with lattice oxygen at ~750 K. Barteau and coworkers [110–112] further observed progressively less decarboxylation of acetic acid on TiO₂ and MgO surfaces and concluded that decarboxylation of carboxylic acids is favored on reducible oxides. This conclusion is in
agreement with our proposal for decarboxylation of acetic acid and acrylic acid on the highly reducible Bi$_2$Mo$_3$O$_{12}$.

Massoth et al. [107] and White et al. [113] observed selective dimerization of propylene to hexadiene on Bi$_2$O$_3$ and proposed the formation of allyl species through hydrogen abstraction of propylene. This catalyst, however, lacks the oxidative functionality of lattice oxygen active sites that are present on Bi-Mo formulations. We propose that propylene dimerization still occurs on Bi$_2$Mo$_3$O$_{12}$, but to a much lesser extent and the C$_6$ intermediate undergoes cracking to ethylene and butadiene as well as cyclization and oxidative dehydrogenation to benzene.

The proposed mechanistic network in Figure 2.8 collates a diverse body of literature on oxidation chemistries catalyzed by Mo-based oxidic materials and provides a compendious description of elementary-step pathways that are likely involved in the formation of byproducts in the partial oxidation of propylene on mixed-metal oxides. This formalism is consistent with the effects of water and co-feeds that we discuss above and suggests the existence and involvement of multiple catalytic sites in propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ formulations.

**2.4. Conclusion**

Application of Wojciechowski’s criterion to the products formed during propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K up to 25% propylene conversion revealed that acrolein, acetaldehyde, acetone, and acetic acid are primary unstable products. Acrylic acid, ethylene, butadiene, and benzene were classified as secondary products, while CO and CO$_2$ were identified as both primary and secondary products. Co-processing small amounts of
acetaldehyde, acetone, acetic acid, and acrylic acid, separately, into the reaction gas mixture comprising initially of 6 kPa propylene, 7 kPa oxygen, and 7 kPa water revealed over-oxidation and carbon-carbon bond scission pathways involved in the consumption of these oxygenates (Figure 2.6). Varying the initial amount of water in the co-feed experiments showed that the conversion of propylene to acrolein and acetaldehyde, the over-oxidation of acrolein to acrylic acid, and the decomposition of acetone to acetic acid and acetaldehyde are independent of water partial pressure. Water showed a promotional effect on the synthesis of acetaldehyde from acrolein, acetone from propylene, and acetic acid from acetaldehyde and acrylic acid as well as an inhibitory effect on the decomposition of acetic acid to CO\textsubscript{x} and acrylic acid to acetaldehyde and ethylene.

A mechanistic network describing the elementary steps and relevant surface intermediates for all reactions is postulated that is consistent with the kinetic effects observed in all co-feed experiments (Figure 2.8). Four different types of active sites are proposed to exist on the catalyst surface under our reaction conditions: nucleophilic lattice oxygen, surface hydroxyl groups, electrophilic adsorbed oxygen species, and an active site for decarboxylation of carboxylic acids. Lattice oxygen active sites are proposed to catalyze propylene oxidation to acrolein, acetone decomposition, and aldehyde oxidation to the corresponding acid while adsorbed oxygen species carry out propylene fragmentation to acetaldehyde and acetic acid. Surface hydroxyl groups are postulated to participate directly in the formation of acetone, acetaldehyde, and acetic acid. Decomposition pathways of acetic acid and acrylic acid are postulated to occur on the same active sites that are dominantly covered with adsorbed water. The quantitative assessment of the effects of various co-feeds in this study enables the systematic description of the
mechanistic origins and kinetics for the formation and consumption of all major byproducts in propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K and can be extended to other metal oxide systems.
Chapter 3. Mechanisms for C-C Bond Cleavage and Formation

during Acrolein Production on a Mixed Metal Oxide Catalyst

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3.1. Introduction

The partial oxidation of propylene to acrolein on multi-component metal oxide catalysts constitutes the first step in the upgrading of propylene to high valued acrylate-based polymers and chemicals [114]. The oxidation of propylene on Bi-Mo-based formulations generates C₁ – C₃ aldehydic and acidic compounds as major side products including but not limited to CO/CO₂, formaldehyde, acetaldehyde, acetic acid, allyl alcohol, and acrylic acid [115,116]. The minor byproducts of this process consist of C₄ and higher oxygenates and hydrocarbons [16]. These compounds, even at ppm level concentrations, adversely affect the production of acrolein and acrylic acid by inducing the formation of high-boiling point tarry compounds, causing fouling in the reactor, plugging transfer lines, and deteriorating desired product quality [16].

The catalytic cycle for acrolein synthesis, as proposed by Grasselli et al. [92] and later by Zhai et al. [81], follows a Mars-van Krevelen-type mechanism and comprises the following sequence of steps: (i) activation of the allylic C-H bond in propylene to form a surface allyl intermediate, (ii) incorporation of a lattice oxygen to the propylene-derived allyl species, (iii) cleavage of a C-H bond of the allyloxide species followed by acrolein desorption to generate a lattice vacancy site, and (iv) surface reoxidation with gas-phase oxygen. Results from steady-state kinetic measurements of propylene oxidation [72,77,81],
oxidation reactions of allyl alcohol, allyl azide, and allyl iodide as probe molecules [42,90], isotopic tracer experiments with deuterated propylene and allyl alcohol and, separately, oxygen-$^{18}$O [80,90,117,118], and DFT calculations [95,103,119] all support this mechanism. Based on mechanistic proposals for gas-phase reactions analogous to the ones involved in acrolein synthesis, Wong et al. [120] postulated an elementary-step kinetic model describing the formation and consumption of acrolein on a metal oxide catalyst with two acrolein-derived surface species [CH$_2$=O] and [CH$_2$=CHO] as the major precursors for the formation of side products including acrylic acid, acetone, acetaldehyde, acetic acid, formaldehyde, formic acid, CO, and CO$_2$. In the previous chapter, we developed a detailed reaction network and kinetic model that rigorously captures the formation and consumption of all C$_3$ and smaller products during propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K and proposed decarbonylation of aldehydic compounds, decarboxylation of carboxylic acids, and reactions of organic compounds with surface-adsorbed oxygen species as the three primary mechanisms for the formation of C$_1$ and C$_2$ products. In the same report, we proposed the existence of four different types of active sites on the surface of Bi$_2$Mo$_3$O$_{12}$ during propylene oxidation to acrolein: (i) nucleophilic lattice oxygen, (ii) electrophilic adsorbed oxygen, (iii) surface hydroxyl groups, and (iv) active sites for decarboxylation of carboxylic acids. The precursors and mechanisms for the formation of C$_4$ and higher byproducts on industrially relevant catalysts, however, remain elusive.

In this work, we report the evolution of product selectivity as a function of propylene conversion and initial synthesis rates of 20 C$_2$ – C$_6$ products observed at selectivities >0.0001% during propylene oxidation at 623 K in the presence of different co-fed probe molecules on a molybdenum-based catalyst promoted with cobalt and nickel.
The reaction rates were assessed under conditions that permit strict kinetic control at high propylene chemical conversions (0 – 70%) in a gradient-less recirculating batch reactor. We elucidate the reaction mechanisms, identify the existence and the involvement of relevant surface intermediates, and develop an extensive reaction network describing the formation of all C₂ – C₆ products and illustrating the underlying mechanisms for C-C bond cleavage and formation reactions. C-C bond cleavage reactions that lead to the formation of C₂ and C₁ products are shown to occur via three mechanisms: (i) the decarbonylation of aldehydes and decarboxylation of carboxylic acids; (ii) total oxidation reactions, and (iii) reactions of organic compounds with surface-adsorbed oxygen species. The formation of C₄ products (butadiene, crotonaldehyde, methyl vinyl ketone) is shown to occur via addition reactions between a propylene-derived surface allyl (C₃H₅) intermediate and formaldehyde. Similarly, C₆ byproducts (hexadiene, benzene) are formed via addition reactions of the same allyl (C₃H₅) species with propylene and allyl alcohol. C₅ products (methylfuran, furfural, pentadiene), on the other hand, are synthesized via an acrolein-derived surface ethenyl (C₂H₃) species in its reactions with acrolein and propylene. These mechanistic insights can guide process conditions and catalyst development to minimize the formation of undesired products.

3.2. Materials and methods

Catalytic reactions were performed in a recirculating batch reactor on a packed catalyst bed in a quartz tube (0.4 cm inner diameter, 0.32 cm³ catalyst bed volume) equipped with a K-type thermocouple penetrating the axial and radial centers of the catalyst bed. Isothermal reaction conditions were maintained using two cartridge heaters (Omega
Engineering Inc., CIR-2100, 600 W) inserted inside two split-tube aluminum sleeves regulated by a Watlow temperature controller (96 Series). Intra-particle and inter-phase mass and energy transport limitations, as well as transport limitations within the catalyst bed, were negligible as assessed by criteria originally proposed by Mears,[100] Anderson,[101] and Weisz-Prater[102]. The total volume of the reactor was 535 cm$^3$. A syringe pump (KDS Scientific, KDS-100) was employed to introduce the liquid to the feed. The inlet of the liquid port was maintained at 383 K, while all transfer lines was maintained at 433 K, which is above the boiling temperature of all co-feed molecules, to prevent condensation of the reactants and products. Our carbon balance closed within 98% for all experiments, indicating that condensation of reactants or products were not presented.

Catalyst particles with sizes between 180 and 425 μm (80–40 mesh) were obtained by pressing and sieving the catalyst powder. The catalyst bed was heated to 623 K from ambient conditions with a rate of 0.083 K s$^{-1}$ in dry air (0.83 cm$^3$ s$^{-1}$ at NTP conditions) prior to kinetic measurements. The catalytic oxidation of propylene was performed at 623 K with 13.0 mg catalyst diluted in 300 mg quartz sand (180 and 425 μm) with an initial feed composition of 7.5 kPa propylene (99.99%, Matheson TriGas), 57 kPa air (21% oxygen and 79% nitrogen, Ultra Zero Certified grade, Matheson TriGas), 9 kPa water (de-ionized), and 89 kPa helium (grade 4.7, Minneapolis Oxygen Company). For co-feed experiments, 0.1 – 1.0 M solutions of the following compounds were prepared in de-ionized water: formaldehyde (methanol-free, 16 wt/v% in water, Thermo-Scientific), acetaldehyde (99.5%, Sigma-Aldrich), propanal (99.5%, Sigma-Aldrich), acetone (99.7%, Sigma-Aldrich), acetic acid (99.5%, Sigma-Aldrich), acrylic acid (99.7%, Sigma-Aldrich), propionic acid (99%, Sigma-Aldrich), allyl alcohol (99%, Sigma-Aldrich), 1,5-hexadiene
(99%, Sigma-Aldrich). The initial molar ratio of the co-feed and water in the reacting mixture as assessed by gas chromatography always matched that of the stock solution. Acrolein was fed as a gas mixture of 2% acrolein and 16% nitrogen in helium (Matheson Trigas). For isotopic tracer experiments, propylene-$^{13}$C$_3$ (99 atom % $^{13}$C, Sigma-Aldrich), acrylic acid-$^{13}$C$_3$ (99 atom % $^{13}$C, Sigma-Aldrich), and H$_2^{18}$O (99 atom % $^{13}$C, Sigma-Aldrich) was used.

The initial reactant mixture with and without co-feeds was recirculated at 7 cm$^3$ s$^{-1}$ in the reactor for 30 minutes using a micro-recirculating pump (Metal Bellows, MB-21) before being diverted to the catalyst bed. The contents of the reacting gas mixture were sampled at three-minute intervals using a multi-position valve (Vici-Valco, EMT6ST16MWE) until 45 min and 35-minute intervals afterwards and separated using an Agilent 6890 gas chromatograph (GC) equipped with an HP-Plot/Q column (30.0 m x 320 μm x 0.20 μm) for all organic products in series with a MolSieve-5A column (30.0 m x 320 μm x 0.20 μm) for nitrogen, oxygen, and CO. The separated compounds were quantified using a flame ionization detector (FID) for all C$_3$ and smaller organic compounds, a thermal conductivity detector (TCD) for water, nitrogen, oxygen, CO, and CO$_2$, and mass spectrometry for all C$_4$ – C$_7$ products.

The net synthesis rate of a species was estimated by fitting a sextic polynomial to the molar quantity of that species as a function of reaction time and calculating the first order derivative. The net synthesis rate and selectivity of a species were extrapolated to zero propylene conversion to calculate the initial synthesis rate and initial selectivity of that product. The isotopologue distribution of selected organic species was determined from mass fragmentation patterns using the method described by Price and Iglesia [121].
The mass fragmentation patterns were corrected for the natural abundance of $^{13}$C atoms following the method described by Moseley [122].

3.3. Results and discussion

3.3.1. Product rank and stability analysis

Propylene oxidation over the catalyst used in this study (623 K, initial 7.5 kPa propylene, 12.0 kPa oxygen, 9.3 kPa water) results in the formation of 27 products (at ~70% propylene conversion) as listed in Table 3.1. The desired product, acrolein, is formed at ~88% selectivity. The major side products with selectivity exceeding 0.1% include formaldehyde, CO, CO$_2$ (C$_1$ products), acetaldehyde, acetic acid, ethylene (C$_2$ products), acrylic acid, allyl alcohol, propanal, and acetone (C$_3$ products). The minor products with selectivity exceeding 0.0001% include butadiene, crotonaldehyde, methyl vinyl ketone (C$_4$ products), linear isomers of pentadiene, 2- and 3-methylfuran, 2- and 3-furfural (C$_5$ products), linear isomers of hexadiene, benzene (C$_6$ products), toluene, benzaldehyde (C$_7$ products), three esters allyl acrylate, allyl acetate, and methyl acrylate, and trace amounts of methanol and acetylene.
Table 3.1. Rank, stability, and selectivity (on a carbon basis) of all products during propylene oxidation to acrolein on the mixed oxide catalyst in this study. Reaction parameters: 623 K, initial reaction mixture comprised of 7.5 kPa propylene, 12 kPa oxygen, and 9 kPa water.

<table>
<thead>
<tr>
<th>Rank and stability</th>
<th>Product</th>
<th>Carbon selectivity (%)</th>
<th>Carbon selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial(^a)</td>
<td>At 17% propylene conversion</td>
</tr>
<tr>
<td>Primary unstable</td>
<td>Allyl alcohol</td>
<td>60 ± 3</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Propanal</td>
<td>0.61 ± 0.03</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>0.10 ± 0.008</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Hexadiene isomers</td>
<td>0.15 ± 0.004</td>
<td>0.025</td>
</tr>
<tr>
<td>Primary and secondary unstable product</td>
<td>Acrolein</td>
<td>36 ± 3</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>Methyl vinyl ketone</td>
<td>(3.5 ± 1.4) x 10(^{-3})</td>
<td>14 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Pentadiene isomers</td>
<td>(2.4 ± 0.4) x 10(^{-3})</td>
<td>4.1 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>2- and 3-methylfuran</td>
<td>(8.7 ± 2.1) x 10(^{-4})</td>
<td>22 x 10(^{-4})</td>
</tr>
<tr>
<td>Primary and secondary stable product</td>
<td>CO</td>
<td>0.19 ± 0.09</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>0.65 ± 0.15</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>0.24 ± 0.01</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Acetaldehyde</td>
<td>0.41 ± 0.05</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>(6.0 ± 1.4) x 10(^{-3})</td>
<td>11 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Butadiene</td>
<td>(2.7 ± 1.2) x 10(^{-3})</td>
<td>6.7 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Crotonaldehyde</td>
<td>(1.1 ± 0.2) x 10(^{-3})</td>
<td>1.7 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>3-Furfural</td>
<td>(1.9 ± 0.2) x 10(^{-3})</td>
<td>5.0 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>2-Furfural</td>
<td>(1.2 ± 0.2) x 10(^{-3})</td>
<td>5.5 x 10(^{-3})</td>
</tr>
<tr>
<td>Secondary stable product</td>
<td>Acetic acid</td>
<td>0.02 ± 0.03</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Acrylic acid</td>
<td>0.03 ± 0.05</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>Methyl acrylate</td>
<td>-(^b)</td>
<td>1.0 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>-</td>
<td>8.4 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>-</td>
<td>4.4 x 10(^{-4})</td>
</tr>
<tr>
<td>Secondary unstable product</td>
<td>Benzene</td>
<td>0.003 ± 0.011</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Allyl acetate</td>
<td>(2.6 ± 3.4) x 10(^{-3})</td>
<td>9.1 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Allyl acrylate</td>
<td>(3.7 ± 4.2) x 10(^{-3})</td>
<td>11 x 10(^{-3})</td>
</tr>
</tbody>
</table>

\(^a\): Extrapolated values to zero propylene conversion. The standard deviations indicate errors from extrapolation, thus the initial selectivities of secondary products are statistically indistinguishable from zero.

\(^b\): Did not observe at propylene conversions below 5%.
The rank of each product in the reaction network and its stability is identified by the trend of its selectivity as a function of propylene conversion. The products are divided into five categories (Table 3.1 and Figure 3.1): (i) primary unstable products with continuously decreasing selectivities from initial non-zero values (e.g. allyl alcohol), (ii) primary and secondary unstable products with selectivities that attain a maximum from initial non-zero values (e.g. acrolein), (iii) primary and secondary stable products with continuously increasing selectivities from initial non-zero values (e.g. acetaldehyde), (iv) secondary unstable products with selectivities that attain a maximum from initial zero (e.g. benzene), and (v) secondary stable products with continuously increasing selectivities from initial zero values (e.g. acrylic acid). Allyl alcohol, propanal, acetone, and hexadiene are identified as primary unstable products, indicating that they are formed directly from propylene and react to generate other products as the reaction progresses. All $C_1$ products (formaldehyde, CO, and CO$_2$) are identified as primary and secondary stable products, suggesting that they are formed from the fragmentation and combustion of both propylene and other organic compounds in the system. Acrylic acid and acetic acid appear as secondary products, suggesting their formation only from other products. Due to the qualitative nature of this analysis, the assignment of each product in one of the five categories above does not reveal the kinetically insignificant formation and consumption pathways of that product. Instead, the detailed connectivity of the reaction network for all $C_6$ and smaller products is elucidated via a series of co-feed and isotopic tracer experiments.
3.3.2. Interconversion of C₃ compounds.

The interconversion of C₃ compounds (propylene, allyl alcohol, acrolein, acrylic acid, propanal, and acetone) is mediated by transformations that preserve the C-C backbone. We performed a series of co-feed experiments with acrolein, acrylic acid, propanal, propionic acid, and acetone, and an isotopic tracer experiment with allyl alcohol-$^{13}$C₀ – propylene-$^{13}$C₃ mixtures to probe the reaction pathways that mediate C₃ interconversion. The results from these studies are summarized in Figure 3.2, box a.
3.2.1. Sequential propylene oxidation to allyl alcohol, acrolein, and acrylic acid

The identification of allyl alcohol as a primary unstable product and acrolein as a primary and secondary unstable product suggests a pathway for acrolein synthesis from propylene via allyl alcohol as an intermediate. The Mars-van Krevelen-like mechanism for acrolein synthesis on bismuth molybdate oxides as proposed by Grasselli et al. [92] proceeds via a surface allyloxide intermediate. Bell and coworkers [74,81,103] recently proposed a similar mechanism for propylene oxidation on bismuth molybdates and bismuth-vanadium-molybdenum mixed oxides. Burrington et al. [90] also investigated the oxidation of allyl alcohol on α-bismuth molybdate (Bi₂Mo₃O₁₂) in the presence of propylene and oxygen and noted the rapid oxidation of allyl alcohol to acrolein, illustrating the formation of a surface allyloxide intermediate from allyl alcohol.
To confirm the existence of an acrolein synthesis pathway involving allyl alcohol as an intermediate and to compare the relative rates of the two formation pathways of acrolein – from allyl alcohol and directly from propylene without an allyl alcohol intermediate – we performed an isotopic tracer experiment in which 0.7 kPa allyl alcohol-\(^{13}\)C\(_0\) (fully unlabeled allyl alcohol) was co-processed with 6 kPa propylene-\(^{13}\)C\(_3\) (fully \(^{13}\)C-labeled propylene), 12 kPa oxygen, and 8 kPa water. The isotopologue distribution of propylene remained 100% propylene-\(^{13}\)C\(_3\) up to 80% propylene conversion (Figure 3.3), illustrating the absence of propylene formation pathways from the reaction products. The isotopologue distributions of allyl alcohol and acrolein consisted of only \(^{13}\)C\(_0\) and \(^{13}\)C\(_3\) isotopologues at all propylene conversions up to 80% (Figure 3.3), confirming the absence of C-C bond formation reactions of C\(_2\) and C\(_1\) products to form either allyl alcohol or acrolein. The co-processed allyl alcohol-\(^{13}\)C\(_0\) was fully consumed at propylene conversions exceeding 10% with an initial consumption rate of \(~290\ \mu\text{mol min}^{-1} \ (\text{m}^2\text{cat})^{-1}\) (Figure 3.3). Concurrently, allyl alcohol-\(^{13}\)C\(_3\) was formed with an initial rate of \(~9.3\ \mu\text{mol min}^{-1} \ (\text{m}^2\text{cat})^{-1}\)\(^1\), demonstrating the rapid oxidation of allyl alcohol. The initial isotopologue distribution of acrolein consisted of \(~90\%\) acrolein-\(^{13}\)C\(_0\) (Figure 3.3), showing that acrolein is formed predominantly by the oxidation of propylene via an allyl alcohol intermediate.

Co-processing 2.0 kPa acrolein with a reaction mixture consisting initially of 6 kPa propylene, 16.5 kPa oxygen, and 8.4 kPa water increased the formation rate of acrylic acid from 0.0 to 1.1 \(\mu\text{mol min}^{-1} \ (\text{m}^2\text{cat})^{-1}\). This co-feed experiment, together with the assignment of acrylic acid as a secondary product, confirms the formation of acrylic acid from over-
oxidation of acrolein. Co-processing 0.26 kPa acrylic acid with 7.7 kPa propylene, 12.0 kPa oxygen, and 9.0 kPa water did not affect the initial formation rate of any C₃ products, showing the absence of rearrangement and reduction pathways of acrylic acid to other C₃ compounds.

