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It is entitled:
The Mechanism of Propane Ammoxidation over the ab Plane of the Mo-V-Te-Nb-O M1 Phase Probed by Density Functional Theory

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The Mechanism of Propane Ammoxidation over the $ab$ Plane of Mo-V-Te-Nb-O M1 Phase Probed by Density Functional Theory

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Abstract

The selective ammonoxidation of propane into acrylonitrile catalyzed by the bulk Mo-V-Te-Nb-O system received considerable attention because it is more environmentally benign than the current process of propylene ammonoxidation and relies on a more abundant feedstock. This process consists of a series of elementary steps including propane oxidative dehydrogenation (ODH), ammonia and \( \text{O}_2 \) activation, and N-insertion into \( \text{C}_3 \) surface intermediates. However, the limited fundamental understanding of the reaction mechanism and the roles of the different cations have hindered the progress in further improving the activity and selectivity of these catalysts required for the commercial application.

In this thesis, we present and discuss the results of the density functional theory (DFT) calculations performed to investigate the overall propane ammonoxidation pathway employing the cluster models of the proposed selective and active sites present in the surface ab plane of the so-called M1 phase, which is the main catalytic phase present in the bulk mixed Mo-V-Te-Nb oxides. The activation energies for the oxidative dehydrogenation (ODH) of propane and sequentially formed intermediates (isopropyl, propene, and allyl) were calculated for different surface cation sites. Propane activation on \( \text{V}^{5+}=\text{O} \) was found to be the rate-limiting step \( (E_a = 1.2 \text{ eV}) \), consistent with the current proposed reaction mechanism for propane activation on the bulk mixed Mo-V-Te-Nb oxides and the current understanding of \( \text{V}^{5+} \) as the active site for alkane activation present in V-based mixed oxides.
Furthermore, a linear relationship was established between the H adsorption energy and the activation energy for H abstraction from various C3 intermediates, which is highly useful for predicting the energy barriers of H abstraction from C3 species based solely on H adsorption energy. The energy barriers of ammonia activation on different surface sites and NH insertion into the allyl species were investigated and discussed in terms of the hypothetical reaction pathway reported in the literature. These elementary reaction steps were indicated to be energetically barrier-less. The formation of acrylonitrile over Te=O as the H abstraction site from the surface absorbed precursor was found to be a barrier-less step. The overall reaction pathway was then explored using micro-kinetic models to study the selectivity of propane ammoxidation to acrylonitrile on the Mo-V-Te-Nb-O M1 phase. The calculated coverages of surface intermediates on Mo and V active sites from the micro-kinetic model indicated that NH is the dominant species on the surface as compared to surface O species which may explain why the M1 phase is so selective in transforming the gas-phase π-allyl intermediate into acrylonitrile as opposed to combustion products. This thesis reports the very first theoretical study of a complete mechanism of propane ammoxidation over surface \( ab \) planes of bulk mixed Mo-V-Te-Nb-O M1 phase. Improved understanding of the surface structure – reactivity relationships for propane ammoxidation to acrylonitrile over this model mixed metal oxide system gained in this research offers a possibility of not only molecular engineering of such mixed metal oxide catalysts for propane (amm)oxidation, but also fundamentally advancing the field of selective alkane (amm)oxidation over bulk mixed metal oxides.
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Chapter 1. Summary

1.1 SELECTIVE (AMM)OXIDATION OF LOWER ALKANES

The catalysis community has been interested in the selective (amm)oxidation of lower alkanes, e.g., ethane and propane, for a long time because of the low cost and high abundance of alkanes as compared to alkenes and their environmentally friendly nature [1, 2]. Propene ammoxidation is currently employed on industrial scale to produce acrylonitrile, which is a major chemical intermediate and a top 50 chemical in the world. However, propane as a major component of natural gas is a more abundant and cheaper feedstock than propene, especially due to increasing shale gas production in the recent years according to Annual Energy Outlook Reports for 2013 and 2014 published by the U.S. Department of Energy [3, 4]. Therefore, propane ammoxidation to acrylonitrile is of particular interest due to its significant economic and environmental advantages. Heterogeneous catalysts that have been investigated to date for this reaction and shown potential for this transformation include supported and bulk vanadia, molybdenum-based mixed oxides, and vanadium-based mixed oxides [2]. Among all catalysts that have been studied for selective propane ammoxidation, the bulk mixed Mo-V-Te-Nb-O system is the most promising catalyst due to its high activity and selectivity [2]. However, further improvement of this catalyst to make it a commercial success requires the understanding of the reaction mechanism and establishing the fundamental structure-reactivity relationships for the various surface active sites present in these catalysts. Quantum chemistry-based theoretical methods, especially the density functional theory (DFT), are powerful tools that can probe the electronic structure and catalytic properties of mixed
metal oxides. Therefore, DFT was employed in this PhD thesis research to develop the fundamental understanding of the structure-reactivity relationships for the surface cation sites and the microkinetic model of the propane ammoxidation pathway over the Mo-V-Te-Nb-O M1 phase catalyst.

1.2 SELECTIVE AMMOXIDATION OF PROPANE OVER MO-V-TE-NB-O M1 PHASE

In this thesis, DFT was employed to elucidate the locations of metal cations in the surface \( ab \) plane of the Mo-V-Te-Nb-O M1 phase and describe the entire propane ammoxidation pathway via thermodynamic and kinetic parameters, such as the reaction, \( \Delta E \), and activation energies, \( E_{\text{act}} \), reaction rate constants, \( k \), and the equilibrium constants, \( K \). This theory together with available experimental reaction data were employed to develop the microkinetic model to predict the distribution of surface \( \text{NH}_x \) and \( \text{OH}_x \) species under realistic reaction conditions, probe the kinetics of a complete reaction pathway and provide further critical insights into the role of each surface cation that are key for further improvement of this highly promising catalytic system.

The Mo-V-Te-Nb-O M1 phase is a highly promising catalyst for direct propane ammoxidation to acrylonitrile. Although the presence of Nb is highly beneficial for the selectivity to acrylonitrile, direct evidence of Nb location is lacking because structural methods cannot distinguish Nb \((Z=41)\) from Mo \((Z=42)\) in the M1 phase. To tackle this issue, we instead turned to a Ta variant of the M1 phase, because Ta is chemically similar to Nb, but much heavier \((Z=73)\) showing a good \(Z\)-contrast against Mo. We conducted high-angle annular dark-field (HAADF) scanning transmission electron microscopy
STEM and density functional theory (DFT) to study the Ta location in a Mo-V-Te-Ta-O M1 phase produced via hydrothermal synthesis. The HAADF STEM and DFT results indicated that Ta predominantly occupies the pentagonal bipyramidal site (S9), thereby validating the previous hypothesis that Ta and Nb both prefer the S9 site [5].