3.3.2.2. Propylene oxidation to acetone and propanal

The assignment of propanal and acetone as primary unstable products suggests direct formation pathways of these two products from propylene oxidation. Decreasing the initial water amount from 7.4 to 2.2 kPa in the presence of 5.5 kPa propylene and 8.8 kPa...
oxygen decreased the initial formation rates of propanal from 0.082 to 0.044 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)) and of acetone from 0.041 to 0.023 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)), illustrating the positive dependency of the formation rates of propanal and acetone on water pressure. We observed a similar promotional effect of water pressure on the synthesis rate of acetone during propylene oxidation on Bi\(_2\)Mo\(_3\)O\(_{12}\) in Chapter 2 and proposed that surface hydroxyl groups catalyze the oxidation of propylene to acetone. We attribute the promotional effect of water pressure to the increase in the concentration of surface hydroxyl groups with increasing water pressure. Along the same lines, we postulate that surface hydroxyl groups act as active surface species for the formation of propanal and acetone on the catalyst used in this study. The proposed mechanism for the synthesis of propanal (or acetone) includes: (i) an addition reaction between propylene and a surface hydroxyl group to generate a surface 1-propoxide (2-propoxide) intermediate, (ii) cleavage of the \(\alpha\)C-H bond of the surface propoxide species followed by desorption of the propanal (acetone) product to form a lattice vacancy site, and (iii) surface reoxidation with gas-phase oxygen. This mechanism is in line with previously proposed mechanisms for propylene oxidation to acetone on Co-Mo and Sn-Mo mixed metal oxide catalysts [68,96,123]. Co-processing 17 Pa propanal and 26 Pa acetone, separately, with a reaction mixture consisting of 8 kPa propylene, 12 kPa oxygen, and 8 kPa water did not affect the initial synthesis rate of any other C\(_3\) products, illustrating the absence of oxidation pathways of propanal or acetone to other C\(_3\) products, most notably the oxidative dehydrogenation of propanal to acrolein.
3.3.3. Formation pathways of C₂ and C₁ products and mechanisms for C-C bond cleavage

3.3.3.1. C-C bond cleavage via decarbonylation and decarboxylation reactions

Co-processing 2.0 kPa acrolein and 0.26 kPa acrylic acid, separately, with a reaction mixture initially comprised of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased initial ethylene formation rates from 7.5 to 13.7 and 35.7 nmol min⁻¹ (m² cat)⁻¹, respectively, demonstrating the existence of fragmentation pathways of acrolein and acrylic acid to ethylene and C₁ compounds. Similar reaction pathways were observed during propylene oxidation on Bi₂Mo₃O₁₂ as shown in Chapter 2. We postulate that acrolein and acrylic acid undergo decarbonylation and decarboxylation reactions, respectively, to form a surface ethenyl (C₂H₃) intermediate which reacts additively with a surface hydrogen adatom to generate ethylene (Figure 3.2). The initial synthesis rate of acetaldehyde remained constant in both co-feed experiments, demonstrating that the ethenyl intermediate was not oxidized further to acetaldehyde. Addition reaction pathways of this ethenyl intermediate to form C₅ byproducts are discussed in Section 3.3.4. Formation pathways of C₄ and higher products and mechanisms of C-C bond formation.

Co-processing 0.017 kPa propanal and 0.017 kPa propionic acid, separately, with a reaction influent mixture of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased initial acetaldehyde formation rate from 0.63 to 1.11 and 0.90 µmol min⁻¹ (m² cat)⁻¹, respectively, demonstrating the decomposition pathways of propanal and propionic acid to acetaldehyde. We postulate that propanal and propionic acid decompose via decarbonylation and decarboxylation reactions, respectively, similar to the decomposition pathways of acrolein and acrylic acid, to form a surface ethyl (C₂H₅) intermediate which undergoes rapid oxidation to acetaldehyde (Figure 3.2). The mechanism for the oxidation
of this ethyl intermediate to acetaldehyde is proposed to resemble the oxidation of the surface allyl intermediate (C₅H₅) to acrolein [92].

Co-processing 0.42 kPa acetaldehyde and 0.08 kPa acetic acid, separately, with a reaction mixture comprising 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased initial formation rates of formaldehyde from 0.54 to 1.35 and 0.63 µmol min⁻¹ (m²cat)⁻¹, of CO from 0.58 to 1.07 and 0.67 µmol min⁻¹ (m²cat)⁻¹, and of CO₂ from 1.58 to 2.36 and 1.74 µmol min⁻¹ (m²cat)⁻¹, suggesting that acetaldehyde and acetic acid also participate in decarbonylation and decarboxylation reactions, respectively. We propose that the resulting surface C₁ intermediate undergoes subsequent oxidation reactions to form formaldehyde, CO, and CO₂. Co-processing 0.026 kPa acetone with the reaction mixture increased acetaldehyde initial formation rate from 0.63 to 0.75 µmol min⁻¹ (m²cat)⁻¹ and acetic acid initial formation rate from 0.00 to 0.20 µmol min⁻¹ (m²cat)⁻¹, illustrating the decomposition of acetone to acetaldehyde and acetic acid. Similar decomposition pathways of acetone were reported for a Bi₂Mo₃O₁₂ formulation [116]; we propose that acetone undergoes C-C bond cleavage to form a surface acetyl (CH₃CO) intermediate which can react with a surface hydrogen adatom to form acetaldehyde or is further oxidized to acetic acid.

The decomposition pathways of acrolein, propanal, acetaldehyde, acrylic acid, propionic acid, acetic acid, and acetone demonstrate cleavage of the C-C bond adjacent to a carbonyl group (acrolein, propanal, acetaldehyde, acetone) or a carboxyl group (acrylic acid, propionic acid, acetic acid) as one mechanism for the fragmentation of the carbon backbone of propylene and the formation of C₂ and C₁ byproducts. Figure 3.4 details a proposed step-wise mechanism for the decarbonylation of acrolein and decarboxylation of acrylic acid. An addition reaction between a nucleophilic lattice oxygen center, the
proposed active site for the formation of acrolein from propylene on bismuth molybdate oxides [92], and the electrophilic C=O center on acrolein forms a surface chemisorbed acrolein species. This chemisorbed acrolein species can undergo one of three transformations: (i) cleavage of the carbon-lattice-oxygen-bond resulting in the desorption of acrolein, (ii) αC-H bond scission with assistance from an adjacent active site to form a surface acyl (C$_2$H$_3$CO) intermediate, and (iii) cleavage of the αC-C single bond with assistance from an adjacent active site to form a surface ethenyl (C$_2$H$_3$) species and a surface formyl (HCO) species. The surface acyl species can desorb as acrylic acid generating a lattice vacancy site. Serwicka et al. [97] noted the appearance of an IR band at 1715 cm$^{-1}$ and a group of bands between 1250 − 1400 cm$^{-1}$ in IR studies of acrolein adsorption at 383 K on molybdenum heteropoly acid (K$_3$PMo$_{12}$O$_{40}$) and assigned these bands to a C=O stretch and CH$_2$ vibrations, respectively, and proposed the existence of an acyl intermediate during acrolein adsorption and oxidation to acrylic acid. Tichy [98] proposed a similar mechanism for the formation of acrylic acid from acrolein on Mo-V oxide. The surface formyl species can react additively with a surface hydrogen adatom to form formaldehyde or undergo hydrogen abstraction to generate CO. Acrylic acid, similarly, chemisorbs via an addition reaction between a nucleophilic surface lattice oxygen and the C=O bond. Cleavage of the C-C single bond generates a surface ethenyl species (C$_2$H$_3$) and a surface carboxyl (OCOH) species which undergoes hydrogen abstraction to form CO$_2$. This mechanism is in agreement with all experimental observations in this report and the proposed reaction pathways of C$_3$ and smaller carbonyl and acidic compounds in our catalytic system.
3.3.2. C-C bond cleavage via reactions of surface adsorbed oxygen species and total combustion

Figure 3.3 shows the isotopologue distribution of acetaldehyde as a function of propylene conversion during the oxidation of 0.7 kPa allyl alcohol-$^{13}$C$_0$ and 6 kPa propylene-$^{13}$C$_3$ mixtures in the presence of 9 kPa oxygen and 8 kPa water. The isotopologue distribution of acetaldehyde extrapolated to zero propylene conversion contained 60% acetaldehyde-$^{13}$C$_0$, in contrast to the isotopologue distribution of acrolein which contained 90% acrolein-$^{13}$C$_0$, indicating the existence of parallel oxidation pathways from propylene and allyl alcohol to acetaldehyde. The proposed direct oxidation of
propylene to acetaldehyde is in agreement with the assignment of acetaldehyde as a primary and secondary product. The initial synthesis rate of acetaldehyde increased from 0.56, 0.63, to 0.80 μmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)), while that of acrolein increased from 40, 43, to 47 μmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)), as oxygen partial pressure was increased from 8.5, 12.2, to 17.2 kPa, respectively, showing that the formation rate of acetaldehyde depends more strongly on the oxygen partial pressure than the acrolein formation rate; this suggests an oxygen-mediated mechanism for acetaldehyde formation from propylene different from the Mars-van Krevelen mechanism for acrolein synthesis. Surface-adsorbed oxygen species have been observed via electron paramagnetic resonance (EPR) spectroscopy on oxide formulations such as MoO\(_3\), Bi\(_2\)Mo\(_3\)O\(_{12}\), and Bi\(_2\)MoO\(_6\) that are catalytically active for selective oxidation of propylene to acrolein [44,48–51]. Volodin and Cherkashin investigated the reaction of surface-adsorbed oxygen species on ZnO with gas phase methane at 90 K and reported the appearance of a new EPR signal attributed to a surface bound CH\(_3\) radical-like species, indicating that the adsorbed oxygen species caused facile dehydrogenation of methane [54]; this demonstrates the electrophilic nature of these species. The stoichiometric reaction of surface-adsorbed oxygen species with propylene on V\(_2\)O\(_5\) at room temperature yielded acetaldehyde (at 40% selectivity) and C\(_3\) oxygenates (propanal, propylene oxide, acetone, and acrolein) [52]. We postulate that surface-adsorbed oxygen species also catalyze the formation of acetaldehyde from propylene and allyl alcohol on the mixed metal oxide catalyst in this study. Reactions of organic compounds with surface-adsorbed oxygen species is another pathway for the fragmentation of the carbon backbone of propylene.

Co-processing 0.42 kPa acetaldehyde with a reaction mixture comprised of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased the initial formation rate of acetic
acid from 0.00 to 0.44 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)), confirming the over-oxidation of acetaldehyde to acetic acid. The formation pathways of acetic acid from acetaldehyde and acetone concur with the assignment of acetic acid as a secondary product.

The initial formation rates of all C\(_1\) products (formaldehyde, CO, and CO\(_2\)) in the oxidation of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water summed up to 2.7 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)) which is larger than the sum of the initial formation rates of all C\(_2\) products (ethylene, acetaldehyde, acetic acid), 0.64 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)). Co-processing 2.0 kPa acrolein to this reaction mixture increased the sum of the initial formation rates of all C\(_1\) products to 4.8 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)) while increasing the sum of the initial formation rates of all C\(_2\) products to 0.89 µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)). These two experiments demonstrate the existence of direct oxidation/combustion of propylene and acrolein to C\(_1\) products (C\(_3\) → 3C\(_1\)) in addition to the fragmentation of propylene and acrolein to C\(_2\) and C\(_1\) products (C\(_3\) → C\(_2\) + C\(_1\)). In the previous chapter, we noted that the direct oxidation of C\(_3\) compounds to C\(_1\) products is negligible during propylene oxidation to acrolein on Bi\(_2\)Mo\(_3\)O\(_{12}\) at 623 K. This discrepancy is attributed to the highly unselective nature of the industrial catalyst used in this study towards the formation of C\(_1\) products (sum of CO, CO\(_2\), and HCHO yields less than 3% at 25% propylene conversion) compared to Bi\(_2\)Mo\(_3\)O\(_{12}\) (sum of C\(_1\) yields 24% at 25% propylene conversion). The total combustion of organic compounds, which is kinetically minor on Bi\(_2\)Mo\(_3\)O\(_{12}\), becomes a major pathway for formaldehyde/CO/CO\(_2\) formation on the industrial formulation and represents the third mechanism for C-C bond cleavage during acrolein synthesis on the mixed metal oxide catalyst in this study.
3.3.4. Formation pathways of C₄ and higher products and mechanisms of C-C bond formation

3.3.4.1. Formation pathways of C₄ products via C₃H₅ surface intermediate

Co-processing 1.3 kPa of formaldehyde with the reaction mixture consisting of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased the initial formation rate of butadiene from 3.6 to 19 nmol min⁻¹ (m²cat)⁻¹, of crotonaldehyde from 0.53 to 9.1 nmol min⁻¹ (m²cat)⁻¹, and of methyl vinyl ketone from 4.2 to 6.4 nmol min⁻¹ (m²cat)⁻¹, demonstrating existence of formation pathways of C₄ products from formaldehyde. The isotopologue distribution of butadiene during the oxidation reactions of 0.7 kPa allyl alcohol-¹³C₀ and 6 kPa propylene-¹³C₃ mixtures in the presence of 9 kPa oxygen and 8 kPa water contained ~80% butadiene-¹³C₄ and ~15% butadiene-¹³C₃ at all propylene conversions up to 80% except at propylene conversions less than 10% in which case the mole fraction of butadiene-¹³C₀ was as high as 20% (Figure 3.5). The isotopologue distributions of crotonaldehyde and methyl vinyl ketone were not recorded due to their low selectivity (less than 0.01% at 70% propylene conversion). This observation suggests that butadiene was formed via an addition reaction of a C₃ species which primarily contained ¹³C₃ isotopologues and a C₁ species with a mixed ¹³C₀ and ¹³C₁ isotopologue distribution. The isotopologue distribution of propylene contained propylene-¹³C₃ at all conversions during the isotopic experiment as noted above (Section 3.3.2.1. Sequential propylene oxidation to allyl alcohol, acrolein, and acrylic acid, Figure 3.3); hence, we propose that butadiene, crotonaldehyde, and methyl vinyl ketone were formed via an addition reaction between formaldehyde and a propylene-derived surface species. The isotopologue
distribution of butadiene in this isotopic experiment at propylene conversions less than 10% contained up to 20% butadiene-$^{13}$C$_0$, indicating that the surface intermediate also contained $^{13}$C$_0$ isotopologues at these conversions. This description matches the identity of the surface allyl (C$_3$H$_5$) intermediate formed in the oxidation of the allyl alcohol – propylene mixture at low propylene conversions (less than 10%) via both hydrogen abstraction of propylene-$^{13}$C$_3$ and dehydroxylative chemisorption of allyl alcohol-$^{13}$C$_0$. At propylene conversions exceeding 10% the co-fed allyl alcohol was fully consumed (Figure 3.3); thus, the surface allyl intermediate contained primarily $^{13}$C$_3$ isotopologues. The formaldehyde reacts additively with the propylene-derived allyl (C$_3$H$_5$) intermediate in a

Figure 3.5. Isotopologue distributions of butadiene, benzene, furfural, and pentadiene linear isomers as a function of propylene conversion during oxidation reactions of 0.7 kPa allyl alcohol-$^{13}$C$_0$, 6 kPa propylene-$^{13}$C$_3$, 9 kPa oxygen, and 8 kPa water at 623 K.
Prins-type condensation reaction to generate a surface butenyl oxide intermediate which undergoes abstraction of either the $\alpha$-H (to the C-O bond) to form the C4 carbonyl byproducts or the $\beta$-H to form butadiene (Figure 3.6).

3.3.4.2. Formation pathways of C6 products via C3H5 surface intermediate

The assignment of hexadiene (lumping all linear isomers) as a primary unstable product indicates the direct formation of hexadiene from propylene. White et al. [113] and Massoth et al. [107] observed the selective formation of hexadiene on Bi2O3 during the
oxidation of propylene and proposed dimerization of propylene to hexadiene via a surface
propylene-derived allyl intermediate as the reaction mechanism. We propose that
propylene dimerization occurs on the mixed metal oxide catalyst used in this study to form
hexadiene, but to a much lesser extent compared to propylene oxidation to acrolein
considering the low selectivity of hexadiene. Co-processing 0.41 Pa 1,5-hexadiene, 0.45
Pa 1,3-hexadiene, and 0.53 Pa 2,4-hexadiene (~3x the maximum amount of hexadiene
formed in the absence of the co-feeds), separately, with a reaction mixture containing 6
kPa propylene, 9 kPa oxygen, and 8 kPa water increased the initial formation rate of
benzene from 7 to 27, 15, and 17 nmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)), respectively, confirming the
formation of benzene from hexadiene in agreement with the assignment of benzene as a
secondary product. We postulate that the linear isomers of hexadiene formed in propylene
dimerization undergo cyclization and subsequent oxidative dehydrogenation to form
benzene.

The isotopologue distribution of benzene during the oxidation of 0.7 kPa allyl
alcohol\(^{13}\text{C}_0\) and 6 kPa propylene\(^{13}\text{C}_3\) mixtures in the presence of 9 kPa oxygen and 8 kPa
water at propylene conversions exceeding 20% contained 70 – 80% benzene\(^{13}\text{C}_6\) (Figure
3.5), confirming the formation of benzene from the fully labeled propylene\(^{13}\text{C}_3\) via
hexadiene intermediates. At propylene conversions below 20%, the isotopologue
distribution of benzene contained up to 40% benzene\(^{13}\text{C}_0\) and benzene\(^{13}\text{C}_3\). This
observation suggests that the formation of hexadiene and, subsequently, of benzene occurs
via addition reactions between a surface allyl (C\(_3\)H\(_5\)) species and either propylene or allyl
alcohol (Figure 3.6). At propylene conversions less than 20% in the isotopic experiment
with allyl alcohol\(^{13}\text{C}_0\) and propylene\(^{13}\text{C}_3\), the surface allyl intermediate contained both
the $^{13}$C$_0$ isotopologue derived from the dehydroxylative chemisorption of allyl alcohol-$^{13}$C$_0$ and the $^{13}$C$_3$ isotopologue derived from propylene-$^{13}$C$_3$. Reactions of the surface allyl-$^{13}$C$_0$ species with allyl alcohol-$^{13}$C$_0$ to form hexadiene-$^{13}$C$_0$ and propylene-$^{13}$C$_3$ to form hexadiene-$^{13}$C$_3$ and those of the surface allyl-$^{13}$C$_3$ species with allyl alcohol-$^{13}$C$_0$ to form hexadiene-$^{13}$C$_3$ and propylene-$^{13}$C$_3$ to form hexadiene-$^{13}$C$_6$ explain the observed isotopologue distribution of benzene.

The proposed mechanisms for the formation pathways of C$_4$ and C$_6$ byproducts demonstrate that surface allyl (C$_3$H$_5$) species, derived from hydrogen abstraction of propylene or dehydroxylative chemisorption of allyl alcohol, constitute the primary surface-bound reactants for C-C bond formation reactions with compounds containing C=C (propylene, allyl alcohol) and C=O (formaldehyde) functionality. Co-processing 0.42 kPa acetaldehyde and 2.0 kPa acrolein, separately, with the reaction mixture did not increase the initial formation rates of pentadiene or hexadiene, showing that Prins-like condensation reactions of the surface allyl species and carbonyl compounds is limited to formaldehyde. This limitation is rationalized based on the absence of steric hindrance at the C=O center of formaldehyde compared to other carbonyl compounds.

3.3.4.3. Formation pathways of C$_5$ products via C$_2$H$_3$ surface intermediate

Co-processing 2.0 kPa of acrolein and 0.26 kPa acrylic acid, separately, with the reaction mixture consisting of 7 kPa propylene, 12 kPa oxygen, and 8 kPa water increased the initial formation rate of pentadiene (lumping all linear isomers) from 1.1 to 3.0 and 15 nmol min$^{-1}$ (m$^2$cat)$^{-1}$, of methylfuran (2- and 3- isomers) from 0.53 to 1.6 and 2.7 nmol min$^{-1}$ (m$^2$cat)$^{-1}$, and of furfural (2- and 3- isomers) from 1.8 to 6.1 and 3.2 nmol min$^{-1}$
(m²cat)⁻¹, respectively, demonstrating that C₅ products are formed from acrolein and acrylic acid.

The isotopologue distribution of 2-furfural during the oxidation of 0.7 kPa allyl alcohol-¹³C₀ and 6 kPa propylene-¹³C₃ mixtures in the presence of 9 kPa oxygen and 8 kPa water contained 40 – 70% furfural-¹³C₅ together with furfural-¹³C₀, furfural-¹³C₂, and furfural-¹³C₃, each at 10 – 20% selectivity (Figure 3.5). The mole fractions of furfural-¹³C₁ and furfural-¹³C₄ isotopologues were negligible at all propylene conversions. The isotopologue distributions of 3-furfural and 2- and 3-methylfuran (Figure 3.7) showed similar trends. Based on this observation, we propose that furfural and methylfuran isomers are formed via an addition reaction between acrolein and a surface ethenyl (C₂H₃) species derived from the decarbonylation of acrolein and decarboxylation of acrylic acid as discussed in Section 3.3.3. Formation pathways of C₂ and C₁ products and mechanisms for C-C bond cleavage above. The addition reaction produces a surface C₅ intermediate that undergoes, subsequently, cyclization, oxidative dehydrogenation, and either abstraction of a surface hydrogen adatom to generate methylfuran or further oxidation to furfural (Figure 3.6). The surface ethenyl species comprised only ¹³C₀ and ¹³C₂ isotopologues during the isotopic experiment with allyl alcohol-¹³C₀ and propylene-¹³C₃ since its precursors, acrolein and acrylic acid, contained only ¹³C₀ and ¹³C₃ isotopologues. Reactions of the ethenyl-¹³C₀ intermediate with acrolein-¹³C₀ and acrolein-¹³C₃ to form the ¹³C₀ and ¹³C₃ isotopologues of methylfuran and furfural, respectively, and those of the ethenyl-¹³C₂ intermediate with acrolein-¹³C₀ and acrolein-¹³C₃ to form the ¹³C₂ and ¹³C₅ isotopologues, respectively, explain the observed isotopologue distributions of methylfuran and furfural isomers.
In contrast to methylfuran and furfural isomers, the isotopologue distribution of pentadiene during the isotopic experiment with allyl alcohol-$^{13}$C$_0$ and propylene-$^{13}$C$_3$ contained only pentadienes-$^{13}$C$_3$ and pentadienes-$^{13}$C$_5$ (Figure 3.5), demonstrating that

Figure 3.7. Isotopologue distributions of 3-furfural, 2- and 3-methylfuran as a function of propylene conversion during oxidation reactions of 0.7 kPa allyl alcohol-$^{13}$C$_0$, 6 kPa propylene-$^{13}$C$_3$, 9 kPa oxygen, and 8 kPa water at 623 K.
pentadiene isomers were formed from an addition reaction between a surface ethenyl intermediate which contained only $^{13}$C0 and $^{13}$C2 isotopologues and propylene which contained only $^{13}$C3. This addition reaction produces a surface pentenyl (C$_5$H$_9$) intermediate which undergoes hydrogen abstraction to generate linear isomers of pentadiene (Figure 3.6). The mole fraction of pentadiene-$^{13}$C0 was 12% at ~9% propylene conversion, suggesting that the surface ethenyl intermediate can also react with allyl alcohol to form pentadiene. The complete consumption of the co-fed allyl alcohol at ~10% propylene conversion during the isotopic experiment with allyl alcohol-$^{13}$C0 and propylene-$^{13}$C3 is consistent with the decreasing mole fraction of pentadiene-$^{13}$C0 at propylene conversions exceeding 10%.

The second mechanism for C-C bond formation and, especially, for the appearance of C$_5$ hexadiene and cyclic oxygenate products in the partial oxidation of propylene, therefore, involves the addition reactions between the acrolein (acrylic acid)-derived surface ethenyl (C$_2$H$_3$) intermediate and organic compounds containing C=C bonds (propylene, allyl alcohol, acrolein).

3.3.5. Reversibility of water adsorption on the mixed metal oxide catalyst in this study

To probe the reversibility of water adsorption on the mixed metal oxide catalyst under reaction conditions, we performed an oxidation reaction of 8 kPa propylene with 12 kPa oxygen in the presence of 9 kPa H$_2^{18}$O and 1 kPa H$_2^{16}$O. The molar fraction of H$_2^{18}$O decreased with propylene conversion as H$_2^{16}$O was formed from the oxidation of propylene. The isotopologue distribution of acrolein, acetaldehyde, and acetone matched the isotopologue distribution of H$_2$O at propylene conversions as low as 3% (Figure 3.8);
Furthermore, the isotopologue distribution of CO$_2$, acrylic acid, and acetic acid matched the binomial distribution of H$_2$O isotopologues (Figure 3.9), demonstrating that oxygen atoms in the aldehyde and carboxylic acid products originate from a common pool of oxygen atoms that is equilibrated with oxygen atoms contained in water. The adsorption of water on a lattice oxygen – vacancy site pair provides a mechanism for the incorporation of oxygen atoms from water into the catalyst lattice site. The oxygen atoms of the lattice sites of the catalyst are, in turn, incorporated into the oxygenate products via the Mars-van Krevelen mechanism. The matching isotopologue distributions of the oxygenate products and water at propylene conversions as low as 3% (and all propylene conversions up to 30%) demonstrates the rapid and reversible adsorption of water on the mixed metal oxide catalyst under our reaction conditions.

Figure 3.8. Mole fractions of $^{18}$O isotopologues of water, acrolein, acetaldehyde, and acetone as a function of propylene conversion in the oxidation of 8 kPa propylene, 12 kPa oxygen, 9 kPa H$_2^{18}$O, and 1 kPa H$_2^{16}$O at 623 K in a gas-phase batch reactor on the mixed metal oxide catalyst in this study.
We consolidate our findings from our series of transient kinetic measurements, co-feed experiments, and isotopic tracer experiments into the mechanistic network in Figure 3.10 detailing the formation and consumption of 22 C_1 – C_6 gas phase species during the oxidation of propylene on a molybdenum-based mixed metal oxide catalyst doped with nickel and cobalt.
Figure 3.10. Mechanistic network for the oxidation of propylene on the molybdenum-based mixed metal oxide catalyst used in this research.
The mechanistic scheme represented in Figure 3.10 considers the oxidation of propylene to occur on lattice oxygen sites following a Mars-van Krevelen-type mechanism [39] comprising the following sequence of steps: (i) activation of the allylic C-H bond in propylene followed by incorporation of a lattice oxygen \((O_L)\) to form a surface allyl species \((C_3H_5O_L)\) (reaction 1), (ii) cleavage of a C-H bond of the surface allyl species followed by acrolein desorption to generate a lattice vacancy site \((V)\) (reaction 5), and (iii) surface reoxidation with gas-phase oxygen (reaction 2). Surface hydroxyl groups \((OH)\) desorb as water (reaction 39). This reaction mechanism is in agreement with the proposed mechanism for propylene oxidation on reducible bismuth-molybdenum-based mixed metal oxides by Grasselli and coworkers [42,92,124] and by Bell and coworkers [81,104] and is supported by kinetic measurements [72,77,81,83,124], oxidation studies with probe molecules [90,91], isotopic tracer experiments with deuterated propylene and oxygen-\(^{18}\)O [40,80,118,125,126], and DFT calculations [95,103,104].

The propylene-derived surface allyl species \((C_3H_5O_L)\) can either desorb with a surface hydrogen adatom to form allyl alcohol (reaction 6) or undergo C-H bond cleavage to form acrolein. This surface allyl species can also be formed by dehydroxylative adsorption of allyl alcohol on a lattice vacancy – lattice oxygen site pair (reaction 7) as evinced in oxidation reactions of propylene-\(^{13}\)C/allyl alcohol-\(^{12}\)C mixture. The same isotopic experiment, together with co-feed experiments with formaldehyde, demonstrated that this allyl intermediate \((C_3H_5O_L)\) reacts additively with formaldehyde to form butadiene (reaction 8) and crotonaldehyde (reaction 9), the observed C\(_4\) products. This surface allyl intermediate also reacts additively with propylene to form hexadienes (reaction 10) and eventually benzene (reaction 11), the observed C\(_6\) products.
Our mechanistic network also includes an acrolein- (reaction 14) and acrylic acid-derived (reaction 15) ethenyl intermediate (C\textsubscript{2}H\textsubscript{3}O\textsubscript{L}) which can (i) react with a surface hydrogen adatom to form ethylene (reaction 16), (ii) react additively with propylene to form pentadiene (reaction 17) or cyclopentene (reaction 19) and (iii) react with acrolein to form 2- and 3-methyl furan (reactions 21 and 23, respectively) and 3- and 2-furfural (reactions 25 and 27, respectively). Evidence supporting the postulated reaction pathways from acrolein and acrylic acid to C\textsubscript{5} products via a surface ethenyl intermediate includes the noted increase in the formation rates of C\textsubscript{5} products in co-feed experiments with acrolein and acrylic acid and the isotopologue distribution of C\textsubscript{5} products in experiments with propylene-\textsuperscript{13}C\textsubscript{3}/allyl alcohol-\textsuperscript{12}C\textsubscript{3} mixtures. Wong et al. [120] proposed a similar surface intermediate in their microkinetic model for propylene oxidation on multicomponent metal oxide catalysts to explain the formation of acetone, acetaldehyde, acetic acid, and C\textsubscript{1} products.

3.4. Conclusion

The selectivity trends of 25 products formed during the oxidation of 7.5 kPa propylene, 12 kPa oxygen, and 9 kPa water at 623 K on the mixed metal oxide industrial formulation catalyst used in this study up to 70% propylene conversion revealed that: (i) allyl alcohol, propanal, acetone, and hexadiene are primary unstable products, (ii) acrolein, methyl vinyl ketone, linear isomers of pentadiene, 2-, and 3-methylfuran are primary and secondary unstable products, (iii) CO, CO\textsubscript{2}, formaldehyde, acetaldehyde, ethylene, butadiene, crotonaldehyde, 2-, and 3-furfural are primary and secondary stable products, (iv) acetic acid, acrylic acid, methyl acrylate, toluene, and benzaldehyde are secondary
stable products, and (v) benzene, allyl acetate, and allyl acrylate are secondary unstable products.

Co-processing allyl alcohol and acrolein with the initial reaction gas mixture evinced the sequential oxidation of propylene to allyl alcohol, acrolein, and acrylic acid. Varying the initial amount of water in the influent gas mixture showed the positive dependence of acetone and propanal initial formation rates on water partial pressure, leading us to propose surface hydroxyl groups as active surface species for the formation of these two $C_3$ oxygenates. Co-processing three aldehydes (acrolein, propanal, acetaldehyde) and three carboxylic acids (acrylic acid, propionic acid, acetic acid), separately, with the reacting gas mixture revealed decarbonylation of aldehydes and decarboxylation of carboxylic acids as one mechanism for C-C bond cleavage to form $C_2$ and $C_1$ products. The strong dependency of acetaldehyde initial formation rate on oxygen partial pressure, compared to that of acrolein, implicates the reaction of propylene and surface-adsorbed oxygen species as the second mechanism for the fragmentation of C-C backbone. The excess formation of $C_1$ products (CO, CO$_2$, formaldehyde) compared to $C_2$ compounds (acetaldehyde, acetic acid, ethylene) suggests total oxidation of organic compounds to $C_1$ products as a third mechanism for the breaking of C-C bonds.

Co-feed experiments with formaldehyde and the transient isotopologue distribution of butadiene during oxidation reactions of 0.7 kPa allyl alcohol-$^{13}$C$_0$ and 6 kPa propylene-$^{13}$C$_3$ mixtures demonstrated the formation of $C_4$ products (butadiene, crotonaldehyde, methyl vinyl ketone) from the addition reaction of a propylene-derived surface allyl (C$_3$H$_5$) intermediate and formaldehyde. The transient isotopologue distribution of benzene in the same isotopic tracer experiment, together with results from hexadiene co-feed experiments,
confirmed that addition reactions of the surface allyl (C₃H₅) intermediate with allyl alcohol or propylene result in the formation of C₆ products (hexadiene linear isomers and benzene). These studies show that addition reactions of surface allyl species with C=C and C=O double bonds are a mechanism for C-C bond formation. Separate co-feed experiments of acrolein and acrylic acid, together with the transient isotopologue distributions of furfural, methylfuran, and pentadiene in the oxidation reaction of allyl alcohol-¹³C₀ and propylene-¹³C₃ mixtures, evinced the formation of C₅ products (pentadiene linear isomers, 2- and 3-methylfuran, and 2- and 3-furfural) from the addition reaction of an acrolein (acrylic acid)-derived surface ethenyl (C₂H₃) intermediate with propylene and acrolein. The addition reaction of this surface ethenyl species with organic compounds containing C=C double bonds constitutes the second mechanism for C-C bond formation and synthesis of C₄ and higher products during propylene oxidation.

The systematic assessment of the kinetic effects of various co-feeds and the transient evolution of isotopically labeled compounds in this study enables the mechanistic description of pathways mediating the formation and cleavage of C-C bonds during acrolein production at 623 K.
4.1. Introduction

A reaction kinetic model is a compilation of expressions for net synthesis rate of all compounds in the reacting mixture. The development of a kinetic model consists of three steps: (i) the construction of the reaction network which contains detailed pathways between all compounds in the system and thus indicates the number of formation and consumption terms in the rate expression for each compound, (ii) the identification of reaction mechanism for all pathways in the reaction network, collectively summarized in a mechanistic network, which indicates the functional form of each term in the rate expressions, and (iii) the estimation of the kinetic and thermodynamic parameters in the rate expressions such that the synthesis rates can be evaluated at different reaction conditions, establishing the predictive power of the kinetic model. The construction of a kinetic model, thus, constitutes a logical expansion of the studies of reaction and mechanistic network via codifying the qualitative information of the reaction mechanisms into numerical kinetic parameters and quantitative mechanistic descriptors that further refines our understandings of the reacting system.
Given the connectivity of the reaction network but without the detailed understanding of the reaction mechanisms, the rate expression of each pathway can be casted in the empirical form of power law kinetics, most notably pseudo-first-order kinetics. Kube et al. [28] constructed kinetic models for the oxidation of ethane and propane on three catalyst formulations: MoVTeNb tertiary oxide, vanadium oxide supported on SiO₂, and vanadium-free carbon nanotubes, using pseudo-first-order rate expressions in the organic reactant and zero-order in oxygen. The predicted selectivities of all observed C₁ – C₃ products as a function of the hydrocarbon conversions fit with experimental data for both ethane and propane oxidation on all three formulations, providing supports for the proposed reaction networks. The simplicity of the rate expressions does not limit the versatility of the pseudo-first-order kinetic model in extracting mechanistic information of oxidation reactions on metal oxide catalysts. The main utility of a pseudo-first-order kinetic model stems from assessing the relative magnitudes of the formation and consumption rates of a species in the reaction network, thus revealing its main precursors and products. The kinetic model of Kube et al. [28] for the oxidation of ethane on three distinct catalyst formulations identifies COₓ as the sole products of ethylene consumption on vanadium oxide supported on mesoporous silica and vanadium-free carbon nanotube, while acetic acid is the main product on MoVTeNb mixed oxide. An identical trend was observed for propane oxidation; propylene is shown to undergo rapid total oxidation to COₓ on vanadium oxide supported on mesoporous silica and carbon nanotube while it is oxidized selectively to acrylic acid on MoVTeNb mixed oxide. These observations correlated well with the measured selectivities of COₓ and carboxylic acids on the three formulations. The authors also identified combustion of
ethylene and propylene to be the main formation pathways of CO\textsubscript{x} on all three formulations by comparing the rate constants and direct fluxes for all total oxidation reactions. Mechanistic understanding of the oxidation reaction can be extracted from comparing the first-order rate constants across different reaction conditions and catalyst composition. Tu et al. [127] systematically introduced neutral silica networks on the surface of MoVTeNb mixed oxide in increasing quantity by controlled silylation and observed a decrease in the first-order rate constants for propane to CO\textsubscript{x}, acrylic acid to CO\textsubscript{x}, and acrylic acid to acetic acid during propane partial oxidation to acrylic acid. The decrease in rate constants correlates well with the decrease in BET surface area and pyridine desorption, suggesting that the effect of silylation on MoVTeNb mixed oxide is to eliminated surface hydroxyl groups which act as Brønsted acid sites.

Armed with the understanding of (i) the types of active sites on reducible metal oxides, (ii) the common transformations of organic compounds on metal oxide surfaces which retain, extend, or reduce the carbon backbone of the reactant, and (iii) the identities of recurring C\textsubscript{2} and C\textsubscript{3} surface intermediates that we discussed in Chapters 2 and 3, a kinetic model for oxidation reaction on metal oxide catalysts can be expanded to include the evolution of active surface species and their formation and consumption pathways. Miller and Bhan construct a kinetic model for acrolein oxidation on a vanadium-based multicomponent metal oxide formulation considering surface coverage of lattice oxygen, vacancy site, surface hydroxyl groups, and carbon-containing intermediates [128]. For each of the reactions in the kinetic model, a step-wise mechanism was proposed based on the known transformations of organic compounds on reducible metal oxide surface. The rate expression was then derived with the assumption that either (i) the cleavage of the first
C-H or C-C bond or (ii) the formation of the first C-C bond is the rate-limiting step. Linke et al. [129] and Savara et al. [130] followed a similar approach in their constructions of the kinetic models for the catalytic oxidation of ethane on Mo$_1$V$_{0.25}$Nb$_{0.12}$Pd$_{0.0005}$O$_x$ and benzyl alcohol on carbon-supported palladium nanoparticles, respectively.

The mechanistic network-based kinetic models retain all the predictive power of the pseudo-first-order kinetic models: validation and refinement of reaction network and identification of major and minor pathways [130–133]. The inclusion of surface species and intermediates significantly broadens the available mechanistic details from the kinetic model. The coverage of the surface-bound species and, thus, the state of the reducible oxide surface can be inferred readily from the kinetic model [134,135]. The knowledge of the evolution of surface species as a function of reaction conditions allows for expansion of the range of experiments available for simulation. The transient and isotopic tracer experiments that provide valuable information on identifying surface intermediates and reaction mechanisms (Chapter 3) can now assist in the estimation of kinetic parameters and validation of the kinetic model. Miller et al. [128] constructed a kinetic model for acrolein oxidation on a multicomponent metal oxide catalyst considering surface intermediates derived from acrolein and acrylic acid. They then forward simulated the evolution of all carbon isotopologues of 25 observable C$_1$ – C$_6$ products as a function of reaction time during a series of acrolein oxidation experiments in the presence of acrylic acid$_{13}$C$_3$ and observed quantitative fit between the simulated and experimental isotopologue distributions of all 25 products, verifying the degradation of acrylic acid to surface C$_2$ intermediates which act as precursors to other byproducts in the system. Suprun et al. [136] combined the kinetic model for 1-butene oxidation to acetic acid over VO$_x$ – TiO$_2$ with a
plug-flow reactor model, allowing them to simulate the evolution of molar amounts and isotopologue distributions of the products and reactants during switching and Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments. Goodness-of-fit between the simulated and experimental data rejected the kinetic model with CO₂ formation from 1-butene oxidation in favor of the kinetic model with acetic acid as the main precursor to CO₂. Balcaen et al. [137] utilized the same method to estimate the kinetic parameters in their kinetic model for the oxidative dehydrogenation of propane over vanadium-based commercial catalyst using experimental data from Temporal Analysis of Products experiments.

In this chapter, we develop two kinetic models for the oxidation of propylene on molybdenum-based mixed metal oxide catalysts. Based on the reaction network proposed for propylene oxidation on Bi₂Mo₃O₁₂ in Chapter 2, pseudo-first-order rate expressions in the oxygenate reactant were considered for all reaction pathways, promotional and inhibitory dependencies on water pressure were added to describe the kinetics of all steps that were affected by water. The resulting kinetic model quantitatively describes the kinetic behavior of all species and provides critical insights into the underlying mechanistic pathways involved in over-oxidation and carbon-carbon bond scission reactions on Bi₂Mo₃O₁₂ catalyst. We extend this kinetic mode by deriving the net synthesis rate of each product from the mechanistic network with a parametrization scheme based on a description of the catalyst surface in terms of lattice oxygen atoms, surface hydroxyl groups, and vacancy sites in addition to surface intermediates derived from C₁ – C₆ species and our proposed mechanistic scheme in Chapter 3 (Figure 3.10) to develop the second kinetic model for the oxidation of propylene on the molybdenum-based mixed metal oxide
catalyst used in Chapter 3. The kinetic parameters in the model were rigorously estimated from a set of 30 experimental oxidation reactions of propylene we conducted utilizing a gas phase recirculating gradient-less batch reactor at different reaction conditions and in the presence of various probe molecules. The kinetic model reveals the state of catalyst surface to be fully oxidized, i.e., the surface coverage of lattice oxygen atoms is greater than 0.90, while the sum of surface coverages of vacancy sites, surface hydroxyl groups, surface allyl species, and surface ethenyl species is less than 0.10 at all reaction conditions in our study. The kinetic model highlights the main formation and consumption pathways of the surface allyl species (C₃H₅O₅) and surface ethenyl species (C₂H₃O₅), the main precursors to C₄ – C₆ products.

4.2. Pseudo-first-order kinetic model of propylene oxidation on Bi₂Mo₃O₁₂

4.2.1. Development of kinetic model from reaction network

We developed a kinetic model for all observed C₁ – C₃ products during propylene oxidation on Bi₂Mo₃O₁₂ consistent with our proposed reaction network in Chapter 2 (Figure 2.6); the net synthesis rate of a species is formulated in typical fashion as the sum of rates from all formation pathways less the sum of rates from consumption pathways (Table 4.1). Ratios of reaction quotients to equilibrium constants for all reactions calculated at 623 K and 25% propylene conversion are much less than 1, reflecting that the reacting mixture was not approaching equilibrium thus the reverse reaction rates were not included in the rate expressions. We adopted a pseudo-first-order kinetic expression in the organic reactant for all reactions that were not promoted or inhibited by water. The reactions that were promoted by water were considered to have reaction rates with a first order
dependence on the organic reactant pressure and a first order dependence on water pressure while the reactions that were inhibited by water were considered to have inverse first order dependence on water pressure. The temporal evolution of eight C₁ – C₃ species during propylene oxidation was accurately captured by this pseudo-first-order kinetic model with seventeen rate parameters at all reaction conditions (>4000 data points). The estimated rate constants and resulting fits are summarized in Table 4.2 and in Figures Figure 4.1 to Figure 4.5. The presented kinetic model is refined by minimizing the number of necessary parameters while remaining statistically consistent with all reaction pathways identified from our experimental observations.

Since C₁ products besides COₓ were not observed, COₓ is proposed to be the byproduct for all decomposition reactions of C₃ compounds (propylene, acrolein, acrylic acid, acetone) to C₂ products (acetaldehyde, acetic acid, ethylene). The net synthesis rate of COₓ, thus, includes the rate of all these decomposition reactions (Equation 8, Table 4.1). COₓ is also formed from total combustion of acetaldehyde, acetone, and acetic acid; the stoichiometry of a C₂-₃ species reacting to form a COₓ species is appropriately considered.