Besides the issue of Nb location in the Mo-V-Te-Nb-O M1 phase, the mechanism of propane ammoxidation over the M1 phase involving a transfer of eight-electrons from propane in a series of oxidative H-abstraction and N-insertion steps, remains poorly understood. We have conducted a DFT study of propane ammoxidation over cluster models of the proposed active and selective center present in the surface \textit{ab} planes of the M1 phase including the steps of adsorption of propane, isopropyl (CH$_3$CHCH$_3$), and H, which are involved in the initial methylene C-H bond scission in propane on these active site models [6]. Among the surface oxygen species, the telluryl oxo (Te=O) was found to be the most nucleophilic. The adsorption of propane on the M1 surface is weak regardless of the nature of the MOx species involved, whereas isopropyl and H adsorption exhibits strong preference in the order of Te=O > V=O > bridging oxygens > empty Mo apical site, suggesting the importance of TeOx species for H abstraction. The adsorption energies of isopropyl and H and, consequently, the reaction energy of the initial dehydrogenation of propane are strongly dependent on the number of \textit{ab} planes of the M1 phase included in cluster model, which stresses the need to employ multilayer cluster models to correctly capture the energetics of surface chemistry on this mixed metal oxide catalyst.
To better understand the roles of different surface cations present in the M1 phase in propane ammoxidation, DFT calculations (GGA-PBE) were performed to investigate the adsorption of C3 (propane, isopropyl, propene, and allyl) and H species on the proposed active center present in the $ab$ plane of the M1 phase [7]. Modified cluster models are employed to isolate the closely spaced $V=O$ and $Te=O$ from each other and to vary the oxidation state of the V cation. While propane and propene adsorb with nearly zero adsorption energy, the isopropyl and allyl radicals bind strongly to $V=O$ and $Te=O$ with adsorption energies, $\Delta E$, being $\leq -1.75$ eV, but appreciably more weakly on other sites, including Mo=O, bridging oxygen, and empty metal apical sites ($\Delta E > -1$ eV). Atomic H binds more strongly to $Te=O$ ($\Delta E \leq -3$ eV) than to all other sites, including $V=O$ ($\Delta E = -2.39$ eV). The reduction of surface oxo groups by dissociated H and their removal as water are thermodynamically favorable except when both H atoms are originally bonded to $Te=O$. Consistent with the strong binding of H, $Te=O$ is markedly more active in abstracting the methylene H from propane ($E_a \leq 1.01$ eV) than $V=O$ ($E_a = 1.65$ eV on $V^{5+}=O$ and 1.95 eV on $V^{4+}=O$). The surprisingly high activity and weak binding of $Te=O$ moieties to the oxide framework predicted by theory raise the question of whether such $Te=O$ groups are indeed present at the surface of the M1 phase catalyst under realistic reaction conditions.

The process of selective propane ammoxidation over the Mo-V-Te-Nb-O M1 phase is proposed to consist of a series of elementary steps including propane oxidative dehydrogenation (ODH), ammonia and $O_2$ activation, NH$_x$ insertion into C$_x$ surface intermediates, etc. DFT calculations were performed here to investigate three sequential
H abstraction steps that successively convert propane into isopropyl, propene, and allyl on cation sites in the proposed selective and active center present in the \(ab\) plane of the Mo-V-Te-Nb-O M1 phase [8]. The initial H abstraction from propane was found to be the rate-limiting step of this process, consistent with both the proposed reaction mechanism for propane ammoxidation on the bulk Mo-V-Te-Nb oxides and current understanding of V\textsuperscript{5+} as the active site for alkane activation on V-based oxides. Te=O was found to be significantly more active than V\textsuperscript{5+}=O for the H abstraction from propane, which suggests that the surface and bulk Te species may be different. The role of Mo=O is most likely limited to being an H acceptor from isopropyl to form propene under ammoxidation conditions.

DFT calculations were subsequently performed to investigate the energetics of ammonia adsorption and activation in the proposed active center present in the \(ab\) plane of the M1 phase [9]. The formation of NH\(_x\) (\(x = 0, 1, 2, 3\)) species was found to be highly favored on reduced, oxo-depleted metal sites. The reduced Mo site was indicated to be the most favorable site for ammonia activation by comparing the reaction energy profiles for the sequential dehydrogenation of ammonia on the various surface metal sites. The activation barrier for the initial H abstraction from ammonia was found to depend strongly on the surface sites that stabilize H and NH\(_2\), and was as low as 0.28 eV when NH\(_2\) was stabilized by the reduced Mo site and H was abstracted by the telluryl oxo group. The subsequent step of surface NH insertion into a gas-phase \(\pi\)-allyl intermediate was also found to have a low activation energy barrier of 0.03 eV on the reduced Mo site.
Finally, DFT theory and cluster models were employed to investigate the mechanism of propane ammoxidation to acrylonitrile on the proposed active center present in the \( ab \) plane of the Mo-V-Te-Nb-O M1 phase, focusing specifically on three sequential H abstraction steps from allyl-imido surface intermediate to acrylonitrile. The transition states and activation barriers for the H abstraction from imido, methyl H abstraction, and methane H abstraction from the allyl on the Mo=O oxo groups have been determined using a combination of CI-NEB and dimer methods. Since Mo=O was previously found to be the least preferred surface site for the H abstraction steps from C3 species, the activation barriers on Mo=O can provide the upper limit for the energy required to completes this series of reaction steps. The activation barriers for the H abstraction from methyl and methine group are calculated to be 1.26 and 1.62 eV, respectively, and that for the H abstraction from the imido species was negligibly small. Both barriers were lower than the activation energies for the initial H abstraction from propane and propene on the same Mo=O site. Therefore, the final formation of acrylonitrile by H abstraction is not the rate-limiting step for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase.