An alternative kinetic model employing Langmuir-Hinshelwood rate expressions for the reactions that were inhibited by water was also investigated. The rate constants for reactions that were not inhibited by water are statistically indistinguishable from those rate constants where water inhibition was modeled via an inverse first-order dependence.
Table 4.1. Rate expressions for the net synthesis rates of eight gas-phase species during propylene oxidation on Bi₂Mo₃O₁₂ at 623 K.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Rate Expression</th>
</tr>
</thead>
</table>
| (1) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{C_2H_4}}{dt} = k_1 P_{C_3H_6} - (k_{11} + k_{17}) P_{C_2H_5CHO} - k_3 P_{C_2H_5CHO} P_{H_2O}
\] |
| (2) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{CH_3CHO}}{dt} = k_2 P_{C_3H_6} + k_3 P_{C_2H_5CHO} P_{H_2O} + k_6 \frac{P_{C_2H_5COOH}}{P_{H_2O}} + k_7 P_{CH_3COCH_3} - k_4 P_{CH_5CHO} P_{H_2O} - k_5 P_{CH_5CHO}
\] |
| (3) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{CH_3COCH_3}}{dt} = k_8 P_{C_3H_6} P_{H_2O} - (k_7 + k_9 + k_{10}) P_{CH_3COCH_3}
\] |
| (4) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{C_3H_6}}{dt} = -(k_1 + k_2 + k_{14} + k_{16}) P_{C_3H_6} - k_8 P_{C_3H_6} P_{H_2O}
\] |
| (5) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{C_2H_5COOH}}{dt} = k_{11} P_{C_2H_5CHO} - (k_6 + k_{12}) \frac{P_{C_2H_5COOH}}{P_{H_2O}} - k_{13} P_{C_2H_5COOH} P_{H_2O}
\] |
| | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{CH_3COOH}}{dt} = k_{14} P_{C_3H_6} + k_4 P_{CH_3CHO} P_{H_2O} + k_9 P_{CH_3COCH_3} + k_{13} P_{C_2H_5COOH} P_{H_2O} - k_{15} \frac{P_{CH_3COOH}}{P_{H_2O}}
\] |
| | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{C_3H_5}}{dt} = k_{16} P_{C_3H_6} + k_{17} P_{C_2H_5CHO} + k_{12} \frac{P_{C_2H_5COOH}}{P_{H_2O}}
\] |
| | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{COX}}{dt} = k_2 P_{C_3H_6} + k_3 P_{C_2H_5CHO} P_{H_2O} + k_6 \frac{P_{C_2H_5COOH}}{P_{H_2O}} + k_7 P_{CH_3COCH_3} + k_{14} P_{C_3H_6} + k_9 P_{CH_3COCH_3} + k_{13} P_{C_2H_5COOH} P_{H_2O} + k_{16} P_{C_3H_6} + k_{17} P_{C_2H_5CHO} + k_{12} \frac{P_{C_2H_5COOH}}{P_{H_2O}} + 2k_9 P_{CH_3CHO} + 3k_{10} P_{CH_3COCH_3} + 2k_{15} \frac{P_{CH_3COOH}}{P_{H_2O}}
\] |
Table 4.2. Estimated values for the kinetic parameters of the net rates of synthesis of eight species: acrolein, acetaldehyde, acetone, propylene, acrylic acid, acetic acid, ethylene, and CO\textsubscript{x} during propylene oxidation on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} at 623 K using the model presented in equations 1 – 8 of Table 4.1 and all collected kinetic data. The corresponding units for the parameters are: $k_1, k_2, k_5, k_7, k_9, k_{10}, k_{11}, k_{14}, k_{16}, k_{17}$: μmol min\(^{-1}\) (m\(^2\) cat\(^{-1}\)) kPa\(^{-1}\);
$k_3, k_4, k_8, k_{13}$: μmol min\(^{-1}\) (m\(^2\) cat\(^{-1}\)) kPa\(^{-2}\);
$k_6, k_{12}, k_{15}$: μmol min\(^{-1}\) (m\(^2\) cat\(^{-1}\)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated value</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$0.251 \pm 0.002$</td>
<td>propylene to acrolein</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$0.043 \pm 0.002$</td>
<td>propylene to acetaldehyde</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$0.028 \pm 0.003$</td>
<td>acrolein to acetaldehyde</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$0.015 \pm 0.006$</td>
<td>acetaldehyde to acetic acid</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$2.71 \pm 0.07$</td>
<td>acetaldehyde to CO\textsubscript{x}</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$12.4 \pm 0.5$</td>
<td>acrylic acid to acetaldehyde</td>
</tr>
<tr>
<td>$k_7$</td>
<td>$2.3 \pm 0.3$</td>
<td>acetone to acetaldehyde</td>
</tr>
<tr>
<td>$k_8$</td>
<td>$0.00376 \pm 0.00008$</td>
<td>propylene to acetone</td>
</tr>
<tr>
<td>$k_9$</td>
<td>$2.0 \pm 0.2$</td>
<td>acetone to acetic acid</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>$1.4 \pm 0.3$</td>
<td>acetone to CO\textsubscript{x}</td>
</tr>
<tr>
<td>$k_{11}$</td>
<td>$0.325 \pm 0.008$</td>
<td>acrolein to acrylic acid</td>
</tr>
<tr>
<td>$k_{12}$</td>
<td>$0.98 \pm 0.04$</td>
<td>acrylic acid to ethylene</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>$0.12 \pm 0.01$</td>
<td>acrylic acid to acetaldehyde</td>
</tr>
<tr>
<td>$k_{14}$</td>
<td>$0.016 \pm 0.001$</td>
<td>propylene to acetic acid</td>
</tr>
<tr>
<td>$k_{15}$</td>
<td>$10.8 \pm 0.3$</td>
<td>acetic acid to CO\textsubscript{x}</td>
</tr>
<tr>
<td>$k_{16}$</td>
<td>$0.00086 \pm 0.00017$</td>
<td>propylene to ethylene</td>
</tr>
<tr>
<td>$k_{17}$</td>
<td>$0.011 \pm 0.002$</td>
<td>acrolein to ethylene</td>
</tr>
</tbody>
</table>
Figure 4.1. Experimental and simulated molar amounts of C3 and smaller compounds with respect to time during propylene oxidation on 400 mg Bi2Mo3O12 at 623 K with initial reaction mixture consisting of 6 kPa propylene, 7 kPa oxygen, (●) (–––) 7 kPa, (◇) (––––) 4 kPa, and (□) (– – – –) 2 kPa water, separately.
Figure 4.2. Experimental and simulated molar amounts of C₃ and smaller compounds with respect to time during propylene oxidation on 400 mg Bi₂Mo₃O₁₂ at 623 K with initial reaction mixture consisting of 6 kPa propylene, 7 kPa oxygen, (Δ) (—) 7.4 kPa and 0.37 kPa, (○) (---) 8.7 kPa and 0.18 kPa, (⋆) (-----) 8.1 kPa and 0.09 kPa, (◇) (----) 3.0 kPa and 0.13 kPa, (□) (-----) 1.6 kPa and 0.12 kPa water and acetaldehyde, respectively.
Figure 4.3. Experimental and simulated molar amounts of C₃ and smaller compounds with respect to time during propylene oxidation on 400 mg Bi₂Mo₃O₁₂ at 623 K with initial reaction mixture consisting of 6 kPa propylene, 7 kPa oxygen, (Δ) (—) 7.0 kPa and 0.14 kPa, (○) (— — —) 7.2 kPa and 0.07 kPa, (★) (••••) 7.4 kPa and 0.04 kPa, (◇) (— — ——) 3.7 kPa and 0.15 kPa, (□) (——) 1.4 kPa and 0.12 kPa water and acetone, respectively.
Figure 4.4. Experimental and simulated molar amounts of C\textsubscript{3} and smaller compounds with respect to time during propylene oxidation on 400 mg Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} at 623 K with initial reaction mixture consisting of 6 kPa propylene, 7 kPa oxygen, (Δ) (-----) 5.0 kPa and 0.25 kPa, (○) (---) 5.9 kPa and 0.15 kPa, (★) (····) 6.7 kPa and 0.09 kPa, (◇) (------) 3.3 kPa and 0.15 kPa, (□) (----) 1.3 kPa and 0.09 kPa water and acrylic acid, respectively.
Figure 4.5. Experimental and simulated molar amounts of C₃ and smaller compounds with respect to time during propylene oxidation on 400 mg Bi₂Mo₃O₁₂ at 623 K with initial reaction mixture consisting of 6 kPa propylene, 7 kPa oxygen, (Δ) (---) 6.0 kPa and 0.30 kPa, (○) (— —) 6.6 kPa and 0.18 kPa, (☆) (••••) 7.1 kPa and 0.11 kPa, (◇) (-----) 2.7 kPa and 0.11 kPa, (□) (→→) 1.1 kPa and 0.08 kPa water and acetic acid, respectively.
4.2.2. Assessment of the relative magnitude of rates for individual pathways from the kinetic model developed

The rate constant for propylene conversion to acrolein is much larger (>5x) than those for propylene conversion to acetaldehyde, acetic acid, ethylene, and acetone, consistent with the observed high selectivity (~75% on a carbon basis at conversions <1%) to acrolein during propylene oxidation on Bi$_2$Mo$_3$O$_{12}$. The first order dependence on propylene partial pressure for acrolein formation rate is consistent with various kinetic measurements of acrolein synthesis on Bi$_2$Mo$_3$O$_{12}$ at similar conditions reported in the literature [77,81].

The predicted formation rate of acrylic acid from acrolein at 25% propylene conversion, calculated using the rate expression shown in Equation 5 of Table 4.1, is 0.26 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ which is comparable to the acrolein consumption rate to acetaldehyde at identical reaction conditions (0.21 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$). Acrolein, therefore, is consumed with nearly equal selectivity in over-oxidation and C-C bond cleavage reactions to form acrylic acid and acetaldehyde, respectively, on Bi$_2$Mo$_3$O$_{12}$ at 623 K.

The simulated acetaldehyde formation rate from acrolein at 25% chemical conversion (0.21 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$) is comparable to the acetaldehyde formation rates from propylene, 0.18 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, and from acrylic acid, 0.09 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$. The simulated acetaldehyde molar amounts (Figure 4.1), however, fail to capture the magnitude of this effect, possibly due to the high predicted contribution of acetaldehyde synthesis from acrylic acid which is inhibited by water. The predicted acetaldehyde synthesis rate from acetone at 25% propylene conversion is 0.06 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$,
showing that acetone is not a major precursor to acetaldehyde under our reaction conditions.

The rate constant for acetone conversion to acetic acid ($k_9$), 2.0, is higher than those for acetic acid formation from propylene ($k_{14}$), 0.016, acetaldehyde ($k_4$), 0.015, and acrylic acid ($k_{13}$), 0.12 with water partial pressures ranging from 2 to 7 kPa, demonstrating that acetone has a high intrinsic reactivity for acetic acid formation. The contribution of the acetone conversion pathway to acetic acid net synthesis rate at 25% propylene conversion, 0.051 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, however, is comparable to the contributions from propylene, 0.065 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, acetaldehyde, 0.020 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, and acrylic acid, 0.070 μmol min$^{-1}$ (m$^2$ cat)$^{-1}$, due to the higher concentrations of these compounds compared to acetone. Acetic acid, therefore, is synthesized at equal rates (at 25% propylene conversion) from its four precursors under our reaction conditions.

The total combustion reactions from propylene, acrolein, and acrylic acid to CO$_x$, when added to the kinetic model, have three rate constants of order $10^{-6}$ μmol min$^{-1}$ (m$^2$ cat)$^{-1}$ kPa$^{-1}$ which are much smaller than the corresponding rate constants for the consumption of these three species, justifying the absence of CO$_x$ formation pathways from total combustion of C$_3$ species in Figure 2.6. CO$_x$ are formed mainly from sequential steps: fragmentation of C$_3$ species (propylene, acrolein, acrylic acid, and acetone) to C$_2$ products (acetaldehyde, acetic acid, and ethylene) and the decomposition of these C$_2$ compounds. We postulate that the decomposition of acetaldehyde and acetic acid follow mechanistic pathways analogous to those for their respective C$_3$ compounds, acrolein and acrylic acid, in which the aldehyde undergoes decarbonylation and the acid undergoes decarboxylation to a surface C$_1$ intermediate which is rapidly oxidized to CO$_x$. 

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All attempts to fit the formation rate of ethylene to the experimental data failed except for a kinetic expression presented in Table 4.1 which includes terms describing ethylene formation pathways from propylene and acrolein, both of which are unaffected by water pressure. The proposed pathways for ethylene formation are consistent with chemical intuition: the highly oxidizing reaction environment renders deoxygenation reactions of acetaldehyde and acetic acid to ethylene improbable. Co-processing acetaldehyde and acetic acid with the reacting gas mixture also did not affect the synthesis rate of ethylene. Figure 4.6 shows a comparison between the net synthesis rate of ethylene observed experimentally and that predicted using the pseudo-first-order kinetic model shown in equation 7 as well as the contribution of individual reaction pathways to ethylene formation as a function of propylene conversion. The non-zero initial formation rate of ethylene, i.e., at zero product concentration, suggests a minor synthesis pathway from propylene. The major contributors to the synthesis rate of ethylene are those involving

![Graph showing observed and predicted net rate of ethylene synthesis](image)

Figure 4.6. Observed (●) and predicted (○) net rate of ethylene synthesis from equation 7 together with deconvolution of the net rate into its components from (□) propylene, (■) acrolein, and (■) acrylic acid.
acrolein and acrylic acid as reactants consistent with the assignment of ethylene as a secondary product.

4.3. Kinetic model of propylene oxidation on a multicomponent molybdenum-based catalyst

4.3.1. Parametrization and development of rate expressions

The 39 reactions in our mechanistic network presented in Chapter 3 (Figure 3.10) are presented as stoichiometrically balanced reactions in Table 4.3.

The formation of surface hydroxyl groups on molybdenum-based metal oxides is a necessary step in the catalytic cycle of propylene oxidation on reducible oxide catalysts via a Mars-van Krevelen mechanism [81] and hydroxyl groups have been observed experimentally via IR spectroscopy and in probe molecule adsorption studies [63–66]. We performed propylene oxidation on the mixed metal oxide catalyst in this study in the presence of H_2^{18}O-H_2^{16}O mixtures (Chapter 3) to demonstrate that surface hydroxyl groups are in quasi-equilibrium with gas phase water from a kinetics standpoint. The surface coverage of hydroxyl groups in the kinetic model, θ_{H\text{O}}, thus, is calculated from an algebraic equation as a function of gas-phase water pressure (Equation 26, Table 4.6).

Adams and Jennings [125] observed a decrease of 45% in the first-order rate constant for the oxidation of propylene to acrolein on bismuth molybdate at 723 K when they switched the reactant from C_3H_6 to C_3D_6, demonstrating that cleavage of a C-H bond is the rate-determining step during propylene oxidation under their reaction conditions. David and Keulks [77] and, recently, Zhai et al. [81] proposed rate expressions for the oxidation of propylene to acrolein with a quasi-equilibrated propylene adsorption step followed by rate-
Table 4.3. Reaction scheme for the kinetic model developed for propylene oxidation on molybdenum-based mixed metal oxide catalyst used in the study in Chapter 3. Notation: O_L: lattice oxygen site, V: vacancy site, HO: surface hydroxyl group, C_3H_5O_L: surface allyl intermediate, C_3H_6O_L: surface ethenyl intermediate, C_3H_5CHO: acrolein, C_2H_5COOH: acrylic acid, C_3H_6OH: allyl alcohol, C_3H_5CHO: crotonaldehyde, C_5H_8: cyclopentene, 2-C_4H_5OCH_3: 2-methyl furan, 2-C_4H_5CHO: 2-furfural.

| (1) | C_3H_6 + 2 O_L → C_3H_5O_L + HO |
| (1b) | 2 HO ⇋ H_2O + O_L + V |
| (1c) | k_1 |
| (2) | O_2 + 2 V → 2 O_L |
| (3) | C_2H_3CHO + O_L → C_2H_3COOH + V |
| (4) | C_3H_5COOH + 3 O_2 → 3 CO_2 + 2 H_2O |
| (5) | C_3H_5O_L + HO → C_3H_5OH + O_L |
| (6) | C_3H_5O_L + HO → C_3H_5OH + O_L |
| (7) | C_3H_5OH + V + O_L → C_3H_5O_L + HO |
| (8) | C_3H_5O_L + HCHO + V → C_4H_6 + HO + O_L |
| (9) | C_3H_5O_L + HCHO → C_3H_5CHO + HO |
| (10) | C_3H_5O_L + C_3H_6 → C_4H_10 + HO |
| (11) | C_4H_10 + 4 O_L → C_6H_6 + 4 HO |
| (12) | C_6H_6 → C_4H_6 + C_2H_4 |
| (13) | C_6H_6 + 7.5 O_2 → 6 CO_2 + 3 H_2O |
| (14) | C_2H_3CHO + 2 O_L → C_2H_5O_L + CO + HO |
| (15) | C_2H_5COOH + 2 O_L → C_2H_5O_L + CO_2 + HO |
| (16) | C_2H_5O_L + HO → C_2H_4 + 2 O_L |
| (17) | C_2H_5O_L + C_3H_6 → C_3H_8 + HO |
| (18) | C_3H_8 + 7 O_2 → 5 CO_2 + 4 H_2O |
| (19) | C_2H_5O_L + C_3H_6 → cC_3H_8 + HO |
| (20) | cC_3H_8 + 7 O_2 → 5 CO_2 + 4 H_2O |
| (21) | C_2H_5O_L + C_2H_3CHO → 2-C_4H_5OCH_3 + HO |
| (22) | 2-C_4H_5OCH_3 + 6 O_2 → 5 CO_2 + 3 H_2O |
determining C-H bond cleavage. Thus, we propose that propylene adsorbs on a lattice oxygen site in a quasi-equilibrated step and subsequently reacts with an adjacent lattice oxygen site, resulting in a rate expression containing a product of propylene partial pressure and a square of the surface coverage of lattice oxygen (entry 1b, Table 4.3 and entry 1, Table 4.4). The rate constant in this rate expression is, thus, an apparent kinetic parameter consisting of a product of an equilibrium constant for propylene adsorption and the rate constant for the C-H bond breaking event. We propose a similar reaction sequence, that is a reactant adsorbed on a lattice oxygen site in a quasi-equilibrated step reacting with an adjacent lattice oxygen site in a rate-determining step to form a reactive intermediate that undergoes rapid successive reactions to form products for the oxidation of, acrolein to

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(23)</td>
<td>C_2H_3O_L + C_2H_3CHO → 3-C_4H_3OCH_3 + HO</td>
</tr>
<tr>
<td>(24)</td>
<td>3-C_4H_3OCH_3 + 6 O_2 → 5 CO_2 + 3 H_2O</td>
</tr>
<tr>
<td>(25)</td>
<td>C_2H_3O_L + C_2H_3CHO + 3 O_L → 3-C_4H_3OCHO + 3 HO + V</td>
</tr>
<tr>
<td>(26)</td>
<td>3-C_4H_3OCHO + 5 O_2 → 5 CO_2 + 2 H_2O</td>
</tr>
<tr>
<td>(27)</td>
<td>C_2H_3O_L + C_2H_3CHO + 3 O_L → 2-C_4H_3OCHO + 3 HO + V</td>
</tr>
<tr>
<td>(28)</td>
<td>2-C_4H_3OCHO + 5 O_2 → 5 CO_2 + 2 H_2O</td>
</tr>
<tr>
<td>(29)</td>
<td>C_3H_6 + O_L → C_2H_5CHO + V</td>
</tr>
<tr>
<td>(30)</td>
<td>C_2H_5CHO + 3 O_L → CH_3CHO + CO + 2 HO + V</td>
</tr>
<tr>
<td>(31)</td>
<td>C_2H_5CHO + 4 O_2 → 3 CO_2 + 3 H_2O</td>
</tr>
<tr>
<td>(32)</td>
<td>C_3H_6 + O_L → CH_3COCH_3 + V</td>
</tr>
<tr>
<td>(33)</td>
<td>CH_3COCH_3 + 2 O_L → CH_3COOH + HCHO + 2 V</td>
</tr>
<tr>
<td>(34)</td>
<td>CH_3COCH_3 + 4 O_2 → 3 CO_2 + 3 H_2O</td>
</tr>
<tr>
<td>(35)</td>
<td>C_3H_6 + O_2 → CH_3CHO + HCHO</td>
</tr>
<tr>
<td>(36)</td>
<td>C_3H_5OH + 0.5 O_2 → CH_3CHO + HCHO</td>
</tr>
<tr>
<td>(37)</td>
<td>CH_3CHO + O_L → CH_3COOH + V</td>
</tr>
<tr>
<td>(38)</td>
<td>CH_3COOH + 2 O_2 → 2 CO_2 + 2 H_2O</td>
</tr>
<tr>
<td>(39)</td>
<td>2 HO ⇋ H_2O + O_L + V</td>
</tr>
</tbody>
</table>
acrylic acid (reaction 3, Table 4.3), acetaldehyde to acetic acid (reaction 37), propanal to acetaldehyde (reaction 30), acetone to acetic acid (reaction 33), hexadiene to benzene (reaction 14) and butadiene and ethylene (reaction 15), and the decarbonylation of acrolein and decarboxylation of acrylic acid to the surface ethenyl species (C₂H₅OCH₃), generating their respective rate expressions listed in Table 4.4 (entries 3, 37, 30, 33, 14, and 15).

Table 4.4. Rate equations for the kinetic model based on the reactions in Table 4.3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>r₁ = 0.5 × k₉₃₆₋₉₃₅ P₉₃₀ H₆O₅</td>
<td>r₂₀ = k₉₅₈₋₉₅₈ P₉₅₈</td>
</tr>
<tr>
<td>r₂ = k₀₂ P₀₂ V</td>
<td>r₂₁ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₃ = k₉₂₃₋₉₂₃ C₉₂₃ P₉₂₃ H₃CHO H₆O₅</td>
<td>r₂₂ = k₂₄₃₋₂₄₃ P₂₉₂ H₃OCH₃</td>
</tr>
<tr>
<td>r₄ = k₉₂₃₋₉₂₃ C₉₂₃ P₂₉₂ H₃OCH₃</td>
<td>r₂₃ = 0.5 × k₂₉₂₋₃₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₅ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₄ = k₃₉₂₃₋₃₄₉₃₂₇ P₃₉₂ H₃OCH₃</td>
</tr>
<tr>
<td>r₆ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₅ = 0.5 × k₂₉₂₋₃₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₇ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₆ = k₃₉₂₃₋₃₄₉₃₂₇ P₃₉₂ H₃OCH₃</td>
</tr>
<tr>
<td>r₈ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₇ = 0.5 × k₂₉₂₋₃₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₉ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₈ = k₂₄₃₋₃₄₉₃₂₇ P₂₉₂ H₃OCH₃</td>
</tr>
<tr>
<td>r₁₀ = 0.5 × k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₂₉ = k₃₉₂₃₋₂₄₉₃₂₇ P₉₂₃ H₃OCH₃</td>
</tr>
<tr>
<td>r₁₁ = k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₃₀ = k₂₉₂₋₂₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₂ = k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₃₁ = k₂₉₂₋₂₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₃ = k₉₂₃₋₉₂₃ C₉₂₃ H₆O₅</td>
<td>r₃₂ = k₂₉₂₋₂₄₉₃₂₇ H₃O₅ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₄ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₃ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₅ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₄ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₆ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₅ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₇ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₆ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₈ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₇ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
<tr>
<td>r₁₉ = 0.5 × k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
<td>r₃₈ = k₂₉₂₋₂₄₉₃₂₇ P₂₉₂ H₃CHO</td>
</tr>
</tbody>
</table>
We propose a reaction between two surface species in an elementary step to form the product for the reactions of the surface allyl intermediate (C\textsubscript{3}H\textsubscript{5}O\textsubscript{L}) to acrolein (reaction 5) and allyl alcohol (reaction 6) and of the surface ethenyl intermediate (C\textsubscript{2}H\textsubscript{3}O\textsubscript{L}) to ethylene (reaction 16), generating the rate expressions for these reactions containing a product between the surface coverages of the corresponding two surface species (entry 5, 6, and 16, Table 4.4). We further propose an Eley–Rideal-type mechanism between a surface species and a gas-phase molecule as the rate-determining step to form reactive intermediates that undergo rapid conversion to the products for the reactions of the surface allyl intermediate (C\textsubscript{3}H\textsubscript{5}O\textsubscript{L}) with formaldehyde to form butadiene (reaction 8) and crotonaldehyde (reaction 9) and with propylene to form hexadiene (reaction 10), as well as reactions of the surface ethenyl intermediate (C\textsubscript{2}H\textsubscript{3}O\textsubscript{L}) with propylene to form pentadiene (reaction 17) and cyclopentene (reaction 19) and with acrolein to form 2- and 3-methyl furan and 2- and 3-furfurals (reactions 21, 23, 25, 27). Applying the pseudo-steady-state hypothesis for the reactive intermediates yielded the corresponding rate expressions (entries 8, 9,10, 17, 19, 21, 23, 25, and 27, Table 4.4). A similar Eley-Rideal mechanism is proposed for the addition reaction of propylene and surface hydroxyl groups to form surface 1- and 2-propyloxide intermediates which undergo rapid oxidation to form propanal and acetone, respectively, yielding the rate expressions for the formation of propanal and acetone shown in entries 29 and 31, Table 4.4. This mechanism is consistent with the proposed mechanism for the formation of acetone during propylene oxidation on Sn-Mo mixed oxide catalysts [67,68,96].