The microkinetic model based on the results of the DFT calculations was further developed to investigate the surface species coverage on Mo-V-Te-Nb-O M1 phase during propane ammoxidation and their impact on the selectivity to acrylonitrile. The model is based on a reaction mechanism consisting of 8 steps starting from the adsorption of gas phase ammonia and oxygen on surface active site to the formation of \( \pi \)-allyl intermediate. The selectivity to acrylonitrile and CO\(_x\) is determined by the ratio of surface coverage of nitrogen to the one of oxygen. The calculated reaction rate constant
and equilibrium constant indicated that: 1) the kinetic parameter analysis showed that oxygen can compete with ammonia in occupying the surface active sites; 2) formation of water from surface hydroxyl and the release of water is quick step featured with exothermic process and high reaction rate constant. The calculated surface species coverage reflected these observations: the main surface species is surface imido NH at Mo site with 0.48 coverage followed by surface oxygen at Mo^{5+} site. Therefore 49% of products from propane ammoxidation is acrylonitrile as selective product which is in agreement with predication in the maximum selectivity to acrylonitrile. Further studies to reach more accurate selectivity to acrylonitrile and CO\textsubscript{x} from propane ammoxidation over Mo-V-Te-Nb-O M1 phase requires a more complicated microkientic model that not only considers the surface Mo and V^{5+} sites but also the catalytic performance of Te and Nb surface sites together with the cooperation and synergy between different surface active sites.
Chapter 2 Background

2.1 INTRODUCTION

Acrylonitrile is an important chemical intermediate that is widely used in the manufacture of useful plastics, such as polyacrylonitrile. It is currently produced by the selective catalytic ammoxidation of propene known as the Sohio process, which produces more than 10 billions pounds worldwide annually [1, 2, 10]. In recent decades the acrylonitrile production by catalytic ammoxidation of propane gained considerable interest as a potential replacement of the Sohio process because of the abundance and environmental friendliness of this natural gas feedstock. According to Annual Energy Outlook Reports for 2013 and 2014 published by the U.S. Department of Energy [3, 4] and 2013 propane market outlook by Propane Education and Research Council [11], increasing shale gas production in the United States may have an added beneficial economic impact on this process by further lowering propane costs.

For example, in 2006, Asahi Kasei, one of the biggest global chemical companies, opened the first acrylonitrile production plant in Thailand using propane as feedstock but shut it down in 2007 [12]. However, after numerous process improvements, they restarted this plant again in January 2013. Despite this initial commercial promise, further improvement of the selectivity of the M1 phase catalysts to acrylonitrile is highly desirable for a widespread adoption of this novel catalytic technology as a lower lost and environmentally friendly alternative to the current Sohio process. The V-based metal oxides, including supported vanadia and V-based mixed metal oxides have received significant attention in the catalysis community as candidate catalysts for propane
ammonoxidation. However, the current experimental techniques have limited ability to establish the nature of the active and selective surface sites present in complex multicomponent mixed metal oxides and develop fundamental molecular structure-reactivity relationships that are needed for their improvement for a commercially viable propane ammonoxidation process.

On the other hand, theoretical modeling has been demonstrated to be a powerful tool to explore the electronic structure of metal oxides and establish elementary steps of alkane ODH over metal oxide surfaces, such as vanadium and molybdenum oxides [13–19]. Based on experimental findings that propane ammonoxidation over vanadium-based oxides catalysts occurs through sequential steps of propane ODH to propylene followed by its ammonoxidation, we first review the results of previous theoretical studies that explored the electronic structure of supported VOₓ and bulk V-based mixed oxides and the molecular structure-reactivity relationships in alkane ODH and ammonoxidation. We then review the results of previous experimental studies of propane ammonoxidation over the M1/M2 catalytic system and discuss the reaction pathway proposed by Grasselli et al. [1, 2, 20]. Lastly, we identify the gaps in understanding the activity and selectivity of the Mo-V-Te-Nb-O M1/M2 system in propane ammonoxidation.

Despite extensive experimental studies of the bulk mixed Mo-V-Te-Nb-O system, many challenges remain. It has been shown that it contains two major crystalline phases, so-called M1 and M2 phases. The differences in their crystal structures and chemical composition of two phases, especially the presence of V⁵⁺ only in the M1 phase, led many researchers to conclude that M1 phase was the only phase responsible for the propane activation. The M2 phase containing only V⁴⁺ was unable to activate propane, but was
proposed to be active in the ammoxidation of the propene intermediate. Grasselli et al. (Figure 1) proposed an early hypothetical model of a complete reaction pathway based on some general understanding of the roles of vanadium and other metal cations in the ODH of lower alkanes established for other mixed metal oxide catalysts.

Table 1. Experimental compositions based on different characterization techniques [21].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1(Te–Nb)</td>
<td>(Te\textsubscript{IV}O\textsubscript{1.3}V\textsuperscript{VI}\textsubscript{3.3}V\textsuperscript{V}\textsubscript{0.3}Mo\textsuperscript{VI}\textsubscript{2.0}Mo\textsuperscript{VI}\textsubscript{13.3}Nb\textsuperscript{V}\textsubscript{2.0}O\textsubscript{56}</td>
</tr>
<tr>
<td>M1(Sb–Nb)</td>
<td>(Sb\textsuperscript{III}O\textsubscript{0.4}Sb\textsuperscript{IV}O\textsubscript{0.1}V\textsuperscript{IV}\textsubscript{2.7}V\textsuperscript{V}\textsubscript{0.3}Mo\textsuperscript{VI}\textsubscript{4.8}Mo\textsuperscript{VI}\textsubscript{9.7}Nb\textsuperscript{V}\textsubscript{2.2}O\textsubscript{56}</td>
</tr>
<tr>
<td>M2(Te)</td>
<td>(Te\textsuperscript{IV}O\textsubscript{2.1}V\textsuperscript{IV}\textsubscript{1.5}V\textsuperscript{V}\textsubscript{0.2}Mo\textsuperscript{VI}\textsubscript{0.8}Mo\textsuperscript{VI}\textsubscript{13.5}O\textsubscript{18}</td>
</tr>
<tr>
<td>M2(Sb)</td>
<td>(Sb\textsuperscript{III}O\textsubscript{0.55}Sb\textsuperscript{IV}O\textsubscript{0.1}V\textsuperscript{IV}\textsubscript{1.0}V\textsuperscript{V}\textsubscript{0.4}Mo\textsuperscript{VI}\textsubscript{0.2}Mo\textsuperscript{VI}\textsubscript{3.8}O\textsubscript{18}</td>
</tr>
<tr>
<td>M2(Tc–Nb)</td>
<td>(Te\textsuperscript{IV}O\textsubscript{1.8}V\textsuperscript{IV}\textsubscript{1.2}V\textsuperscript{V}\textsubscript{0.1}Mo\textsuperscript{VI}\textsubscript{0.6}Mo\textsuperscript{VI}\textsubscript{3.7}Nb\textsuperscript{V}\textsubscript{0.4}O\textsubscript{18}</td>
</tr>
<tr>
<td>M2(Sb–Nb)</td>
<td>(Sb\textsuperscript{III}O\textsubscript{0.4}Sb\textsuperscript{IV}O\textsubscript{0.1}V\textsuperscript{IV}\textsubscript{1.1}V\textsuperscript{V}\textsubscript{0.3}Mo\textsuperscript{VI}\textsubscript{0.4}Nb\textsuperscript{V}\textsubscript{0.3}O\textsubscript{18}</td>
</tr>
</tbody>
</table>

![Orthorhombic Space group Pna2](image)

Figure 1. *ab* Planes of M1 (left) and M2 (right) phases [22, 23]
Figure 2. Hypothetical pathway of propane ammoxidation over $ab$ planes of the Mo-Te-V-Nb-O M1 phase [24].

Due to the importance of vanadium for selective oxidations, in the following sections, we review the major results of prior theoretical studies focused on the structures and reactivities of V-based oxides employed for oxidative transformations of propane.

2.2 PROPANE OXIDATION OVER UNSUPPORTED AND SUPPORTED VANADIA CATALYSTS

The efforts in designing improved catalysts for selective propane oxidation started by exploring the ability of bulk vanadia to activate C-H bonds as the initial step in oxidative dehydrogenation (ODH) of lower alkanes to alkenes, especially that of propane. Lower alkane ODH over metal oxide surfaces was proposed to proceed via a Mars-van Krevelen redox mechanism, where hydrogen is abstracted from alkane by the surface lattice
oxygen and the resulting oxygen vacancies are re-oxidized by the absorbed O$_2$ [25–27]. There are three different types of lattice oxygen present in the bulk vanadia: terminal oxygen (O1), oxygen bridging two V centers (O2), and oxygen bridging three V centers (O3).

One of the early studies of surface oxo sites present in vanadia was reported by the Hermann group [28]. They modeled V$_2$O$_5$(010) surface using a V$_{10}$O$_{31}$H$_{12}$ cluster model as a single layer and V$_{20}$O$_{62}$H$_{24}$ cluster model as a bilayer. Hydrogen binding energies on three different O sites were calculated for single H atom adsorption on each site using DFT with a gradient-corrected (RPBE) functionals. It was shown that OH was most stable on terminal oxo site O1 exhibiting the highest H adsorption energy followed by the bridging oxo site O2. Adding a second H atom to the oxo sites showed the similar trend that O1 and O2 were the two most stable sites for H adsorption. In this study, the removal of O, OH, and H$_2$O from the V$_2$O$_5$(010) surface oxo sites by fully relaxing the structure with oxygen vacancy was also investigated. It was found that removing oxygen is difficult indicated by a large vacancy formation energy ranging from 6.5–7.2 eV. However, the addition of hydrogen onto the oxo site made the oxygen removal easier, especially in the case of formation of water on the oxo site. The findings that H adsorption was favored at terminal O site O1 and the removal of water from the surface oxo site was easy leading to an oxygen vacancy suggested V$_2$O$_5$(010) as a good catalytic surface for hydrocarbon oxidation reactions with enhanced yield of ODH products.

The importance of the O1 site present at the vanadia surface for hydrocarbon oxidation was subsequently studied in more detail for the initial H abstraction from propane. Gilardoni et al. [29] studied propane oxidation to propene using DFT
calculations and finite cluster models $\text{V}_4\text{O}_{14}$ to represent the $\text{V}_2\text{O}_5$(010) surface. They observed the formation of $i$-propoxide on the surface O1 site and hydroxyl on all three oxygen sites through the methylene H abstraction. The second H abstraction from the methyl group is performed by the bridging hydroxyl group followed by a simultaneous release of water and propene in a concerted process. These findings are in agreement with the results of the isotopic labeling studies [17, 30], in which the formation of the propoxide and hydroxyl by cleaving the methylene C-H bond in propane was found to be irreversible. Moreover, the observation of a simultaneous release of water molecule is in good agreement with earlier findings [28] that the formation of water facilitates oxygen removal, which is one of the reasons that vanadia is highly active in hydrocarbon oxidations. However, the estimated activation energy for the ODH of propane to propene on the $\text{V}_2\text{O}_5$(010) surface from the second H abstraction was 15 kcal/mol or 0.65 eV compared to 9.4 kcal/mol for first H abstraction to form $i$-propoxide. It suggested that the initial H abstraction is not the rate-limiting step of propane ODH on $\text{V}_2\text{O}_5$(010) surface in this study based on the estimated activation energies, which is in disagreement with other studies as discussed below using period slab models. This might due to the use of the finite cluster models that cannot represent the structure of the $\text{V}_2\text{O}_5$(010) surface in terms of describing the activity of each oxygen site in H abstraction from C$_3$ species.

Besides showing the importance of surface oxo center for propane activation, theoretical studies of propane ODH over vanadia also focused on the nature of the rate-limiting step and its associated activation energy barrier that can be directly validated against the experimental activation energy. Rozanska et al. [15] explored propane ODH
using O=V(OH)$_3$ cluster model and compared the energy barriers calculated by different quantum chemistry methods. The cluster structure was optimized by the hybrid B3LYP functional with triple-$\zeta$ plus polarization basis sets (TZVP) on all atoms. Since B3LYP is known to produce systematically low energy barriers, a single point energy calculation by a wavefunction-based electron correlation CCSD(T)/TZVP was then performed on the optimized structure from B3LYP/TZVP to estimate the error of the B3LYP method. The estimated error due to B3LYP was 20-30 kJ/mol as compared to much more accurate CCSD(T) results. However, the error was even larger for the rate-limiting step of initial H abstraction from propane: the energy barrier for the initial H abstraction during propane ODH was 205 kJ/mol using CCSD(T) and only 163 kJ/mol using B3LYP.
Figure 3. The structure of the V$_2$O$_5$(010) surface. Vanadium atoms are shown in blue and oxygen atoms are shown in red. Three different types of oxygen sites in bulk structure (O1, O2, and O3) are labeled accordingly. Site O2’ and O3’ are equivalent to O2 and O3, respectively, in the bulk structure, but non-equivalent in the V$_2$O$_5$ surface. Hence, they are labeled accordingly for the V$_2$O$_5$(010) surface [31].