Co-feed experiments with 2-methylfuran, 2-furfural, and benzene demonstrated the consumption of these C\textsubscript{5} and C\textsubscript{6} products; we further observed the formation of C\textsubscript{7} and
higher products including toluene, benzaldehyde, benzoic acid, maleic anhydride, and phthalic anhydride. Since our kinetic model focuses on the formation and consumption of primary and secondary C\(_6\) and smaller products, we simplified the model to consider consumption of C\(_5\) and C\(_6\) species as total oxidation reactions (reactions 13, 18, 20, 22, 24, 26, and 28). Due to the low selectivity of the heavy C\(_4^+\) products (cumulative selectivity less than 0.1% on a carbon basis at 70% propylene conversion), the formation rate of C\(_1\) products from the minor C\(_4\) and higher compounds is expected to be much lower than that from propylene and the major C\(_3\) and smaller products; thus, this simplification does not significantly affect the values of the formation rates of the C\(_1\) products. We further simplified the model by adopting power-law kinetics for the rate expressions of the total oxidation of organic compounds to C\(_1\) products (entries 4, 13, 18, 20, 22, 24, 26, 28, 31, 34, and 38, Table 4.4). Since all reactions in the model are highly exothermic oxidation reactions with vanishingly small values of the approach to equilibrium at all reaction conditions employed in this study, we reduced the number of parameters in the model further by assuming that all reactions in the model are irreversible and thereby eliminated 38 overall equilibrium constants from the kinetic model.

4.3.2. Estimation of kinetic parameters

To estimate the 39 kinetic parameters of the model, we compiled a dataset totaling 15,000 data points consisting of molar amounts of 22 gas phase species at different reaction times from 30 batch reactions. The batch reactions were performed at 623 K with ~7 kPa initial propylene pressure, 8 – 18 kPa initial oxygen pressure, 4 – 13 kPa initial water pressure, and with co-feed of 12 different products, separately, including: formaldehyde,
Table 4.5. Initial composition of the reacting mixture for the oxidation of propylene at 623 K on the molybdenum-based mixed metal oxide catalyst used in Chapter 3 in the presence of different co-feed compounds. The reactor pressure was ~130 kPa with helium as make-up.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Propylene pressure / kPa</th>
<th>Oxygen pressure / kPa</th>
<th>Water pressure / kPa</th>
<th>Co-feed compound</th>
<th>Co-feed pressure / kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>8.3</td>
<td>12.1</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(2)</td>
<td>7.7</td>
<td>12.1</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3)</td>
<td>7.1</td>
<td>12.1</td>
<td>10.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(4)</td>
<td>7.2</td>
<td>14.8</td>
<td>9.6</td>
<td>Acrolein</td>
<td>1.2</td>
</tr>
<tr>
<td>(5)</td>
<td>7.2</td>
<td>12.0</td>
<td>12.7</td>
<td>Formaldehyde</td>
<td>1.1</td>
</tr>
<tr>
<td>(6)</td>
<td>7.2</td>
<td>12.1</td>
<td>11.8</td>
<td>Formaldehyde and benzene</td>
<td>1.1 and 0.005</td>
</tr>
<tr>
<td>(7)</td>
<td>7.1</td>
<td>12.0</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(8)</td>
<td>6.1</td>
<td>16.5</td>
<td>8.4</td>
<td>Acrolein</td>
<td>2.0</td>
</tr>
<tr>
<td>(9)</td>
<td>7.4</td>
<td>12.1</td>
<td>11.1</td>
<td>Formaldehyde</td>
<td>1.1</td>
</tr>
<tr>
<td>(10)</td>
<td>7.4</td>
<td>12.1</td>
<td>9.4</td>
<td>Acetaldehyde</td>
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<td>7.5</td>
<td>12.2</td>
<td>9.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(12)</td>
<td>7.5</td>
<td>12.2</td>
<td>9.0</td>
<td>Propanal</td>
<td>0.017</td>
</tr>
<tr>
<td>(13)</td>
<td>7.7</td>
<td>12.0</td>
<td>9.0</td>
<td>Acrylic acid</td>
<td>0.26</td>
</tr>
<tr>
<td>(14)</td>
<td>7.0</td>
<td>12.2</td>
<td>12.0</td>
<td>Formaldehyde</td>
<td>1.1</td>
</tr>
<tr>
<td>(15)</td>
<td>7.2</td>
<td>12.3</td>
<td>10.4</td>
<td>2-Methylfuran</td>
<td>0.00028</td>
</tr>
<tr>
<td>(16)</td>
<td>7.2</td>
<td>12.2</td>
<td>9.7</td>
<td>2-Furfural</td>
<td>0.00073</td>
</tr>
<tr>
<td>(17)</td>
<td>8.1</td>
<td>12.2</td>
<td>6.7</td>
<td>Acetic acid</td>
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<tr>
<td>(18)</td>
<td>8.8</td>
<td>12.2</td>
<td>7.5</td>
<td>Acetone</td>
<td>0.025</td>
</tr>
<tr>
<td>(19)</td>
<td>7.8</td>
<td>12.2</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(20)</td>
<td>8.1</td>
<td>17.2</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(21)</td>
<td>7.6</td>
<td>8.5</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(22)</td>
<td>5.5</td>
<td>8.6</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(23)</td>
<td>7.4</td>
<td>13.6</td>
<td>9.3</td>
<td>Acetic acid\textsuperscript{\textsuperscript{13}}C\textsubscript{2}</td>
<td>1.2</td>
</tr>
<tr>
<td>(24)</td>
<td>7.2</td>
<td>13.1</td>
<td>19.7</td>
<td>Acetaldehyde\textsuperscript{\textsuperscript{13}}C\textsubscript{2}</td>
<td>0.91</td>
</tr>
<tr>
<td>(25)</td>
<td>7.5</td>
<td>13.4</td>
<td>14.7</td>
<td>Acetaldehyde\textsuperscript{\textsuperscript{13}}C\textsubscript{2}</td>
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<tr>
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<td>8.2</td>
<td>12.1</td>
<td>4.2</td>
<td>Acrylic acid\textsuperscript{\textsuperscript{13}}C\textsubscript{3}</td>
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<tr>
<td>(27)</td>
<td>8.5</td>
<td>12.3</td>
<td>14.3</td>
<td>Formaldehyde\textsuperscript{\textsuperscript{13}}C</td>
<td>2.7</td>
</tr>
<tr>
<td>(28)</td>
<td>9.8</td>
<td>13.0</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(29)</td>
<td>9.3</td>
<td>13.0</td>
<td>6.6</td>
<td>Acrylic acid\textsuperscript{\textsuperscript{13}}C\textsubscript{3}</td>
<td>0.10</td>
</tr>
<tr>
<td>(30)</td>
<td>8.8</td>
<td>13.1</td>
<td>16.8</td>
<td>Acrylic acid\textsuperscript{\textsuperscript{13}}C\textsubscript{3}</td>
<td>1.2</td>
</tr>
</tbody>
</table>

acetaldehyde, acetic acid, acrolein, allyl alcohol, acrylic acid, propanal, acetone, propionic acid, 2-methyl furan, 2-furfural, and benzene. The reaction conditions for the batch
reactions in this study are summarized in Table 4.5. The procedure for the catalytic batch reaction has been described in Chapters 2 and 3.

The mass and site balance equations relevant for the kinetic model developed are summarized in Table 4.6. Since the C\(_1\) products (CO, CO\(_2\), formaldehyde) were lumped together, the molar amount of formaldehyde used in the rate expressions 8 and 9 of Table 4.4 were interpolated from the measured molar amount of formaldehyde in the experiments. We utilized Bayesian statistics employed in the Athena Visual Studio software package [138] to minimize the residuals between the observed amounts of the gas phase species in the batch reactions and the predicted amounts from the kinetic model. The objective function we utilized in this work is the sum of the natural logarithms of the square of residual. The values of 39 parameters in the kinetic model were estimated simultaneously with the full dataset and are tabulated in Table 4.7 and Figure 4.7.
Table 4.6. Mass balance of gas-phase species and site balance of surface species for the kinetic model for propylene oxidation on the molybdenum-based mixed metal oxide catalyst in Chapter 3 applied to a batch reactor. $S_{\text{cat}}$: surface area of the catalyst in the reactor.

\[
\begin{align*}
(1) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_2\text{H}_3\text{CHO}}}{\text{dt}} = -r_3 + 2r_5 - 2r_{14} - 2r_{21} - 2r_{23} - 2r_{25} - 2r_{27} \\
(2) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_2\text{H}_5\text{OH}}}{\text{dt}} = 2r_6 - 2r_7 - r_{36} \\
(3) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_7\text{H}_6}}{\text{dt}} = 2r_8 + r_{12} \\
(4) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_9\text{H}_{10}}}{\text{dt}} = 2r_{10} - r_{11} - r_{12} \\
(5) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_6\text{H}_6}}{\text{dt}} = r_{11} - r_{13} \\
(6) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_7\text{H}_8\text{CHO}}}{\text{dt}} = 2r_9 \\
(7) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_7\text{H}_8\text{COOH}}}{\text{dt}} = r_3 - r_4 - 2r_{15} \\
(8) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_6\text{H}_8}}{\text{dt}} = r_{12} + 2r_{16} \\
(9) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_7\text{H}_8}}{\text{dt}} = 2r_7 - r_{18} \\
(10) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_7\text{H}_8}}{\text{dt}} = 2r_{19} - r_{20} \\
(11) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{2\text{C}_6\text{H}_8\text{OCH}_3}}{\text{dt}} = 2r_{21} - r_{22} \\
(12) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{3\text{C}_6\text{H}_8\text{OCH}_3}}{\text{dt}} = 2r_{23} - r_{24} \\
(13) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{2\text{C}_6\text{H}_8\text{OCHO}}}{\text{dt}} = 2r_{25} - r_{26} \\
(14) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{2\text{C}_6\text{H}_8\text{OCHO}}}{\text{dt}} = 2r_{27} - r_{28} \\
(15) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{C}_2\text{H}_4\text{CHO}}}{\text{dt}} = r_{29} - r_{30} - r_{31} \\
(16) \quad & \frac{1}{S_{\text{cat}}} \frac{\text{dn}_{\text{CH}_3\text{COCH}_3}}{\text{dt}} = r_{32} - r_{33} - r_{34}
\end{align*}
\]
Table 4.6. (cont)

<table>
<thead>
<tr>
<th>Equation</th>
<th>Expression</th>
</tr>
</thead>
</table>
| (17) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{CH}_2\text{CHO}}}{dt} = r_{30} + r_{35} + r_{36} - r_{37}
\] |
| (18) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{CH}_3\text{COOH}}}{dt} = r_{37} - r_{38}
\] |
| (19) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{C}_2\text{H}_6}}{dt} = -2r_i - 2r_{10} - 2r_{17} - 2r_{19} - r_{29} - r_{32} - r_{35}
\] |
| (20) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{C}_2\text{i}}}{dt} = 2r_4 + 6r_{13} + 2r_{14} + 2r_{15} + 5r_{18} + 5r_{20} + 5r_{22} + 5r_{24} + 5r_{26}
+ 5r_{28} + r_{30} + 3r_{31} + 3r_{34} + r_{35} + r_{36} + 2r_{38}
\] |
| (21) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{O}_2}}{dt} = -r_2 - 3r_4 - 7.5r_{13} - 7r_{18} - 7r_{20} - 6r_{22} - 6r_{24} - 5r_{26} - 5r_{28}
- 4r_{31} - 4r_{34} - 4r_{35} - 0.5r_{36} - 2r_{38}
\] |
| (22) | \[
\frac{1}{S_{\text{cat}}} \frac{dn_{\text{H}_2\text{O}}}{dt} = r_i + 3r_4 + 2r_5 - r_6 + r_7 + r_8 + r_9 + r_{10} + r_{11} + 3r_{13} + r_{14} + r_{15}
-r_{16} + r_{17} + 4r_{18} + r_{19} + 4r_{20} + r_{21} + 3r_{22} + r_{23} + 2r_{24} + 3r_{25} + 2r_{26} + 3r_{27} + 3r_{28} + r_{30} + 3r_{31} + 3r_{34}
\] |
| (23) | \[
\frac{1}{S_{\text{cat}}} \frac{d\theta_{\text{O}_2}}{dt} = -3r_i + 2r_2 - r_3 - r_5 + r_6 - r_7 + 3r_8 + r_9 + r_{10} - 2r_{11} - 3r_{15} = 0
+ 3r_{16} + r_{17} + r_{19} + r_{21} + r_{23} - 2r_{25} - 2r_{27} - r_{29} = 0
\] |
| (24) | \[
\frac{1}{S_{\text{cat}}} \frac{d\theta_{\text{C}_2\text{H}_6}}{dt} = 2r_i - 2r_5 - 2r_6 + 2r_7 - 2r_8 - 2r_9 - 2r_{10} = 0
\] |
| (25) | \[
\frac{1}{S_{\text{cat}}} \frac{d\theta_{\text{C}_2\text{H}_4\text{O}_2}}{dt} = 2r_{14} + 2r_{15} - 2r_{16} - 2r_{17} - 2r_{19} - 2r_{21} - 2r_{23} - 2r_{25} - 2r_{27} = 0
\] |
| (26) | \[
\theta_{\text{HO}}^2 = K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}\theta_{\text{O}_2}\theta_{\text{V}}
\] |
| (27) | \[
\theta_{\text{V}} = 1 - \theta_{\text{O}_2} - \theta_{\text{HO}} - \theta_{\text{C}_2\text{H}_6\text{O}_2} - \theta_{\text{C}_2\text{H}_4\text{O}_2}
\] |
Table 4.7. Estimated values for the kinetic parameters of the rate expressions listed in Table 2 during propylene oxidation on the molybdenum-based mixed metal oxide catalyst used in Chapter 3 at 623 K using the model presented in Tables 4.4 and 4.6 with all collected kinetic data in Table 4.5. The rate constants have units of µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)) (kPa)\(^n\) with n=0 for \(kC3H5-C2H3CHO\), \(kC3H5-C3H5OH\), \(kC2H3-C2H4\) and n=1 for others.

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>Estimated values</th>
<th>Rate constant</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kC3H6-C3H5)</td>
<td>4.6 ± 0.16</td>
<td>(kC5H8-e)</td>
<td>1.3 ± 0.22</td>
</tr>
<tr>
<td>(kO2)</td>
<td>(1.9 \times 10^7 \pm 1.0 \times 10^7)</td>
<td>(kC2H3-2C4H30CH3)</td>
<td>(0.0096 \pm 9.5 \times 10^{-4})</td>
</tr>
<tr>
<td>(K_{H2O})</td>
<td>0.86</td>
<td>(k2C4H30CH3-e)</td>
<td>88 ± 5.1</td>
</tr>
<tr>
<td>(kC2H3CHO-C2H3COOH)</td>
<td>0.32 ± 0.012</td>
<td>(kC2H3-3C4H30CH3)</td>
<td>0.16 ± 0.052</td>
</tr>
<tr>
<td>(kC2H3COOH-e)</td>
<td>1.1 ± 0.042</td>
<td>(k3C4H30CH3-e)</td>
<td>930 ± 290</td>
</tr>
<tr>
<td>(kC3H5-C2H3CHO)</td>
<td>2.6×10(^5)</td>
<td>(kC2H3-3C4H30CHO)</td>
<td>0.10 ± 0.025</td>
</tr>
<tr>
<td>(kC3H5-C3H5OH)</td>
<td>(6.4 \times 10^6 \pm 2.4 \times 10^6)</td>
<td>(k3C4H30CHO-e)</td>
<td>66 ± 17</td>
</tr>
<tr>
<td>(kC3H5OH-C3H5)</td>
<td>(2.4 \times 10^6 \pm 1.4 \times 10^6)</td>
<td>(kC2H3-2C4H30CHO)</td>
<td>(0.028 \pm 0.0026)</td>
</tr>
<tr>
<td>(kC3H5-C4H6)</td>
<td>49 ± 1.5</td>
<td>(k2C4H30CHO-e)</td>
<td>12 ± 1.4</td>
</tr>
<tr>
<td>(kC3H5-C3H5CHO)</td>
<td>33 ± 0.95</td>
<td>(kC3H6-C2H3CHO)</td>
<td>0.84 ± 0.22</td>
</tr>
<tr>
<td>(kC3H5-C6H10)</td>
<td>18 ± 0.43</td>
<td>(kC2H5CHO-C2H3CHO)</td>
<td>(10^{14})</td>
</tr>
<tr>
<td>(kC6H10-C6H6)</td>
<td>120 ± 5.9</td>
<td>(kC2H5CHO-e)</td>
<td>120 ± 5.0</td>
</tr>
<tr>
<td>(kC6H10-C4C2)</td>
<td>33 ± 2.0</td>
<td>(kC3H6-C3HCOCH3)</td>
<td>0.13 ± 0.033</td>
</tr>
<tr>
<td>(kC6H6-e)</td>
<td>0.17 ± 0.079</td>
<td>(kC3H30CH3-C3H3COOH)</td>
<td>6.7 ± 0.42</td>
</tr>
<tr>
<td>(kC2H3CHO-C2H3)</td>
<td>0.012 ± 0.0013</td>
<td>(kC3H30CH3-e)</td>
<td>(10^{14})</td>
</tr>
<tr>
<td>(kC2H3COOH-C2H3)</td>
<td>0.16 ± 0.011</td>
<td>(kC3H6-C3HCHO)</td>
<td>(0.022 \pm 0.0093)</td>
</tr>
<tr>
<td>(kC2H3-C2H4)</td>
<td>6.7 ± 1.7</td>
<td>(kC3H30NH-C3H3CHO)</td>
<td>9.5 ± 1.1</td>
</tr>
<tr>
<td>(kC2H3-C5H8)</td>
<td>0.0093 ± 6.0 \times 10^{-4}</td>
<td>(kC3H30CHO-C3H3COOH)</td>
<td>1.9 ± 0.10</td>
</tr>
<tr>
<td>(kC5H8-e)</td>
<td>15 ± 0.92</td>
<td>(kC3H30CHO-e)</td>
<td>1.8 ± 0.16</td>
</tr>
<tr>
<td>(kC2H3-C5H8)</td>
<td>0.0016 ± 9.2 \times 10^{-5}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.7. Mechanistic network for the oxidation of propylene on the molybdenum-based mixed metal oxide catalyst used in Chapter 3. The number on top of each arrow is the estimated value for the kinetic parameters of the rate expressions listed in Table 4.4.
4.3.3. Statistical evaluation of the kinetic model

The model developed can be used to successfully predict the molar amounts of 22 compounds in the system at all propylene conversions up to 70% in the 30 batch reactions that we performed (Figures 4.8, 4.9, and 4.10) except for 2- and 3-methyl furan and crotonaldehyde at low propylene conversions (less than 20%). The model predicts well the molar amounts of the product in the presence and absence of that product co-fed to the initial reacting mixture, as demonstrated in Figures 4.8 and 4.9 for acrolein and acrylic acid, respectively, illustrating the ability of the kinetic model developed in capturing both the formation and consumption of the major oxidation products. We attribute the lack of fit between the kinetic model and the experimental data for 2- and 3-methylfuran to a missing formation pathway to these two C5 products; however, we currently do not possess mechanistic evidence to propose an alternative reaction pathway that is consistent with all the kinetic and isotopic data we have gathered for this study.

Two parameters, $k_{\text{C}_2\text{H}_5\text{CHO}-\text{CH}_3\text{CHO}}$ and $k_{\text{CH}_3\text{COCH}_3}$, have estimated values of $10^{-14}$ which is the arbitrarily set lower bound for the values of the kinetic parameters in the model, indicating that the data set we gathered for this study is insufficient to probe the kinetically minor pathway for the formation of acetaldehyde from propanal and the combustion of acetone. Hence, we omitted these two parameters in further statistical tests (vide infra).

The 95% confidence intervals of the estimated parameters in Table 5 are calculated from the 90% highest posterior probability interval of each parameter and are within 20% of the estimated value for most of the 37 kinetic parameters in the model. The 95%
confidence intervals for $K_{H2O}$ and $k_{C3H5-C2H3CHO}$ are indeterminate, indicating that the data set we gathered for this study did not contain information to uniquely bound these two parameters simultaneously with the other parameters. The values of $K_{H2O}$ and $k_{C3H5-C2H3CHO}$ were estimated to be $0.4 \pm 0.004$ and $0.24 \pm 0.002$ when all other parameters were fixed at their estimated values in Table 5, indicating that the bounds on the values of $K_{H2O}$ and $k_{C3H5-C2H3CHO}$ are small.
Figure 4.8. Experimental and simulated molar amounts of acrolein, allyl alcohol, butadiene, crotonaldehyde, hexadiene, and benzene as a function of reaction time during propylene oxidation on the molybdenum-based mixed metal oxide catalyst used in Chapter 3 at 623 K in 30 batch reactions listed in Table 4.5.
Figure 4.9. Experimental and simulated molar amounts of acrylic acid, ethylene, pentadiene, cyclopentene, 2-methylfuran, 3-methylfuran, 2-furfural, and 3-furfural as a function of reaction time during propylene oxidation on the molybdenum-based mixed metal oxide catalyst used in Chapter 3 at 623 K in 30 batch reactions listed in Table 4.5.
Figure 4.10. Experimental and simulated molar amounts of acrylic acid, ethylene, pentadiene, cyclopentene, 2-methylfuran, 3-methylfuran, 2-furfural, and 3-furfural as a function of reaction time during propylene oxidation on the molybdenum-based mixed metal oxide catalyst used in Chapter 3 at 623 K in 30 batch reactions listed in Table 4.5.
4.3.4. Model evaluation with isotopic tracer experiments

We performed a series of isotopic tracer experiments in which various amounts of acrylic acid-$^{13}$C$_3$ were co-processed with 7 kPa propylene, 12 kPa O$_2$, and 8 kPa H$_2$O (entries 26, 29, 30, Table 4.5) to further probe the kinetic model developed. Only acrolein-$^{13}$C$_0$ formed from the unlabeled propylene (Figure 4.11) was observed in the effluent. The isotopologue distribution of acrylic acid varied with propylene conversion (Figure 4.11) as the co-fed acrylic acid-$^{13}$C$_3$ was consumed and acrylic acid-$^{13}$C$_0$ was formed from unlabeled acrolein. The surface ethenyl intermediate (C$_2$H$_5$O$_L$) in these experiments, thus, contained only the ethenyl-$^{13}$C$_2$ derived from acrylic acid-$^{13}$C$_3$ and the ethenyl-$^{13}$C$_0$ derived from acrolein-$^{13}$C$_0$ and acrylic acid-$^{13}$C$_0$ (reactions 14 and 15, Table 4.3), resulting in the formation of C$_5$ products containing only isotopologues with either zero or two $^{13}$C atoms according to reactions of the ethenyl intermediate with propylene-$^{13}$C$_0$ or acrolein-$^{13}$C$_0$ (reactions 17, 19, 21, 23, and 25, Table 4.3). This prediction from the kinetic model is in agreement with our experimental observations (Figure 4.12). The isotopologue distributions of C$_5$ products shown in Figure 4.12 were obtained via forward simulation of

![Figure 4.11. Molar amounts of $^{13}$C isotopologues of acrolein and acrylic acid as a function of propylene conversion in the oxidation of 8 kPa propylene-$^{13}$C$_0$, 12 kPa oxygen, 8 kPa H$_2$O, and 0.6 kPa acrylic acid-$^{13}$C$_3$ at 623 K in a gas-phase batch reactor on the mixed metal oxide catalyst in this study.](image-url)
the model developed; specifically, using reactions 14 to 28 and the kinetic parameters reported in Table 4.7. The good agreement between the simulated isotopologue distribution of C₅ products with the experimentally obtained distribution further validates the accuracy of our kinetic model.