Redfern et al. [31] employed the hybrid B3LYP DFT calculations to study propane ODH over the V$_2$O$_5$(010) surface using both vanadia cluster models and periodic slabs composed of (1×2) and (1×3) supercells of (010) single layers. The complete reaction
mechanism included propane adsorption on terminal oxygen O1 and bridging oxygen O2 site followed by the release of water and propene from the surface, as well as the adsorption of dioxygen at the depleted o xo site. They found the energy barriers for the propane adsorption and propene release process to be 45-60 kcal/mol depending on the reaction pathway and spin state of the system. Cheng et al. [32] found that the rate-limiting step of propane ODH is the first H abstraction from propane to form the isopropyl intermediate with a 23.9 kcal/mol activation energy using the B3LYP method and a V₅O₁₅ cluster model. These findings are in good agreement with experimental observations for propane ODH on vanadia that the rate-limiting step is the first H abstraction from the methylene group with the activation energy of 20-30 kcal/mol [18, 30, 33]. Rozanska et al. [13] also examined the positively charged vanadia cluster V₅O₇⁺ model and compared it to other vanadium oxides models. They found that the initial C-H bond cleaving is still the rate-limiting step for propane ODH that occurs on a surface V=O site.

Therefore, extensive theoretical studies of propane ODH employing different V₂O₅(010) models and computational protocols conducted to date indicated that the initial H abstraction from propane by the terminal O1 site is the rate-limiting step with the 20-30 kcal/mol activation energy. These findings are also in good agreement with experimental observations of propane ODH on vanadia catalysts.

Fu et al. [34] employed the periodic DFT to study propane ODH over unsupported V₂O₅(001) surface modeled as a single-layer slab. They investigated various pathways of propane activation to propene and observed quite different behavior of this surface as compared vanadia(010) (Figure 4). In this case as shown in Figure 4, not only
the terminal oxygen O1 was capable of activating the methylene C-H bond in propane, but also the bridging oxygen O2 was able to complete this step with a similar activation energy (30.4 kcal/mol as compared to 27.3 kcal/mol). Moreover, they found that propene formed more easily from i-propoxide and was released from the bridging O sites because of weaker bonding, while the terminal O1 sites were too active leading to propene combustion. Therefore, vanadia(001) surface was found to be less ideal for selective propane ODH to propene. These findings are consistent with the experimental observation [35] that the selectivity to propane is low at high vanadium loadings when bridging O sites are favored and active for propane ODH. Similar to earlier conclusions from the studies on the V_{2}O_{5} (001) surface [REFS!], the O1 site present on the V_{2}O_{5}(010) surface is believed to be the active site responsible for the initial propane activation during propane ODH on the vanadia surface.

Figure 4. Propane ODH on O1 and O2 sites present in the vanadia(001) surface investigated by periodic DFT. The energy units are kcal/mol. The energies of each
intermediate and transition state (TS) (DID YOU ALREADY EXPLAIN WHAT TS IS?) are calculated with respect to the total energies of gas phase propane and the vanadia(001) model [34].

Experimental studies of ODH catalysts have been extended to supported vanadium oxides, since the bulk (unsupported) vanadium oxides showed significant activity in propane ODH. Supported vanadia received significant attention in the catalysis literature because of high propene yields resulting from the highly dispersed nature of these molecular vanadium oxide catalysts. Therefore, two major research topics, i.e. (1) the interactions between the oxide support and vanadia, and (2) the fundamental relationships between the molecular structure and reactivity of the supported vanadia have been at the front and center of theoretical studies aimed at improved understanding of the propane ODH, especially the C-H bond activation step [36].

Extensive experiments and computational studies [19, 37–39] demonstrated that vanadia species supported on the alumina surface are tetrahedral possessing one terminal oxo group and three bridging oxygen atoms anchored to the oxide surface. Kim et al. [19] studied the structure of θ-alumina supported vanadia using both deep UV Raman and B3LYP DFT. The presence of tridendate, bidendate, and molecular monomeric vanadate species (Figure 5) was suggested for dehydrated θ-alumina by matching the observed frequencies with the calculated stretching frequencies from B3LYP for different structures of vanadia monomers supported on alumina. On the other hand, the Raman spectrum indicated the presence of only monodentate species on hydrated support (Figure
5). All four structures on either dehydrated or hydrated alumina show the four-coordinated oxygen environment for vanadium, with three oxygen atoms coordinated to support. Todorova et al. studied vanadium oxides on $\alpha$- and $\kappa$- aluminum oxide supports [37, 38] by DFT combined with statistical thermodynamics. The statistical thermodynamic model was applied to understand the vanadia aggregation on each support under different oxygen partial pressures and surface vanadium concentrations. It was predicted that vanadia film can grow on both $\alpha$- and $\kappa$- aluminum as the vanadia loading increases when the vanadium chemical potential is high. The thick vanadia film formed on the both $\alpha$- and $\kappa$- aluminum oxide support surface featured vanadyl groups with $V^{5+}$ at surface of the film and $V^{3+}$ in the bulk of the multilayer vanadia film.

Cheng et al. [40] studied conversion of propane to propanol by the anatase-supported vanadium oxide monomers and dimers using B3LYP. It was found that the coordination number of the vanadium atom was the key structural parameter in predicting the catalytic activity, especially the ability to activate C-H bonds. The supported VO$_x$ structures with a square-pyramidal coordination environment were shown to be the most active geometry for activating C-H bonds because of its ability to stabilize reduced V cations.
Figure 5. Model structures of vanadia monomer supported on θ-alumina used in DFT calculations [19].

The pathways of propane ODH over supported vanadia were investigated both experimentally and theoretically and compared to those on unsupported, bulk vanadia. Kondratenko et al. [41] studied selective and unselective reaction pathways of the oxidative dehydrogenation of propane over supported vanadia catalysts using steady-state and transient isotope labeling tests. They found that propene is primarily formed via oxidative dehydrogenation of propane by lattice oxygen of VO₅ species similar to earlier findings for propane ODH [17]. Unselective pathway was found to begin from C-C bond breaking in propene that occurred on bare acidic surface of the Al₂O₃ support. Therefore, high vanadia coverage on the oxide support is expected to be beneficial for the selectivity to propene. Alexopoulos et al. [36, 42] conducted extensive studies of propane oxidation over anatase-supported V₂O₅(001) surface using both cluster models and periodic slabs in
DFT calculations. They found that the deposition of a vanadia monolayer onto the anatase support enhanced the Lewis acidity of vanadia and the activity of vanadyl oxygen. This led to a lower binding energy of H on the vanadyl site. Therefore, the propane activation via a methylene C-H bond broken through the H abstraction by vanadyl site is more favorable on supported vanadia surface as compared to unsupported vanadia characterized by a lower activation energy (by 34 kJ/mol).

Theoretical studies of the propane ODH over supported and unsupported $\text{V}_2\text{O}_5(001)$ surface were conducted for other supports than alumina and anatase (Table 1). Rozanska et al. [14] studied the silica substrate by substituting one Si-H in cubic silsesquioxane with a vanadyl group corresponding to a V atom in a 5+ oxidation state in this cluster model. They found that the initial H abstraction from propane occurs on vanadyl site and determined its activation energy to be 123 kJ/mol, which is excellent agreement with the apparent activation energy of $122 \pm 20$ kJ/mol determined for propene formation over $\text{V}_2\text{O}_5/\text{SiO}_2$ [43]. Moreover, they found that the second H abstraction from isopropyl can either happen on a V=O or V-O-Si bridging site. However, as compared to bulk $\text{V}_2\text{O}_5$ and vanadia supported on anatase and alumina, the activation energy of the initial H abstraction from propane by $\text{V}_2\text{O}_5$ on a silica support is not lowered significantly. Accordingly, this supported vanadia catalyst shows lower activity in propane ODH as compared to anatase and alumina supported vanadia [15, 40, 42, 44, 45].

Table 1. Theoretical and experimental activation energies for propane oxidation over bulk and supported vanadia catalysts [42].

<table>
<thead>
<tr>
<th>Method</th>
<th>Catalyst</th>
<th>$E_{\text{act}}$ (kJ/mol)</th>
</tr>
</thead>
</table>

29
Theoretical work

<table>
<thead>
<tr>
<th></th>
<th>V$_2$O$_5$</th>
<th>120 [42]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ML-V$_2$O$_5$/TiO$_2$</td>
<td></td>
<td>86 [42]</td>
</tr>
<tr>
<td>&lt;$1$ML-V$_2$O$_5$/SiO$_2$</td>
<td></td>
<td>123 [14]</td>
</tr>
<tr>
<td>(001) V$_2$O$_5$</td>
<td></td>
<td>115 [34]</td>
</tr>
<tr>
<td>&lt;$1$ML-V$_2$O$_5$/support*</td>
<td></td>
<td>100 [32]</td>
</tr>
</tbody>
</table>

Experimental findings

<table>
<thead>
<tr>
<th></th>
<th>V$_2$O$_5$/TiO$_2$</th>
<th>74 [46]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt% V$_2$O$_5$/TiO$_2$</td>
<td></td>
<td>70 [47]</td>
</tr>
<tr>
<td>5wt% V$_2$O$_5$/TiO$_2$</td>
<td></td>
<td>99 [18]</td>
</tr>
<tr>
<td>10wt% V$_2$O$_5$/ZrO$_2$</td>
<td></td>
<td>80 [47]</td>
</tr>
<tr>
<td>14wt% V$_2$O$_5$/Al$_2$O$_3$</td>
<td></td>
<td>110-120 [48]</td>
</tr>
<tr>
<td>2-30wt% V$_2$O$_5$/Al$_2$O$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3wt% V$_2$O$_5$/SiO$_2$</td>
<td></td>
<td>122 ± 20 [43]</td>
</tr>
</tbody>
</table>

*V$_4$O$_{10}$ cluster model was built in this study to represent the V$_2$O$_5$(001) surface supported on a sphere-shaped substrate.

Although the activation energy can be lowered by introducing favorable interactions between the vanadia species and support, the reaction is still initiated by a secondary C-H bond scission in propane that occurs at the terminal oxygen site (O1). Unlike bulk vanadia, extensive theoretical studies of supported vanadia mainly focused on the model (001) surface, since the reaction on the (010) surface leads to propane combustion [34].
In conclusion, the following observations have been made for propane ODH over bulk and supported vanadia: 1) the initial C-H bond activation from propane is the rate-limiting step; 2) the activation energy for this step is ca. 20-30 kcal/mol calculated using DFT and verified experimentally; 3) the terminal oxygen in $V^{5+}=O$ was shown to be the most active site as compared to bridging oxygen atoms; 4) the coordination environment is important in determining the catalytic activity of terminal oxygens. Vanadate species possessing a square-pyramidal coordination appear to be the most active geometry. Moreover, these theoretical findings have direct relevance to understanding the catalytic performance of isolated vanadyl centers present in V-based bulk mixed metal oxides in propane ODH due to local structural similarities of such mixed metal oxides to bulk and supported vanadia systems.

2.3 THEORETICAL STUDIES OF PROPANE OXIDATION OVER V-BASED BULK MIXED OXIDES

Although bulk and supported vanadium oxides are among the most active and selective catalysts for propane ODH to propene that have been extensively studied in recent decades, the current yield of propene is still limited to ca. 30 mol. % due to high reactivity of propene leading to its combustion at high propane conversion. The search for improved metal oxide catalysts suitable for selective propane activation has expanded to include V-based bulk mixed oxides, such as VMgO, VSB, and Mo-V-O catalysts for propane ammoxidation to acrylonitrile, which is a thermodynamically more stable molecule than propene under redox reaction conditions.
The VMgO system is among the most active and selective catalyst for propane ODH, where the site isolation of V\(^{5+}\) cations in its oxide framework is believed to be beneficial for the high selectivity to propene [49]. Subsequent studies [25, 50] of the V-Mg-Sb-O system demonstrated that antimony further improved the selectivity of the VMgO system by forming isolated Sb-O-V-O sites. Similar effect was observed when the vanadium concentration in this mixed metal oxide matrix was lowered, which also resulted in improved selectivity to propene [51].

The rutile structure of another V-based mixed oxide, VSbO\(_4\) (Figure 6), was probed by theory in order to understand its catalytic behavior in hydrocarbon oxidation. Seitz et al. [52] studied the V and Sb vacancies at the surface of VSbO\(_4\) and their effects on the surface electronic structure and reoxidation properties using DFT. The rutile structure was constructed with 16.67% cation deficiency. V was found to be isolated by surrounding Sb atoms and became oxidized from +3 to +4 oxidation state determined by the Bader charge analysis [53, 54]. The oxidized V atom site is thus a Lewis acid site that could act as an active site for adsorption of ammonia and oxygen molecules during oxidation catalysis. Furthermore, the density of state (DOS) analysis suggested that lattice oxygen is close to a V vacancy site and could be involved in hydrocarbon activation. Irigoyen et al. [55, 56] studied toluene adsorption at the VSbO\(_4\)(110) surface using a semi-empirical method, which is an improvement of the Extended Hückel Molecular Orbital (EHMO) method. Their fragment overlap population analysis and projected density of states results showed that the methyl group in toluene interacts with Sb site when the surface of phenyl fragment in toluene is parallel to VSbO\(_4\)(110) surface on Sb-V site. The C-H bond in the methyl group and Sb-O bond are weakened due to the
interaction between the methyl and this Sb site. Their results also showed the importance of the cation site in activating C-H bond in hydrocarbon but the cation is Sb not the V as showed in the other studies for VSB₅O₄ system. However, their cluster model had a very high net charge of -61. This high negative charge may introduce artificial electronic interactions when studying the adsorption of hydrocarbon species on the surface cation sites.