![Graphs showing molar amounts of isotopologues as a function of propylene conversion.](image)

Figure 4.12. Molar amounts of ¹³C isotopologues of pentadiene, 2-methyl furan, and 2-furfural as a function of propylene conversion in the oxidation of 8 kPa propylene-¹³C₀, 12 kPa oxygen, 8 kPa H₂¹⁸O, and 0.6 kPa acrylic acid-¹³C₃ at 623 K in a gas-phase batch reactor on the mixed metal oxide catalyst in this study. The solid lines represent predictions from simulation of the kinetic model.

4.3.5. Surface coverage of relevant species

Model predictions suggest that the surface coverage of lattice oxygen site (Oₗ) is greater than 0.90 at all propylene conversions up to 70%, indicating that the catalyst surface is fully oxidized under our reaction conditions (Figure 4.13). The surface coverage of the propylene-derived allyl intermediate (C₃H₅Oₗ) is on the order of 10⁻³ and decreases with
propylene conversion, demonstrating the reactive nature of this intermediate. The surface coverage of the ethenyl intermediate (C$_2$H$_3$O$_L$) increases with propylene conversion, illustrating the secondary nature of this intermediate.

The oxidation state of the catalyst surface is controlled by a balance between the reduction of the surface via the removal of lattice oxygen with organic compounds in the system via the Mars-van Krevelen mechanism and reoxidation of vacancy sites with gas-phase oxygen. The rate for propylene oxidation to form the surface allyl intermediate (reaction 1, Table 4.3) decreased from 15 to 4.2 µmol min$^{-1}$ (m$^2$cat)$^{-1}$ as propylene conversion increased from 3% to 70%. This rate is 10x – 1000x higher than the sum of the rates of the reactions of other organic compounds with lattice oxygen (reactions 3, 11, 14, 15, 37, Table 4.3) at all propylene conversions, demonstrating that the reaction of propylene and lattice oxygen to form the surface allyl (C$_3$H$_5$O$_L$) intermediate is the main pathway for the reduction of the catalyst surface. The rate constant for the reaction of propylene with lattice oxygen, $k_{C_3H_6-C_3H_5}$, 4.6 µmol min$^{-1}$ (m$^2$cat)$^{-1}$ kPa$^{-1}$, is six orders of

![Figure 4.13. Surface coverage of reactive species during propylene oxidation on the mixed metal oxide catalyst in this study with the initial reaction mixture consisting of 7.5 kPa propylene, 12 kPa oxygen, and 8 kPa water.](image-url)
magnitude smaller than the rate constant for the reoxidation of catalyst surface with gas
phase oxygen, \( k_{O_2} \), \( 1.9 \times 10^7 \pm 1.0 \times 10^7 \) µmol min\(^{-1}\) (m\(^2\)cat\(^{-1}\)) kPa\(^{-1}\), consistent with the
prediction from the model that the catalyst surface is fully oxidized at all propylene
conversions under our reaction conditions in this study.

We note that this is the preferred result for kinetic modeling of oxidation reactions
on reducible metal oxide catalyst following a Mars-van Krevelen mechanism. Atomic force
microscopy revealed the large scale reconstruction of MoO\(_3\) (010) surface under hydrogen
or methanol atmosphere resulting from crystallographic shear plane formation caused by a
high coverage of vacancy site [23,24], illustrating the ability of reducible metal oxides to
reconstruct under reducing environment. These reconstructions appear in the form of pit
formation with increasing depth exceeding five surface layers with decreasing oxygen
partial pressure. Furthermore, the steps generated along the pits align with the (001) plane
in oxygen-rich environment and with (100) plane in oxygen-deficit environment,
demonstrating the formation of different undercoordinated surface Mo sites as a function
of the gas phase composition. The observed increase in the uptake of hydrogen as
intercalates H\(_x\)MoO\(_3\) with increasing density of (h0l) surfaces demonstrates the difference
in chemisorption properties between the (h0l) planes and the (010) plane of MoO\(_3\) [139].
The kinetic parameters in the model rigorously are functions of the structure of the catalyst
surface, indicated by the coverage of lattice oxygen. The kinetics measurements used for
the estimation of kinetic parameters of the model should be collected at identical surface
coverage of lattice oxygen, most easily obtained with a fully oxidized catalyst surface.
4.3.6. Assessment of the relative magnitude of rates for individual pathways

The rate constant for the consumption of the surface allyl intermediate (C₃H₅O₅L) to form acrolein (reaction 5, Table 4.7), $k_{C3H5-C2H3CHO} = 2.6 \times 10^5 \, \text{µmol min}^{-1} (\text{m}^2\text{cat})^{-1}$, is five orders of magnitude higher than the rate constant for the formation of this intermediate from propylene, $k_{C3H6-C3H5} = 4.6 \, \text{µmol min}^{-1} (\text{m}^2\text{cat})^{-1} \, \text{kPa}^{-1}$ with the surface coverage of the lattice oxygen of order 1 at all reaction conditions. Similarly, the rate constants for the formation of the ethenyl intermediate (C₂H₃O₅L) from acrolein and acrylic acid, $k_{C2H3CHO-C2H3} = 0.012 \, \text{µmol min}^{-1} (\text{m}^2\text{cat})^{-1} \, \text{kPa}^{-1}$ and $k_{C2H3COOCH-C2H3} = 0.16 \, \text{µmol min}^{-1} (\text{m}^2\text{cat})^{-1} \, \text{kPa}^{-1}$, are an order of magnitude smaller than the rate constant for the main consumption pathway of the ethenyl intermediate to ethylene, $k_{C2H3-C2H4} = 6.7 \, \text{µmol min}^{-1} (\text{m}^2\text{cat})^{-1}$.

The consumption rate of the surface allyl intermediate (C₃H₅O₅L) to form acrolein decreased from 16 to 5.2 µmol min⁻¹ (m²cat)⁻¹ as propylene conversion increased from 3% to 70% in an oxidation reaction of 8 kPa propylene, 12 kPa oxygen, and 8 kPa water. In the same reaction, the consumption rate of this intermediate to form butadiene, crotonaldehyde, and hexadiene changed from $1.1 \times 10^{-5}$ to $2.0 \times 10^{-4}$, from $7.1 \times 10^{-6}$ to $1.3 \times 10^{-4}$, and from $1.0 \times 10^{-2}$ to $8.9 \times 10^{-4}$ µmol min⁻¹ (m²cat)⁻¹, respectively. Together with the high consumption rate of propylene to the surface allyl intermediate, from 15 to 4 µmol min⁻¹ (m²cat)⁻¹, compared to the consumption rate of propylene to propanal, from 0.35 to 0.12 µmol min⁻¹ (m²cat)⁻¹, acetone, from 0.05 to 0.02 µmol min⁻¹ (m²cat)⁻¹, and acetaldehyde, from 0.16 to 0.49 µmol min⁻¹ (m²cat)⁻¹, this result is consistent with the high selectivity of acrolein of ~88% at 70% propylene conversion as a primary product.

The rate constant for the reaction of the allyl species (C₃H₅O₅L) with formaldehyde to form butadiene and crotonaldehyde, the sum of $k_{C3H5-C4H6}$ and $k_{C3H5-C3H5CHO}$, 82 µmol
min\(^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), is of the same order of magnitude with the rate constant for the reaction of this allyl intermediate with propylene to form hexadiene, \(k_{\text{C3H5-C6H10}}\), 18 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), demonstrating the comparable reactivity of the surface allyl species with C=O and C=C bonds.

The rate constant for the consumption of acrolein to acrylic acid, \(k_{\text{C2H3CHO-C2H3COOH}}\), 0.32 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), is an order of magnitude higher than the rate constant for the consumption of acrolein to form the surface ethenyl intermediate, \(k_{\text{C2H3CHO-C2H3}}\), 0.012 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), indicating that ~95% of the consumed acrolein is converted to acrylic acid. The rate constant for the formation of the ethenyl intermediate from acrylic acid, \(k_{\text{C2H3CHO-C2H3}}\), 0.16 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), is higher than that from acrolein, \(k_{\text{C2H3CHO-C2H3}}\), 0.012 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), suggesting that decarboxylation reactions occur at faster rates than decarbonylation reactions on the mixed metal oxide in this study. The synthesis rate of the ethenyl intermediate from acrolein increased from \(1.7 \times 10^{-3}\) to \(0.021 \mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\) as propylene conversion increased from 3% to 70% in an oxidation reaction of 8 kPa propylene, 12 kPa oxygen, and 8 kPa water, while the ethenyl intermediate formation rate from acrylic acid increased from \(6.1 \times 10^{-5}\) to \(1.4 \times 10^{-3}\) \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\), demonstrating that acrolein is the main precursor for the ethenyl intermediate.

The rate constant for the reaction of the surface ethenyl species (C\(_2\)H\(_3\)O\(_L\)) with propylene, i.e., the sum of \(k_{\text{C2H3-C5H8}}\) and \(k_{\text{C2H3-C5H8}}\), 0.011 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), is an order of magnitude smaller than the rate constant for the reaction of this intermediate with acrolein, i.e., the sum of \(k_{\text{C2H3-2C4H30CH3}}\), \(k_{\text{C2H3-3C4H30CH3}}\), \(k_{\text{C2H3-2C4H30CHO}}\), and \(k_{\text{C2H3-3C4H30CHO}}\), 0.30 \(\mu\)mol \(\text{min}^{-1}\) (m\(^2\)cat\(^{-1}\) kPa\(^{-1}\), demonstrating the rapid reactivity of the surface
ethenyl species with the C=O bond of acrolein compared to the C=C bond of propylene. This result is in contrast with the equal reactivity of the surface allyl species with C=O bond of formaldehyde and C=C bond of propylene, highlighting the difference between these two key surface intermediates. The consumption rate of the surface ethenyl species to form ethylene increased from $2.7 \times 10^{-4}$ to $8.9 \times 10^{-3} \, \mu\text{mol min}^{-1} \,(\text{m}^2\text{cat})^{-1}$, to form pentadiene and cyclopentene increased from $5.8 \times 10^{-5}$ to $5.2 \times 10^{-4} \, \mu\text{mol min}^{-1} \,(\text{m}^2\text{cat})^{-1}$, and to form oxygenated C$_5$ products increased from $2.5 \times 10^{-5}$ to $2.8 \times 10^{-2} \, \mu\text{mol min}^{-1} \,(\text{m}^2\text{cat})^{-1}$ as propylene conversion increased from 3% to 70% in an oxidation reaction of 8 kPa propylene, 12 kPa oxygen, and 8 kPa water, demonstrating that the surface ethenyl intermediate primarily forms ethylene at propylene conversions below 20% and primarily forms oxygenated C$_5$ products beyond 20% conversion as acrolein concentration in the system increases.

4.4. Conclusion.

A pseudo-first-order kinetic model with additional promotional and inhibitory water dependences to account for the observed effects of water successfully captured the quantitative behavior of the molar amounts of all C$_3$ and smaller products in all co-feed experiments during propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K. The model predicted that acrolein is further oxidized at equal rates to acrylic acid and acetaldehyde and slightly fragmented to ethylene. A deconvolution of acetic acid synthesis rates showed that propylene, acetaldehyde, acetone, and acrylic acid contributed equally to the formation of acetic acid; acetone, however, is shown to have the highest pseudo-first-order rate constant for conversion to acetic acid, demonstrating that acetone has the highest intrinsic reactivity
for acetic acid synthesis. The kinetic model also shows that breakdown of propylene, acrolein, and acrylic acid to CO\(_x\) is insignificant; CO\(_x\), instead, are generated mainly from the fragmentation of C\(_3\) species to C\(_2\) products and from the total oxidation of C\(_2\) compounds.

A kinetic model consisting of 39 reactions detailing the formation and consumption of propylene, oxygen, water, and 19 C\(_1\) – C\(_6\) products was developed to quantitatively describe the kinetics of propylene oxidation on a molybdenum-based mixed metal oxide catalyst used in industrial practice. The reaction pathways in the model proposed are based on a description of the catalyst surface in terms of lattice oxygen atoms, surface hydroxyl groups, and vacancy sites. The kinetic model successfully captures the molar amounts of all 22 gas phase species at all propylene conversions up to 70% during propylene oxidation in 30 experiments we conducted in a gas phase recirculating batch reactor in the presence of various probe molecules, as well as the isotopologue distributions of C\(_5\) products in oxidation experiments of propylene-\(^{13}\)C\(_0\) – acrylic acid-\(^{13}\)C\(_3\) mixtures.

Simulations from the model reveal the fully oxidized nature of the catalyst surface during propylene oxidation at 623 K under all reaction conditions employed in this study, illustrating the rapid re-oxidation of surface vacancy sites with gas-phase oxygen compared to reactions of surface lattice oxygen atoms with organic compounds, most notably propylene. The model highlights the formation and consumption pathways of two key surface intermediates, an allyl species (C\(_3\)H\(_5\)O\(_L\)) and an ethenyl species (C\(_2\)H\(_3\)O\(_L\)), which act as precursors for all heavy C\(_4\) – C\(_6\) products. The model identifies the main formation route for the surface allyl species (C\(_3\)H\(_5\)O\(_L\)) to be the oxidation of propylene on a lattice oxygen site and the main consumption route for this intermediate to be its reaction with a
lattice oxygen atom to form the desired product acrolein. The surface allyl species can react in parallel pathways with equal reactivity with the C=O bond of formaldehyde and the C=C bond of propylene to form C₄ and C₆ products, respectively. The decarboxylation of acrylic acid on a lattice oxygen atom is identified as the most rapid pathway for the formation of the surface ethenyl species (C₂H₃O₅); while acrolein is demonstrated to be the main precursor of this surface intermediate via acrolein decarbonylation on a lattice oxygen atom due to the dominant concentration of acrolein in the system up to 70% propylene conversion compared to that of acrylic acid. The main product of the surface ethenyl species is identified to be ethylene at propylene conversions below 20% and oxygen-containing C₅ compounds at propylene conversions above 20%. The surface ethenyl species, in contrast to the surface allyl species, reacts one to two orders of magnitude more rapidly with the C=O bond of acrolein to form C₅ oxygenate byproducts than with the C=C bond of propylene to form hydrocarbon C₅ byproducts. This kinetic model can now serve as a starting point for the development of reactor models and optimization schemes for the partial oxidation of propylene to acrolein.
Chapter 5. Butanal hydrogenation on supported metal catalysts
for butanol production

5.1. Introduction

The worldwide market for n-butanol, an emerging biofuel and a precursor for the production of plastic monomers, e.g. n-butyl acrylate and n-butyl methacrylate, and specialty solvents, e.g. butyl glycol ethers and n-butyl acetate [140], was valued at $4.2 billion in 2017 and expected to reach $5.6 billion by 2022 [141]. The catalytic hydrogenation of butanal, notably on copper on zinc oxide formulations [142–145], remains the main synthesis pathway of this chemical. The main byproducts of this process include C₈ compounds, especially dibutyl ether and butyl butyrate [146]. Even though the commercial process for the manufacturing of butanol can achieve reaction yield of >99%, the presence of the C₈ compounds in trace quantities significantly complicates the purification of the desired product via azeotrope formation, leading to reduction of the overall yield of the process [147].

Promoted and supported copper on zinc oxide formulations constitute one class of catalyst formulations for the selective hydrogenation of aldehydes to alcohols [142–145]. While an extensive amount of studies dedicated to the understanding of COₓ hydrogenation on supported copper on zinc oxide formulations for methanol synthesis are available, the detailed reaction mechanism, the possibility of distinct sites for hydrogen chemisorption and COₓ adsorption, and the origins of the promotional effect of the zinc oxide on the activity and selectivity of the Cu/ZnO-based catalysts remain hotly-debated topics [148].
Kinetic measurements of methanol synthesis [149,150] and methanol steam reforming [151,152] on Cu/ZnO/Al₂O₃ catalysts agree with rate expressions deduced from a two-site model: one for hydrogen dissociative chemisorption and the other for CO₅ adsorption. Extensive adsorption studies of CO₅, H₂, methanol, and water on a commercial Cu/ZnO/Al₂O₃ catalyst [153] and individual components of the formulation [154], together with co-adsorption studies of the reactants on the commercial catalyst [155], revealed a mismatch between the theoretical isotherms for CO₅ adsorption in the presence of H₂ calculated from individual adsorption isotherms and the experimental data, excluding competitive adsorption of H₂ and CO₅. Edwards et al. studied the adsorption of CO₅-H₂ mixtures, methanol, formaldehyde, and formic acid on Cu/ZnO catalysts [156–158] using transmission infra-red spectroscopy and observed adsorption bands at 3520 and 1660 cm⁻¹ which were assigned to the formation of zinc hydroxyl and zinc hydride groups, respectively. The authors further observed stoichiometric hydrogenation of CO in the absence of hydrogen while the two bands at 3520 and 1660 cm⁻¹ were present and proposed that hydrogen dissociative adsorption on ZnO site is the first step in the catalytic cycle. In contrast, Arena et al. [159] performed TPR measurements of H₂, CO, and CO₂ adsorption, and catalytic testing of a series of Cu-ZnO/ZrO₂ formulations with systematic variation of the Cu and Zn content and observed a systematic increase in the amount of CO₂ adsorption and the conversion of CO₂ with increasing Zn content of the formulation. The authors proposed a dual-site nature of the reaction path with hydrogen chemisorption on Cu sites and CO₂ adsorption of ZnO basic sites. These studies support the proposition of distinct adsorption sites for hydrogen and CO₅ during methanol synthesis on Cu/ZnO-based formulations, even though the nature of the adsorption sites is unclear.
Hansel et al. [160] performed in-situ TEM experiments and observed reversible morphological changes of Cu nanocrystals supported on ZnO under reacting environments. Under hydrogen atmosphere, the exposed facets of the Cu nanoparticles were identified as (111), (110), and (100) low-index planes. Addition of water to the hydrogen gas transformed the Cu nanoparticles into a more spherical morphology with higher fraction of (110) and (100) facets, suggesting adsorption of water on different Cu facets drives the morphological changes of the Cu nanoparticles. The addition of CO, a stronger reductant, to the gas mixture, however, caused the Cu particles supported on ZnO to reshape into a disk-like structure with increasing contact with the ZnO; this reconstruction was not observed for Cu nanoparticles supported on SiO$_2$. This phenomenon was attributed to the lower free energy for the formation of oxygen vacancies on ZnO compared to SiO$_2$; the increased coverage of oxygen vacancies on ZnO in the presence of CO decreases the Cu/ZnO$_x$ interface energy and results in Cu wetting the ZnO surface. Further studies employing in-situ high resolution TEM, neutron diffraction experiments, and DFT calculations suggest the high activity of the Cu/ZnO formulation towards methanol synthesis originates from the presence of steps on Cu surfaces which are stabilized by bulk defects terminating at the surface and are in close vicinity to ZnO$_x$ [161]; the formation of these steps is a direct consequence of the morphological change of Cu nanoparticles under reducing conditions. Ovesen et al. [162] proposed a single-site mechanism for CO$_x$ hydrogenation on Cu/ZnO in which the hydrogenation reaction occurs exclusively on Cu sites and the role of the ZnO component of the formulation is to facilitate the formation of and stabilize the active morphologies of the Cu nanoparticles. DFT calculations on a Cu$_8$ cluster supported on ZnO [163,164] showed that although dissociative adsorption of H$_2$ on
ZnO sited does occur, hydrogen adatoms on Cu sites are responsible for the hydrogenation of CO$_x$. Microkinetic models with the assumption of a single active site, incorporating the structural changes of the catalyst as a function of reaction conditions, show good agreement with experimental data from kinetic measurements [162,165,166]. We utilize a supported Cu/ZnO formulation for the hydrogenation of butanal to butanol in this study and use proposals on the mechanism and site requirements for CO$_x$ hydrogenation discussed above as guidance in our postulations of the mechanism and kinetics for the reactions in this study.

In this work, we report the steady-state kinetic measurements for butanal hydrogenation to butanol at 413 K, as well as the evolution of product selectivity and initial synthesis rates of C$_4$ and C$_8$ byproducts during butanal hydrogenation at 473 K on a supported Cu/ZnO formulation. The reaction rates were assessed under conditions that permit strict kinetic control at high butanal chemical conversions (0 – 90%) in a gradient-less recirculating batch reactor. We propose a dual-site reaction mechanism in which hydrogen and butanal adsorb on distinct active sites consistent with the observed apparent butanal and hydrogen reaction orders from our kinetic measurements. We identify the direct disproportionation reaction of butanal to form butyl butyrate, the formation of dibutyl ether from butanol, and the sequential hydrogenation of 2-ethylhex-2-enal to 2-ethylhexanal and eventually 2-ethylhexanol. These findings can serve as a foundation for the development of a kinetic model for the hydrogenation of butanal on Cu/ZnO-based catalysts.
5.2. Materials and methods

5.2.1. Catalyst preparation and pretreatment

A sample of a Cu/ZnO formulation was obtained containing 50-70% ZnO, 25-40% CuO, 5-15% CaAl$_2$O$_4$, and < 5% graphite. The catalyst was pelletized and sieved between 40-80 mesh (180-420 mm). An intrapellet physical mixture were prepared by mixing the catalyst powder with hexagonal boron nitride (Sigma Aldrich, 98%, ~1 μm) powder using an agate mortar and pestle and then pelleting, crushing, and sieving the mixture to obtain 180-420 μm aggregates. The catalyst was reduced in 5% H$_2$ (Minneapolis Oxygen, 99.999%) in He (Minneapolis Oxygen, 99.999%) at 473 K (with a ramping rate of ~0.017 K s$^{-1}$ from RT) for 3 h and finally at 523 K (with a ramping rate of ~0.017 K s$^{-1}$ from 473 K) for 3 h [161]. Prior to transient kinetic measurements in a batch reactor, the catalyst was exposed to a gas stream (1.12 cm$^3$ s$^{-1}$ at NTP conditions) comprising of ~1%/30%/5%/balance of butanal (Sigma Aldrich, 99.5%), H$_2$, CH$_4$ (Minneapolis Oxygen, 99.999%), and He for 6h.