![Crystal structure of the rutile VSbO₄ phase](image)

Figure 6. Crystal structure of the rutile VSbO₄ phase [52].

Besides modeling the electronic structure of the VSB₅O₄(110) surface, some theoretical studies probed the ammonia and hydrocarbon adsorption and reaction on this catalytic surface. Seitz et al. [57] studied adsorption of ammonia on Lewis and Bronsted acid sites present on the VSB₅O₄(110) surface using DFT performed on a slab model consisting of 12 layers. The crystal orbital overlap population analysis indicated that for
Lewis site nitrogen atom interacts with a surface vanadium-isolated site whereas for Bronsted site nitrogen atom interacts with surface hydrogen atom. Moreover these interactions were limited and did not involve other atoms on the surface and subsurface layers, which suggested weak adsorption of ammonia on the V$_{\text{Sbo}}$(110) surface. Rojas et al. [58, 59] reported a similar conclusion for ammonia adsorption on the V$_{\text{Sbo}}$(110) surface by employing a combined DFT and experimental study. Ammonia was indicated to prefer an isolated V site neighboring two Sb atoms in the rutile structure as a Lewis acid site for adsorption with a weak electrostatic acid–base interaction. Ammonia interacted more strongly with Brønsted acid sites as compared to Lewis acid sites, preferring a two-fold hydroxyl site bridging both V and Sb. Further studies of ammonia dissociation showed that the isolated vanadium Lewis sites were thermodynamically preferred by ammonia dissociation to NH$_2$+H and NH+H. Furthermore, Rojas et al. recently extended their studies to ammoxidation and ODH of lower hydrocarbons (ethane, ethylene, propane, and propylene) on the V$_{\text{Sbo}}$(110) surface [59]. They found that antimony is the preferred adsorption site for propane and propene, which is different from isolated vanadium sites indicated for ammonia adsorption and activation. This indicated that there is no competition between ammonia, propane, and propene for the same activation site. In contrast such competition does occur between ammonia, ethane, and ethylene. This difference in preferred adsorption sites by hydrocarbon species explained why this catalyst is active for propane ODH but not ethane ammoxidation. Also they found that molecular dispersed VO$_x$ species in the system are responsible for transforming propane to propene.
On-going theoretical studies of the VSbO$_4$ system that focused on the electronic structure and reactivity properties of its surface have revealed the following findings: 1) V can be isolated by Sb atoms thus resulting in an oxidized V site. 2) The V site isolation affects the catalytic properties making the V vacancy a favorable adsorption site for ammonia and the surface lattice oxygen close to the V vacancy an active site for hydrocarbon activation. 3) Ammonia is able to interact and weakly bind to the surface V site isolated by Sb atoms. The dissociation of ammonia is thermodynamically favored on isolated V sites.

In recent years, a more robust catalytic system based on bulk multicomponent Mo/V oxides has gained considerable interest due to its high selectivity and activity towards propane ammoxidation to acrylonitrile that approach practical requirements for an industrial catalyst for this lower alkane transformation reaction. This catalytic system is further discussed in the next section.

**2.4 THEORETICAL STUDIES OF MO-V-TE-NB-O M1 PHASE CATALYST**

Selective oxidation catalysis is of great importance to chemical industry because it provides about a quarter of all organic chemicals used worldwide to produce consumer goods [16]. The selective ODH and ammoxidation of inexpensive and abundant alkanes, such as ethane and propane, to ethylene and acrylonitrile, respectively, using mixed metal oxide catalysts represents new environmentally friendly “green” chemical processes that have received considerable attention. Moreover, as the shale gas production dramatically increased in recent years, it is now the largest source of growth in US natural gas supply
that is predicted to continue to grow until 2040 according to Department of Energy Annual Energy Outlook publications in 2013 and 2014 [3, 4]. Consequently, increased supply of propane from shale gas can be expected, which would further improve the process economics of propane ammoxidation. However, the current yield of acrylonitrile from propene in the Sohio process is greater than 80 mol. %, the yield of acrylonitrile in propane ammoxidation over the best bulk multicomponent Mo/V oxides is ca. 60 mol. % [REFS]. In order to successfully compete with the Sohio process, the yield from propane ammoxidation should be improved significantly, which requires better understanding and further improvement of the current bulk multicomponent Mo/V oxide catalysts.

Among the currently researched catalysts for propane ammoxidation [48], the Mo-V-Te-Nb mixed metal oxide discovered by the Mitsubishi Chemical Corporation in 1995 is most active and selective [16, 20, 21, 55]. The Mo-V-Te-Nb oxide consists of two major crystalline phases, M1 and M2 [10, 19]. It has been demonstrated that the M1 phase [37, 46, 47, 54, 56] is primarily responsible for the activity and selectivity of the Mo-V-Te-Nb oxides in propane ammoxidation, whereas the presence of the M2 phase appears to improve the selectivity of the M1 phase at low propane conversion through synergistic effects [1, 17, 27, 32, 48].

The M1 phase crystallizes in the orthorhombic Pba2 space group exhibiting 13 crystallographically distinct metal lattice positions (S1-S13) and has an overall composition of Mo7.8V1.2NbTe0.94O28.9 [19]. The 11 framework sites include octahedral sites (S1-S8, S10 and S11) occupied by V and Mo, and a pentagonal bipyramidal site (S9) occupied by Nb, while the Te=O component is found to be intercalated into hexagonal (S12) and heptagonal (S13) channels in the M1 phase structure [49]. Recent
studies of the M1 phase combining high resolution TEM (transmission electron microscopy), synchrotron X-ray, and powder neutron diffraction methods have shown that V, Mo, and Te are present in the 4+/5+, 5+/6+ and 4+ oxidation states, respectively [9, 10, 42, 51].