5.2.2. Transient and steady state kinetic measurements of butanal hydrogenation

The steady state butanol formation rate was measured using a quartz tube packed bed reactor (4 mm inner diameter) system. The bed temperature was measured with a type K thermocouple located on the external surface of the reactor and maintained at reaction temperature (413 – 473 K) using two cartridge heaters (Omega Engineering Inc., CIR-2100, 600 W) inserted inside two split-tube aluminum sleeves regulated by a Watlow temperature controller (96 Series). Butanal hydrogenation was carried out at 413-473 K and ambient pressure under a gas stream comprising of He (0.6 – 1.6 cm$^3$ s$^{-1}$ at NTP
conditions), H\(_2\) (0.08 – 0.5 cm\(^3\) s\(^{-1}\) at NTP conditions), butanal (0.04 – 5.0 cm\(^3\) s\(^{-1}\) at NTP conditions), and CH\(_4\) as an internal standard for analysis (0.083 cm\(^3\) s\(^{-1}\) at NTP conditions) and under differential reaction conditions (<10% conversion of butanal). The molar amounts of butanal, hydrogen, and products as a function of reaction time in a batch reactor was measured in a recirculating batch reactor as described previously (see Section 2.2. Materials and methods). The initial reactant mixture with and without co-feeds was recirculated at 7 cm\(^3\) s\(^{-1}\) in the reactor for 30 minutes using a micro-recirculating pump (Metal Bellows, MB-21) before being diverted to the catalyst bed. The contents of the reacting gas mixture were sampled at 20-minute intervals.

Liquid butanal (Sigma Aldrich, >99.5%) was delivered into the gas stream at 345 K via syringe pumps (KD scientific KDS-100 and Cole Parmer). The liquid butanal used in this study contained ~0.13 mol% 2-ethylhex-2-enal as the main impurity. Butanol (Sigma Aldrich, ≥ 99.4%), butyric acid (Sigma Aldrich, ≥ 99%), dibutyl ether (Sigma Aldrich, ≥ 99%), butyl butyrate (Sigma Aldrich, 98%), 2-ethyl hexenal (Sigma Aldrich), 2-ethyl hexanal (Sigma Aldrich, 96%), and deionized water was delivered as solutions in butanal. Feed partial pressures were controlled by adjusting the liquid flowrates into the system. Condensation of the reactants and products was avoided via the resistive heating of the transfer lines to temperatures greater than 353 K.

The reactor effluent was separated using an Agilent 6890 gas chromatograph (GC) equipped with an DB-1 column (30.0 m x 320 μm x 3.0 μm) for all organic products in series with a MolSieve-5A column (30.0 m x 320 μm x 20 μm) for hydrogen and methane. The C\(_8^+\) compounds were separated using a DB-1ms column (30.0 m x 320 μm x 0.3 μm). The composition and molar amounts of the effluent were determined using a flame
ionization detector (FID) for butanal and butanol, a thermal conductivity detector (TCD) for water and hydrogen, and mass spectrometry for all other byproducts.

5.2.3. Parameter estimation techniques for kinetic modeling

The rate of each compound during batch reactions was evaluated by a polynomial fit to the transient composition profile of the reactor effluent during reaction. Kinetic parameters for postulated models were estimated from measured rates using Bayesian statistical optimization techniques in the Athena Visual Studio software package (v14.2, W. E. Stewart and M. Caracotsios). Reported confidence intervals for model parameters reflect 95% marginal highest posterior density intervals.

5.3. Butanal hydrogenation on doped Cu/ZnO

5.3.1. Measurement of surface Cu density with N$_2$O

Nitrous oxide adsorption-decomposition has been used previously to quantify surface Cu sites on reduced Cu-based catalysts [159,161,167–172]. A step increase in the amount of nitrogen evolution upon contacting N$_2$O and Cu supported on SiO$_2$ was observed at 373 K, suggesting the transition into bulk oxidation beyond 373 K [173]. Ultraviolet photoelectron spectrum of the Cu on SiO$_2$ upon contacting N$_2$O at 353 K showed peaks at 2.5 and 5.8 eV which were assigned to energy levels of Cu 3d and O 2p$_x$-2p$_y$ of Cu$_2$O, respectively, demonstrating the formation of Cu$_2$O [173]. Reactive frontal chromatography of reduced Cu/ZnO/Al$_2$O$_3$ formulations confirmed the instantaneous decomposition of N$_2$O upon contacting the formulations at 333 K [174]. The N$_2$O consumed as a function of reaction time while recirculating dilute N$_2$O in a batch reactor is shown in Figure 5.1. The
amount of dinitrogen formed as a function of reaction time correlates with the amount of N\textsubscript{2}O consumed; the initial disappearance of N\textsubscript{2}O was employed to quantify the extent of N\textsubscript{2}O adsorption–decomposition. Initial oxygen uptake was found to be 90 \(\mu\)mol g\textsubscript{cat}\(^{-1}\), which corresponds to a 180 \(\mu\)mol surface Cu g\textsubscript{cat}\(^{-1}\), assuming N\textsubscript{2}O to Cu ratio (O/Cu) to be 1:2.

![Graph](image.png)

Figure 5.1. Amount of (●) N\textsubscript{2}O consumed and (■) N\textsubscript{2} formed upon contacting N\textsubscript{2}O with the supported Cu/ZnO formulation used in this study in a recirculating batch reactor.

5.3.2. Kinetics of butanal hydrogenation at 413 K

During butanal hydrogenation (413 K, 1kPa butanal, 30 kPa hydrogen, < 1% butanal conversion) the formation rate of butanol decreased by 56 % after a turn-over number of 108 mol\textsubscript{butanal converted} mol\textsubscript{surface Cu}\(^{-1}\) after 500 min time-on-stream (Figure 5.2). We utilize a standard condition as a reference at a given time-on-stream to assess the consequences of catalyst deactivation on measured reaction rates. After measurement of butanol formation rate at process reaction conditions other than the standard condition (e.g. at a different hydrogen pressure in Figure 5.2), the reaction conditions were restored to the chosen standard condition and the corresponding butanal formation rate was measured. The extent of catalyst deactivation was assessed by calculating the ratio of the butanol
formation rate at standard conditions measured at those two time-on-stream values. The corrected butanol formation rate measured at varying partial pressure conditions was then obtained by multiplying the extent of catalyst deactivation.

![Figure 5.2](image)

Figure 5.2. Butanol formation rate ((○) raw data, (●) butanol rate measured at the standard condition, and (■) corrected butanol formation rate based on experimentally measured butanol formation rate at the standard condition) as a function of time-on-stream. Reaction conditions: 413 K, 1.0 kPa butanal, 3.5-56 kPa H2.

Figure 5.3 show the dependence of butanol formation rate on butanal and H2 partial pressures, respectively, in which the butanal pressure was varied from ~0.04 to ~5.0 kPa and the H2 partial pressure was varied from ~3.5 to ~55 kPa at 413 K. The apparent H2 order was found to be ~0.6, suggesting that dissociative adsorption of hydrogen occurs. The apparent butanal order was found to be ~0.5 at a butanal partial pressure of ~0.04 to ~0.27 kPa and close to zero at butanal partial pressures >1.0 kPa, indicating that the rate-limiting step for butanal hydrogenation to butanol involves surface butanal-derived intermediates. The near half-order (~0.6) dependence of butanol formation rate on H2 pressure (3.5 – 55 kPa, Fig. 5.3) at constant butanal pressures (0.5–3.0 kPa) suggests that
dissociative adsorption of hydrogen occurs on sites that are distinct from those required for butanal adsorption since we would expect inhibition of butanol formation rate by butanal if butanal and molecular hydrogen adsorb competitively on the same site.

![Figure 5.3](image.png)

Figure 5.3. Effect of butanal (left) and hydrogen (right) partial pressures on butanol formation rate. Reaction conditions: (a) 413 K, (●) 34 kPa, (●) 12 kPa H₂; (b) 413 K, (□) 0.5 kPa, (●) 1.0 kPa, (▲) 2.0 kPa, (◇) 3.0 kPa butanal.

We propose the following reaction mechanism to explain the experimentally observed reaction order dependencies of hydrogen and butanal: (i) hydrogen molecules undergo dissociative adsorption on site 1 (S₁) (Equation 5.1), (ii) butanal molecules adsorb on a distinct site, site 2 (S₂) (Equation 5.2), (iii) addition of a hydrogen adatom to the carbon of the C=O bond of butanal generating a surface butoxy intermediate (Equation 5.3), and (iv) desorption of the butoxy intermediate with a second hydrogen adatom to form butanol (Equation 5.4), thus completing the catalytic cycle. This reaction mechanism is consistent with the isotopologue distribution of butanal and butanol during deuteriation of butanal on the Cu/ZnO formulation used in this study at 473 K (see Section 5.3.4. Isotopic experiment with D₂). Based on the assumption that (i) addition of the first hydrogen adatom to the C=O
bond of butanal is the rate-determining step (Equation 5.3), (ii) all other steps are at quasi-equilibrium, and (iii) site 1 (S1) is predominantly empty, an expression for butanol formation rate (Equation 5.5) consistent with the experimental observation of an apparent hydrogen order of ~0.6 at a H2 pressure of ~3.5 to ~55 kPa and a decreasing apparent butanal order from ~0.5 to zero as butanal pressure increased from ~0.04 to 5.0 kPa can be derived. Kinetic and equilibrium constants in equation 5.5 were estimated and are tabulated in Table 5.1. A parity plot for the observed and predicted butanol formation rates from Equation 5.5 and rate parameters in Table 5.1 is shown in Figure 5.4.

\[
(5.1) \quad \text{H}_2 + 2 \text{S}_1 \rightleftharpoons 2 \text{H–S}_1
\]

\[
(5.2) \quad \text{C}_3\text{H}_7\text{CHO} + \text{S}_2 \rightleftharpoons \text{C}_3\text{H}_7\text{CHO–S}_2
\]

\[
(5.3) \quad \text{H–S}_1 + \text{C}_3\text{H}_7\text{CHO–S}_2 \rightarrow \text{S}_1 + \text{C}_3\text{H}_7\text{CH}_2\text{O–S}_2
\]

\[
(5.4) \quad \text{C}_3\text{H}_7\text{CH}_2\text{O–S}_2 + \text{H–S}_1 \rightleftharpoons \text{C}_3\text{H}_7\text{CH}_2\text{OH} + \text{S}_2 + \text{S}_1
\]

\[
(5.5) \quad r_i = \frac{k_3 \times K_{C_3H_7CHO} P_{C_3H_7CHO}}{1 + K_{C_3H_7CHO} P_{C_3H_7CHO}} \times \left( K_{H_2} P_{H_2} \right)^{\frac{1}{2}}
\]

Table 5.1. Estimated values for the kinetic parameters of butanal formation rate on the supported Cu/ZnO catalyst used in this study at 413 K using the model presented in equation 5.5.

<table>
<thead>
<tr>
<th>Rate constant</th>
<th>Estimated values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_3 \left( K_1 \right)^{\frac{1}{2}} [\text{mol min}^{-1} \text{molCu}^{-1} \text{kPa}^{-0.5}])</td>
<td>0.039 ± 0.0021</td>
</tr>
<tr>
<td>(K_2 / \text{kPa})</td>
<td>18 ± 9.3</td>
</tr>
</tbody>
</table>
5.3.3 Reaction network for butanal hydrogenation at 473 K

We observed eight compounds besides butanol during butanal hydrogenation over the supported Cu/ZnO catalyst used in this study (473 K, 1.8 kPa butanal, 50 kPa hydrogen) at ~90% butanal conversion as listed in Table 5.2. The desired product, butanol, is formed at ~99% selectivity at 90% butanal conversion. The byproducts formed at selectivity greater than 0.1C% include: butyric acid, heptan-4-one, 1-butoxybutan-1-ol, 1-butoxybut-1-en, 2-ethylhexanal, butyl butyrate, and dibutyl ether. The impurity 2-ethylhex-2-enal from the butanal feed was continuously consumed as the reaction progressed, resulting in the negative values of its selectivity at all butanal conversions.

The rank of each product in the reaction network and its stability is identified by the trend of its selectivity as a function of butanal conversion [25]. The selectivity of butyric acid, 1-butoxybutan-1-ol, 1-butoxybut-1-en, and 2-ethylhexanal decreased continuously as a function of butanal conversion from an initial non-zero value, indicating that they are primary unstable products. Butyl butyrate and heptan-4-one have constant non-zero
selectivities up to 90% butanal conversion and are identified as primary stable products directly from butanal. Dibutyl ether has a zero initial selectivity that increases as a function of butanal conversion, indicating a secondary stable product which is formed from other products in the system. We performed a series of co-feed experiments to establish the detailed connectivity of the reaction network as follows.

The main impurity in the butanal used in this study is 2-ethylhex-2-enal. The initial partial pressure of 2-ethylhex-2-enal in a feed comprising of 1.7 kPa butanal and 50 kPa hydrogen was ~2.3 Pa, resulting in an initial consumption rate of 2-ethylhex-2-enal of 0.0025 mol⁻¹ min⁻¹ molCu⁻¹. Co-processing 0.03 kPa 2-ethylhex-2-enal to a feed comprising of 1.7 kPa butanal and 50 kPa hydrogen at 473 K increased the initial consumption rate of 2-ethylhex-2-enal to 0.058 mol⁻¹ min⁻¹ molCu⁻¹, confirming the unstable nature of 2-ethy...
ethylhex-2-enal. The initial formation rate of 2-ethylhexanal also increased from 0.0025 to 0.062 mol·1·min⁻¹·molCu⁻¹ in the same co-feed experiment, suggesting that hydrogenation of the C=C bond in 2-ethylhex-2-enal to form 2-ethylhexanal occurs. The molar amount of 2-ethylhexanal as a function of reaction time in the co-feed experiment with 0.03 kPa 2-ethylhex-2-enal increased to a maximum before decreasing; simultaneously we detected the formation of 2-ethylhexanol, demonstrating the sequential hydrogenation of 2-ethylhexanal to 2-ethylhexanol on the Cu/ZnO formulation used in this study at 473 K. We attributed the lack of 2-ethylhexanol formation in the absence of co-fed 2-ethylhex-2-enal to the lower partial pressure of 2-ethylhexanal formed (~1.0 Pa) comparing to the partial pressure of 2-ethylhexanal during butanal hydrogenation in the presence of co-fed 2-ethylhex-2-enal (~15 Pa). We propose that the sequential hydrogenation of 2-ethylhex-2-enal to 2-ethylhexanal and eventually 2-ethylhexanol occurs following the same mechanism for butanal hydrogenation as outlined in Section 5.3.2.

Co-processing 0.03 kPa butyl butyrate into a reaction mixture comprising of 1.7 kPa butanal and 50 kPa hydrogen at 473 K (30x the amount of butyl butyrate formed at 80% butanal conversion) did not decrease the initial formation rate of butyl butyrate, nor did it affect the initial synthesis rate of any compound in the system, consistent with the identification of butyl butyrate as a stable product. Co-processing 13.3 and 7.7 Pa butyric acid or 0.18, 0.31, and 0.44 kPa butanol, separately, to the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂ did not affect the initial formation rate of butyl butyrate, demonstrating the absence of esterification reactions between butyric acid and butanol on the Cu/ZnO formulation used in this study. Chung et al. [175] studied the reaction of formaldehyde on a series of Cu/ZnO formulations with varying content of Cu and ZnO.
over the temperature range between 373 and 573 K and observed a maximum methyl formate yield of 28% on pure Cu and 4% on pure ZnO, suggesting that methyl formate is mainly formed on Cu sites. Cant et al. [176] observed a decrease by a factor ~4 of methanol dehydrogenation rate to formaldehyde on Cu supported on CrO$_3$ when the reactant was switched from CH$_3$OH to CD$_3$OH, indicating that cleavage of the methyl C-H bond on methanol is the rate-limiting step. The authors also reacted a mixture of CH$_3$OH and CD$_3$OH in the ratio of 1:3 on Cu supported on CrO$_3$ and observed the formation of methyl formate-d$_2$, ruling out the formation of methyl formate via an additive reaction of formaldehyde and surface methoxy in favor of a Tischenko-type reaction between two formaldehyde molecules. Miyazaki and Yasumori [177] studied the decomposition of formaldehyde on pure Cu and reported a rate expression as shown in Equation 5.6 that quantitatively captures the formation rate of methyl formate, suggesting methyl formate was formed via dimerization of two adsorbed formaldehyde molecules. We propose that on the Cu/ZnO formulation used in this study butyl butyrate was formed via a similar mechanism, i.e. Tischenko-type reaction between two adsorbed butanal molecules. We posit further that the active sites for butyl butyrate formation coincide with the active site for butanol formation based on the similarity between the functional form of Equation 5.5 and 5.6.

\[
\textit{r}_{\text{methylformate}} = k \times \frac{(K_{\text{HCHO}}P_{\text{HCHO}})^2}{(1 + K_{\text{HCHO}}P_{\text{HCHO}})^2}
\]  

(5.6)

Recirculating a gas mixture consisting of 0.17 kPa water-$^{18}$O, 1.7 kPa butanal, and 50 kPa H$_2$ at 373 K in the absence of the catalyst resulted in the formation of a butanal mixture with 10% butanal-$^{18}$O, demonstrating the rapid scrambling of oxygen in water and
the carbonyl group of butanal. We propose that this scrambling occurs via the equilibrium between butanal, water, and butane-1,1-diol. We noted the presence of ~40 Pa water in the feed comprising of 1.7 kPa butanal and 50 kPa H₂ and attributed this water amount as an impurity in the butanal feed. Co-processing 0.23 kPa water to a feed stream comprising initially of 1.7 kPa butanal and 50 kPa H₂ at 473 K increased butyric acid initial formation rate from 0.011 to 0.11 µmol min⁻¹ gcat⁻¹, demonstrating the positive effect of water pressure on butyric acid formation. We propose that butyric acid is formed via dehydrogenation of butane-1,1-diol which is in equilibrium with gas-phase butanal and water. Co-processing 0, 7.7, and 13.3 Pa butyric acid with the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂ decreased butyric acid initial formation rate from 1.9, 1.2, to 0.4 mol min⁻¹ molCu⁻¹, demonstrating that hydrogenation of butyric acid to butanal and water occurs at our reaction conditions. The calculated initial approach to equilibrium for the reaction of butanal and water to form butyric acid and hydrogen is 0.0, 1.0, and 1.6 for the mixture comprising of 1.7 kPa butanal, 50 kPa H₂, 40 Pa water, and 0, 7.7, and 13.3 Pa butyric acid. We note that the reported enthalpies of formation of butanal and butyric acid both have errors up to 4 kJ mol⁻¹ [178,179], resulting in an estimated equilibrium constant for the reaction with an order-of-magnitude error.

Co-processing 0.18 kPa butanol with the reaction mixture comprising of 1.7 kPa butanal and 50 kPa H₂ increased initial formation rate of dibutyl ether from 0.00 to 5.0 × 10⁻⁴ mol⁻¹ min⁻¹ molCu⁻¹, demonstrating the direct formation of dibutyl ether from butanol. Increasing the initial partial pressure of the co-fed butanol to 0.44 kPa did not increase the initial formation rate of dibutyl ether. Furthermore, butanol formation rate remained invariant at 5.0 × 10⁻⁴ mol⁻¹ min⁻¹ molCu⁻¹ as butanol partial pressure increased.
from 0.41 to 1.46 kPa and butanal pressure decreased from 1.25 to 0.16 kPa, corresponding to butanal conversions between 26% and 90% (Figure 5.5), indicating that dibutyl ether formation rate is independent of butanal or butanol partial pressure. We propose that dibutyl ether is formed on a distinct site from the active site for butanal hydrogenation as discussed in Section 5.3.2. Kinetics of butanal hydrogenation at 413 K. The zero-order dependency of dibutyl ether formation rate on butanol pressure further suggests that this active site is saturated with butanol. Co-processing 0.0, 7.7, and 13.3 Pa butyric acid to the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂ decreased the formation rate of dibutyl ether from $5.0 \times 10^{-4}$, $3.9 \times 10^{-4}$, to $1.7 \times 10^{-4}$ mol⁻¹ min⁻¹ molCu⁻¹ while maintaining the invariancy of dibutyl ether formation rate as a function of reaction time. We posit that butyric acid competitively adsorbs on the active site for dibutyl ether formation.

![Graph](image)

Figure 5.5. Molar amount of dibutyl ether as a function of reaction time during butanal hydrogenation on the supported Cu/ZnO formulation used in this study in a recirculating batch reactor at 473 K with the feed stream initially comprising of (●) 1.7 kPa butanal, 50 kPa H₂, and co-fed (■) 0.18 kPa butanol, (♦) 0.44 kPa butanol, (▲) 7.7 Pa butyric acid, (◆) 13.3 Pa butyric acid.

Based on the steady-state rate measurements at 413 K for butanal hydrogenation to butanol and the co-feed experiments with water, butanol, butyric acid, butyl butyrate, and
2-ethyl-hex-2-enal at 473 K, we propose a mechanistic network for butanal hydrogenation on the Cu/ZnO formulation used in this study as summarized in Figure 5.6. We propose the existence of three types of active sites on the catalyst surface: an active site for hydrogen chemisorption, an active site for aldehyde adsorption including butanal, butane-1,1-diol, 2-ethylhex-2-enal, and 2-ethylhexanal, and an active site for dibutyl ether formation. Butanol, 2-ethylhexanal, and 2-ethylhexanol are formed via additive reactions between chemisorbed hydrogen adatoms and butanal, 2-ethylhex-2-enal, and 2-ethylhexanal, respectively. We propose an equilibrium between butanal, water, and butane-1,1-diol; we also propose that butane-1,1-diol undergoes dehydrogenation on the active site for butanal adsorption to form butyric acid. Butyl butyrate is proposed to form via Tischenko-type reaction between two adsorbed butanal molecules. Butanol is proposed to form dibutyl ether on a distinct site from the active site for butanal hydrogenation; the independence of dibutyl ether formation rate on butanol partial pressure suggests that this active site is covered with butanol. We posit that the hemiacetals of butanal and butanol, 1-butoxybutan-1-ol and 1-butoxybut-1-en, are in equilibrium with butanal and butanol from the rapid formation of

![Figure 5.6. Schematic for proposed reaction pathways and surface intermediates during butanal hydrogenation on the Cu/ZnO formulation used in this study. The surface intermediates are denoted within brackets; the bracket colors indicate the different active sites.](image-url)
the hemiacetals upon mixing liquid butanal and butanol at room temperature (see Section 6.6. Identification of C₈ byproducts during butanal hydrogenation on Cu/ZnO).

5.3.4. Isotopic experiment with D₂

Replacing H₂ in the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂ at 473 K with D₂ decreased the initial synthesis rate of butanol from 380 to 130 µmol min⁻¹ gcat⁻¹, demonstrating an isotope effect on the formation rate of butanol from butanal hydrogenation. The apparent kinetic parameter in the rate expression for butanal hydrogenation to butanol (Equation 5.5), \( k_3 \times K_{C,H,CHO} \times \left( K_{H_2} \right)^{\frac{1}{2}} \), represents the energy difference between gas phase H₂ and butanal molecules and the transition state for the formation of the butyloxide surface intermediate. Assuming that the transition states with H and D have identical energy levels, the rate of butanol formation from butanal and H₂ relative to the rate of butanol formation from butanal and D₂ at identical partial pressures of butanal and H₂ or D₂, \( r_H / r_D \), depends primarily on the difference in the zero-point-energy of H₂ and D₂ which gives an upper bound for the \( r_H / r_D \) ratio of 2.7 at 473 K, comparable to our measured \( r_H / r_D \) of 2.9. The measured \( r_H / r_D \) ratio, thus, is consistent with our postulated rate expression for butanol synthesis from butanal hydrogenation.

The isotopologue distribution of the reactant butanal during the deuteration of 1.7 kPa butanal with 50 kPa D₂ at 473 K comprised of butanal with zero, one, or two deuterium atoms (Figure 5.7). The initial synthesis rate of butanal-d₁ was zero, indicating that there were no direct routes for hydrogen exchange between butanal and surface hydrogen/deuterium adatoms, i.e., chemisorption of butanal on the catalyst surface via cleavage of either aldehydic or a β C-H bond, if it occurs, is not reversible under our
reaction conditions. We attribute the formation of butanal-d₁ to the dehydrogenation of the deuterated butanol product in the system, as shown by the isotopologue distribution of butanol in the deuteration of butanal and co-feed experiments with butanol (vide infra).

Co-processing 0, 0.18, and 0.44 kPa butanol to the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂ decreased initial butanol synthesis rate from 2.1, 2.0, to 1.9 mol⁻¹ min⁻¹ molCu⁻¹. The estimated approach to equilibrium for the hydrogenation of butanal to butanol is 0.0, 0.02, and 0.05 for the reacting mixture comprising of 1.7 kPa butanal, 50 kPa H₂, and 0.0, 0.18, and 0.44 kPa butanol, respectively, suggesting the existence of butanol dehydrogenation at our reaction conditions. Deuteration of 1.7 kPa butanal with 50 kPa D₂ at 473 K on the Cu/ZnO formulation used in this study resulted in the formation of butanol containing C₄H₈D and C₄H₇D₂ fragments only; the parent ion C₄H₉OH could not be observed in our mass spectrometer. The initial formation rate of butanol with C₄H₇D₂ fragment was zero, demonstrating that the deuteration of butanal occurs via addition of two deuterium atoms to the C=O bond, instead of the C=C bond of

![Figure 5.7. Molar amount of (●) d₀, (■) d₁, (◆) d₂, and (▲) d₃ isotopologues of (left) butanal and (right) C₄H₉ fragment from butanol as a function of reaction time during butanal deuteration on the supported Cu/ZnO formulation used in this study in a recirculating batch reactor at 473 K with the feed stream initially comprising of 1.7 kPa butanal and 50 kPa H₂.](image-url)
the enol formed from butanal. Butanol with a C₄H₂D₂ fragment was observed after ~100 min reaction time in the batch reaction, while butanal-d₁ was observed after ~50 min, illustrating that butanal-d₁ (C₃H₇CDO) was formed via removal of HD from C₃H₇CHDOD and was further deuterated to C₃H₇CD₂OD.

5.4. Conclusion

Steady-state kinetic measurements of butanal hydrogenation to butanol on the supported Cu/ZnO formulation used in this study at 413 K revealed a butanol formation rate with an apparent hydrogen order of ~0.5 as H₂ pressures varied between 3.5 and 60 kPa at all butanal partial pressures from 0.5 to 3.0 kPa and a decreasing butanal order between ~0.5 and zero as butanal pressure increased from ~0.04 to ~5.0 kPa. These dependencies of butanol formation rate are consistent with a dual-site mechanism for the hydrogenation of butanal in which butanal and hydrogen adsorb on distinct sites. The calculated butanol formation rate using a rate expression following the dual-site mechanism fit well with the experimental data. Selectivity plots of the products as a function of butanal conversion during butanal hydrogenation at 473 K revealed that: (i) butyric acid, 1-butoxybutan-1-ol, 2-ethylhex-2-enal, and 2-ethylhexanal are primary unstable products, (ii) butyl butyrate and heptan-4-one are primary stable products, and (iii) dibutyl ether is a secondary product. Co-feed experiments with 2-ethylhex-2-enal revealed the hydrogenation of 2-ethylhex-2-enal to form 2-ethylhexanal and 2-ethylhexanol, sequentially. Co-feed experiments with butyl butyrate confirmed the stability of this product and the kinetic irrelevancy of the partial pressure of this compound on the formation rates of other products in the system. The appearance of dibutyl ether as a
secondary product, its constant synthesis rate at butanal conversions ranging from 26 to 90%, and the decreased synthesis rate of dibutyl ether in the presence of co-fed butyric acid suggest the formation of dibutyl ether from butanol on a distinct site from the adsorption sites for H₂ and butanal; this site is rapidly saturated with butanol and is competitively adsorbed by butyric acid. The rapid scrambling of $^{18}$O upon mixing liquid butanal-$^{16}$O and water-$^{18}$O at room temperature, together with the increased initial synthesis rate of butyric acid in co-feed experiments with water, suggest the formation of butyric acid via dehydrogenation of the butane-1,1-diol. The kinetic and mechanistic studies in this work may enable the construction of a mechanistic network for the hydrogenation of butanal on a Cu/ZnO formulation.
Chapter 6. Appendix

6.1. Schematics of gas-phase recirculating batch reactor

Figure 6.1. Schematic of the recirculating batch reactor used for catalyst experiments. MFC indicated gas mass flow controller, P and T indicated pressure transducer and thermocouple, respectively. During reactor charge-up the feed gas mixture (red) was flown through the reactor while the catalyst bed inside the furnace was flushed with helium (blue).
6.2. Heat and mass transfer calculations

The existence of internal mass transfer limitations was estimated by comparing the reaction rate with the diffusion rate following the Weisz-Prater criterion, assuming that the concentration of the reactant on the catalyst pellet surface is close to that in the gas fluid.

\[
\eta \phi^2 = \frac{r_{obs} S \rho_b d_p^2}{4 D_e C_s}
\]

where \(\eta\) is the dimensionless effectiveness factor, \(\phi\) is the dimensionless Thiele modulus, \(r_{obs}\) is the observed rate of propylene consumption in mol s\(^{-1}\) (m\(^2\)cat\(^{-1}\)), \(S\) is the surface area of the catalyst in m\(^2\)cat kgcat\(^{-1}\), \(\rho_b\) is the catalyst pellet density in kgcat (m\(^3\)cat\(^{-1}\)), \(d_p\) is the catalyst pellet diameter in m, \(D_e\) is the effectiveness diffusivity in m\(^2\) s\(^{-1}\) (assumed to be equal to the diffusivity of propylene in air at 623 K since the catalyst is non-porous), and
$C_s$ is the propylene concentration on the catalyst pellet surface in mol m$^{-3}$ (assumed to be equal to the propylene concentration in the gas fluid). Internal mass transfer limitations are negligible when $\eta \phi^2 << 1$, which is confirmed in our reaction system of propylene oxidation to acrolein on Bi$_2$Mo$_3$O$_{12}$ at 623 K (Table 6.1).

Table 6.1. Tabulation of parameters for the calculation of internal mass transfer limitation using Weisz-Prater criterion for propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{obs}}$ (mol (m$^2$cat)$^{-1}$ s$^{-1}$)</td>
<td>$3.5 \times 10^{-8}$ (highest observed)</td>
</tr>
<tr>
<td>$S$ (m$^2$ cat kgcat$^{-1}$)</td>
<td>400</td>
</tr>
<tr>
<td>$\rho_b$ (kg cat (m$^3$ cat)$^{-1}$)</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>$d_p$ (m)</td>
<td>$3 \times 10^{-4}$ (based on average pellet mesh size of 180 – 425 µm)</td>
</tr>
<tr>
<td>$D_e$ (m$^2$ s$^{-1}$)</td>
<td>$5.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_s$ (mol m$^{-3}$)</td>
<td>1.2 (6 kPa propylene at 623 K)</td>
</tr>
<tr>
<td><strong>Calculated Weisz-Prater criterion $\eta \phi^2$</strong></td>
<td><strong>1.5 x 10$^{-5}$</strong></td>
</tr>
</tbody>
</table>

The existence of internal heat transfer limitations can be estimated by calculating the average temperature within the catalyst pellet following the Anderson criterion [101] which assumes a parabolic temperature profile within the spherical catalyst pellet and a Taylor series expansion of the Arrhenius rate expression around $T_s$, the temperature of the catalyst pellet surface.

\[
\frac{T_{\text{ave}}}{T_s} = 1 + \frac{(-\Delta H)r_{\text{obs}}S\rho_b d_p^2}{60\lambda_c T_s^2}
\]

where $T_{\text{ave}}$ is the average temperature within the catalyst pellet in K, $T_s$ is the temperature on the catalyst pellet surface in K (assumed to be equal to the gas phase temperature), $\Delta H$ is the reaction enthalpy in J mol$^{-1}$, and $\lambda_c$ is the heat conductivity of the catalyst particle in W m$^{-1}$ K$^{-1}$. Calculations from Table 6.2 showed that the average temperature in the catalyst
particle was very close to the temperature on the catalyst surface during our propylene oxidation reactions at 623 K.

Table 6.2. Tabulation of parameters for the calculation of internal heat transfer limitation using Weisz-Prater criterion for propylene oxidation on Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} at 623 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H) (J mol(^{-1}))</td>
<td>(-3.5 \times 10^5)</td>
</tr>
<tr>
<td>(r_{\text{obs}}) (mol (m(^2\text{cat}))(^{-1}) s(^{-1}))</td>
<td>(3.5 \times 10^8)</td>
</tr>
<tr>
<td>(S) (m(^2\text{cat kgcat}^{-1}))</td>
<td>400</td>
</tr>
<tr>
<td>(\rho_b) (kgcat (m(^3\text{cat}))(^{-1}))</td>
<td>(3 \times 10^3)</td>
</tr>
<tr>
<td>(d_p) (m)</td>
<td>(3 \times 10^{-4})</td>
</tr>
<tr>
<td>(\lambda_c) (W m(^{-1}) K(^{-1}))</td>
<td>0.1 (estimated from common value for metal oxides)</td>
</tr>
<tr>
<td>(T_s) (K)</td>
<td>623</td>
</tr>
</tbody>
</table>

| Calculated \(T_{\text{ave}}/T_s\) | \(1 + 3.5 \times 10^{-7}\) |

The concentration of propylene on the surface of the catalyst particle is approximated via Mears’s criteria [100], which is essentially a mass balance around a spherical catalyst particle.

\[
\frac{C_s}{C_b} = 1 - \frac{r_{\text{obs}}S\rho_b d_p}{6k_g C_b} \tag{6.3}
\]

where \(C_s\) is the propylene concentration on the catalyst surface in mol m\(^{-3}\), \(C_b\) is the propylene concentration in the gas fluid in mol m\(^{-3}\), and \(k_g\) is the external mass transfer coefficient in m s\(^{-1}\).

In a similar manner, the temperature gradient between the catalyst pellet surface and the gas fluid can be estimated via an energy balance around the spherical catalyst pellet.

\[
\frac{T_s}{T_b} = 1 + \frac{(-\Delta H)r_{\text{obs}}S\rho_b d_p}{6h_g T_b} \tag{6.4}
\]
where $T_s$ is the temperature of the catalyst pellet surface in K, $T_b$ is the temperature of the
gas in K, and $h_g$ is the heat transfer coefficient between the gas phase and the catalyst pellet
surface in W m$^{-2}$ s$^{-1}$. Calculations presented in table 6.3 show that external concentration
and temperature gradients were negligible under the reaction conditions used in this
research.

Table 6.3. Tabulation of parameters for the calculation of external heat and mass
transfer limitations using Mears’s criteria for propylene oxidation on Bi$_2$Mo$_3$O$_{12}$ at 623 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (J mol$^{-1}$)</td>
<td>$-3.5 \times 10^5$</td>
</tr>
<tr>
<td>$r_{obs}$ (mol (m$^2$cat)$^{-1}$ s$^{-1}$)</td>
<td>$3.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>$S$ (m$^2$ cat kgcat$^{-1}$)</td>
<td>400</td>
</tr>
<tr>
<td>$\rho_b$ (kg cat (m$^3$ cat)$^{-1}$)</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>$d_p$ (m)</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_g$ (m s$^{-1}$)$^a$</td>
<td>0.54</td>
</tr>
<tr>
<td>$h_g$ (W m$^{-2}$ s$^{-1}$)$^b$</td>
<td>510</td>
</tr>
<tr>
<td>$C_b$ (mol m$^{-3}$)</td>
<td>1.2</td>
</tr>
<tr>
<td>$T_s$ (K)</td>
<td>623</td>
</tr>
</tbody>
</table>

$^a$: Estimated from $Sh$ (Sherwood number) = $k_g d_p/\nu_g$ = 3.0 from Frossling correlation
$Sh = \frac{2}{3} Sc^{0.3}$ with $Re$ (Reynolds number) = $U_b d_p/\nu_g$ = 2.1 where $U_b$ = superficial gas velocity
= 0.54 m s$^{-1}$ (total volumetric flow rate (3 cm$^3$ s$^{-1}$) divided by reaction cross sectional area (0.15 cm$^2$)
and void fraction (0.4)), $\nu_g$ = kinematic viscosity of gas = $7.6 \times 10^{-5}$ m$^2$ s$^{-1}$ (estimated as kinematic viscosity
of air at 650 K), and $Sc$ (Schmidt number) = $\nu_g/D_e$ = 1.4.

$^b$: Estimated from $Nu$ (Nusselt number) = $h_g d_p/\lambda_g$ = 2.8 where $\lambda_g$ = thermal conductivity of gas = 0.055 W
m$^{-1}$ K$^{-1}$ (estimated from value of air at 650 K) from Ranz-Marshall correlation
$Nu = \frac{2}{3} Pr^{0.3}$ with $Re$ (Reynolds number) = 2.1 and $Pr$ (Prandtl number) = 0.7 (estimated as Prandtl number of air at
650 K).
6.3. Statistical evaluation of the pseudo-first-order kinetic model

The estimability of the 17 parameters in the pseudo-steady-state kinetic model for propylene oxidation on Bi₂Mo₃O₁₂ described by equations in Table 4.1 was ranked using the orthogonalization method originally proposed by Yao et al. [180]. From 4032 experimental data points, a scaled sensitivity matrix, Z, with dimension 4032 x 17 was calculated as:

\[ Z_{ij} = \frac{\text{dlog}n_i}{\text{dlog}k_j} \]  

(S5)

where \( n_i \) is the corresponding model prediction at data point \( i \) (amount of one of the eight species at a reaction time in an experiment) and \( k_j \) is one of the 17 kinetic parameters. The first column in Table 6.4 shows the magnitude of each column in the scaled sensitivity matrix, illustrating that the model predictions are most sensitive to parameter \( k_1 \). The first column of the sensitivity matrix \( Z \) was put into a matrix \( Z_1 \) with dimension 4032 x 1. The sensitivity of the model predictions to other parameters was ranked via the following algorithm: (i) ordinary least-squares was used to estimate the values in \( Z \) using \( Z_m \) with \( m \) representing the iteration number, \( \hat{Z}_m = Z_m (Z_m^T Z_m)^{-1} Z_m^T Z \), and the residual matrix was calculated \( R_m = Z - \hat{Z}_m \); (ii) the magnitude of each column in \( R_m \) was calculated and tabulated in the corresponding \( m^{th} \) column in Table 6.4; (iii) the column vector in \( Z \) corresponding to the column with the largest magnitude in \( R_m \) was adjoined to matrix \( Z_m \) generating the \( Z_{m+1} \) matrix with dimension 4032 x (\( m+1 \)). The highest value in each column in Table 6.4, thus, shows that predictions from the kinetic model were most sensitive to the corresponding parameters after the sensitivity effects of the previously ranked parameters had been de-convoluted. The results in Table 6.4 shows that all 17 parameters can be
ranked by the orthogonalization method, suggesting that all parameters in the kinetic model can be estimated reliably. This result is further verified by the correlation matrix of the parameters (Table 6.5) which shows small correlations between the rate parameters used in the kinetic model.

The distributions of residuals between experimental data and predictions from the kinetic model are presented in Figure 6.3. All distributions have zero mean except for propylene indicating that the kinetic model systematically under-predicts the amount of consumed propylene. The residual distributions are not completely normal especially for ethylene and CO\textsubscript{x}, indicating a poor fit between predictions of the kinetic model and the experimental data for these two compounds. Lag plots of the residuals (Figure 6.4) showed systematic correlations for acrolein and acrylic acid, suggesting a certain degree of non-randomness in the variance of the residuals for these products.
Table 6.4. Iterative ranking of the estimability of the kinetic parameters in equations 1-8 of Table 4.1 using orthogonalization method.

<table>
<thead>
<tr>
<th>Iteration</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>29</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$k_2$</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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Figure 6.3. Distributions of residuals between predictions from kinetic model from equation 1-8 of Table 4.1 and experimental data. The red curves are normal distribution fits to the residual distributions.
A sample of 22 wt% Ni supported on SiO2 was synthesized via treatment of Ni(NO3)2 and suspended SiO2 with Na2CO3 at 363 K followed by air treatment of the resulting precipitation at 393 K. Prior to the measurement of reaction rates, the sample was treated in H2 (Minneapolis Oxygen, 99.999%) with a total flow rate of ~0.83 cm3 s−1 at 723
K for 1 h (with a ramping rate of \( \sim 0.083 \text{ K s}^{-1} \) from RT). This formulation had been shown to achieve a C\textsubscript{9} alcohol yield of 92\% in batch and trickle bed reactors in hydrogenation reaction of C\textsubscript{9} aldehyde [181]. The sample powder was pelletized and sieved between 40–80 mesh (180–420 \( \mu \text{m} \)).

This formulation displayed consistent deactivation during butanal hydrogenation (413 K, 1\, kPa butanal, 30 \, kPa hydrogen, < 10\% butanal conversion) with butanal consumption rate decreasing by 90\% after a TON of 1.8 mol aldehyde converted/g catalyst (600 min TOS) at WHSV of 5.0 mol aldehyde/g catalyst/h (Figure 6.5) while maintaining >95\% selectivity towards butanol. Prolonged reduction of the catalyst at 723 K for 16h and re-distillation of the feed butanal did not affect the initial butanal consumption rate or the deactivation profile, indicating that catalyst sintering and feed contamination did not play a significant role in deactivation of the catalyst. Increasing the butanal partial pressure from 1.0 to 4.0 kPa decreased the butanol formation rate from 0.46 mmol min\(^{-1}\) gcat\(^{-1}\) to 0.09 mmol min\(^{-1}\) gcat\(^{-1}\) and concurrently increased the formation rates of butyl butyrate and 2-ethyl 2-hexenal, dimerization products of butanal, from 0.0 to 14.8 and 0.02 to 3.9 mmol min\(^{-1}\) gcat\(^{-1}\), respectively, demonstrating the intensive formation of C\textsubscript{8} byproducts during butanal hydrogenation on the Ni/SiO\textsubscript{2} formulation (Figure 6.5). We attributed the deactivation of the catalyst to the formation and adsorption of these heavy compounds as persistent species on the active sites of the catalyst. Limited by the catalyst deactivation and our inability to perform butanal hydrogenation at high butanal pressure (\( > 1 \) kPa), we decided to explore other catalytic systems for the hydrogenation of butanal.
We observed formation of two byproducts during butanal hydrogenation on the Cu/ZnO formulation used in the study in Chapter 5 and proposed these two products to be 1-butoxybutan-1-ol and 1-butoxybut-1-ene. The retention time of these two products are 13.4 min and 14.0 min on the DB-1 column, between heptan-7-one (13.0 min) and dibutyl ether (14.1 min), consistent with elution time of C₈ compounds. Fragmentation patterns of both compounds on the mass spectrometer comprise of three peaks at m/z of 128, 72, and 57, consistent with the fragmentation pattern of a 1-butoxybut-1-ene ion radical (m/z of 128), the product of dehydration of 1-butoxybutan-1-ol ion radical, following McLafferty rearrangement to give a 1-butanal ion radial (m/z of 72) and α-cleavage of the C-O to give a butyl ion radical (m/z of 57). Both products were formed immediately upon mixing liquid
butanal and butanol at room temperature, consistent with the additive reaction of butanal and butanol to give 1-butoxybutan-1-ol, the hemiacetal of butanal and butanol. Replacing butanol with butanol-d$_{10}$ in the mixture with butanal yielded two products with mass fragmentation patterns containing a peak shift from m/z of 128 to m/z of 137, further confirming the two compounds as additive products of butanal and butanol. Homonuclear correlation spectroscopy (COSY) of the butanal-butanol mixture in CDCl$_3$ reveals J coupling between two protons with chemical shifts of ~5.2 ppm and ~2.6 ppm, consistent with predicted $^1$H NMR spectrum of 1-butoxybutan-1-ol using ChemDraw 15 software. The COSY however failed to locate J coupling between two protons with chemical shifts of ~6.3 ppm and ~4.6 ppm as predicted by $^1$H NMR of 1-butoxybut-1-ene.
Bibliography


[141] Research and Markets, N-Butanol Market by Application (Butyl Acrylate, Butyl Acetate, Glycol Ethers, Direct Solvents, Plasticizers), and Region (Asia Pacific, North America, Europe, Middle East & Africa, South America) - Global Forecast to 2022, 2018.