Propane ammoxidation to acrylonitrile is proposed to occur via a series of steps involving propane oxidative dehydrogenation (ODH), ammonia and O₂ activation, and N-insertion into C₃ surface intermediates. Based on the site isolation concept, Grasselli et al. [16-19] have proposed that the crucial propane activation step occurs on the V⁵⁺=O site through its resonance structure V⁵⁺=O ↔ V⁴⁺•–O•; that the subsequent H abstraction steps forming the allyl intermediate are performed by the Te⁴⁺=O site; and that the Mo⁶⁺ site is active and selective in the NH/O insertion into allyl. All the key catalytic elements needed to transform propane into acrylonitrile are strategically arranged within bonding distances of one another in the proposed active center of the M1 phase (Figure 1). Nb⁵⁺ pentagonal bipyramidal sites do not play a direct catalytic role, and instead stabilize the M1 structure by isolating the active centers. On the other hand, only V⁴⁺ and no V⁵⁺ cations were found in the bulk M2 phase, which may explain the inability of the M2 phase to activate propane [19]. Consistent with this mechanism, the ammoxidiation of propane to acrylonitrile has been found to involve no re-arrangement of the C backbone (Figure 7) [60]. In this study by Shiju et al., the reaction was conducted using propane labeled by ¹³C at the terminal C1. The ¹³C NMR analysis on the products showed a strong signal for =CH₂ group followed by –CN and –CH=, which suggested the lack of structural re-arrangement on C during the ODH of propane to propene.
Figure 7. $^{13}$C NMR spectra of products collected after the ammoxidation reaction of 1-$^{13}$C-labeled propane (a) and unlabeled propane (b). The expanded spectra of the acrylonitrile regions are given in the insets. The peak at 77 ppm is of the solvent, CDCl$_3$ [60].

The hypothetical reaction pathway proposed by Grasselli et al. relies upon the difference in the ability of V$^{5+}$=O and other cations for H abstraction and in the facility of H removal from the different cation centers. Although vanadia (VO$_x$) is a well-known oxidation and ODH catalyst [5, 8, 30, 31, 38, 58] and the presence of Te and Nb is important for the high activity and selectivity [49], the detailed understanding of the roles of the various cations in the Mo-V-Te-Nb oxide is presently poor. The fundamental explanation for the significantly higher activity and selectivity of the Mo-V-Te-Nb oxide in propane ammoxidation to acrylonitrile as compared to compositionally simpler bulk Mo-V and Mo-V-Te oxides remains lacking, in no small part because of the complex
structure of the M1 phase. However, the limited fundamental understanding of this highly promising catalytic system hinders its further improvement that is required to make the process of propane ammoxidation to acrylonitrile a commercial success.

Quantum chemistry-based theoretical approaches have been well established as a powerful tool for generating mechanistic insights that are otherwise unavailable. So far, only a handful of theoretical studies have been performed to better understand the structure and catalytic behavior of the Mo-V-Te-Nb-O M1 and M2 phases [61–65]. Fu et al. [65] has studied the V distribution in the bulk M1 structure by developing a cost-efficient DFT-based method where a large number of M1 phase configurations calculated using periodic DFT were treated by the Boltzmann statistics to find the optimal V distribution. They found that the V atom occupies S2 site predominantly which is in good agreement with experimental observations. Moreover, they found a negative correlation for the arrangement of V-V pairs suggesting the preference for isolated V sites in the M1 structure.

Recently, Goddard et al. [61, 64] applied their reactive force field (ReaxFF) method to prepare the M1 phase models with Mo-V-Te-Nb-O and Mo₃VOₓ compositions. The NVT-MD simulations of the bulk structure at 300 K confirmed the stabilizing role of Te⁴⁺ and Nb⁵⁺ in the bulk M1 phase. Mo and V in the bulk M1 phase were found to preferentially occupy separate columns rather than mixing in the same column of alternating Mo and V sites. They also found that after allowing 20 propane molecules to react with Mo₃VOₓ, three propane molecules penetrated one of the heptagonal channels (Figure 8) and that one has lost an H to a V=O.
Goddard et al. [63] also studied propene activation over the M2 phase by employing Monte Carlo techniques based on ReaxFF. They found that the Te$^{5+}$ oxo chains are critical for activating propene but not propane in the M2 phase.

Figure 8. Cross-section of the final configuration from the propane/ Mo$_2$VOx ReaxFF–RD simulation illustrating the shape and size of heptagonal channels C7$_1$ and C7$_2$ from the top and side of the slab. Channel C7$_2$ with an average radius of 4.6 Å contains three propane molecules (channel length ca. 18 Å) while channel C7$_1$ is smaller with an average radius of 4.1 Å and remains empty [61].

In conclusion, the Mo-V-Te-Nb-O M1 phase is one of the most promising catalysts displaying both high selectivity and activity in propane ammoxidation. In the
past, extensive experimental and theoretical studies have been conducted to understand
the VO_x, VMeO_x, and Mo-V-Te-Nb-O systems in terms of their bulk and surface
electronic structure and related catalytic behavior of each system. The importance of V^{5+}
cations in activating hydrocarbon species has been confirmed for both vanadia and V/SbO
catalysts. In addition, the isolated V site surrounded by Sb cations in V/SbO_4 was found to
be a thermodynamically preferred site for ammonia activation.

However, for the more complex bulk Mo-V-Te-Nb-O system that contains several
metal cations characterized by multiple oxidation states and various partial occupancies,
three major issues must be addressed in order to improve the fundamental understandings
of the structure and catalytic behavior of the M1 phase: 1) investigating the Nb location
in the bulk and surface M1 structure which cannot be determined experimentally due to
similar X-ray, neutron and electron scattering behavior of Mo and Nb centers; 2) probing
the reactivities of surface metal sites in proposed elementary reaction steps which is
highly challenging for the current experimental methods; 3) modeling the entire proposed
propane ammoxidation pathway that has not been done systematically to date. Therefore,
the major objective of this thesis was to address the three above-mentioned fundamental
issues by conducting DFT-based theoretical studies of the M1 phase and its reactivity in
propane ammoxidation, which are described in the following chapters.
REFERENCES


Chapter 3. Nb location in the Mo-V-Te-Nb-O catalyst M1 phase

3.1 CHALLENGE IN LOCATING NB IN BULK M1 PHASE

The mixed metal Mo-V-M-O oxides (M = combination of Nb, Ta, Te, Sb) have attracted significant interest of the catalysis community due to their unique ability to selectively transform propane into important industrial chemicals, such as acrylonitrile and acrylic acid[1–4]. The active and selective catalyst contains two major crystalline phases, M1 and M2[3, 5, 6]. The M1 phase (Figure 1) is primarily responsible for the activity and selectivity in the (amm)oxidation of propane, whereas the M2 phase is unable to activate propane and instead may assist the M1 phase in the (amm)oxidation of the propylene intermediate[3]. However, knowledge of the bulk and surface structures and the catalytic roles of each metal ion in these mixed metal oxides is still limited due to the structural

Figure 1. The crystal structure of Mo-V-Te-Ta(Nb)-O M1 phases in the $ab$ plane. Nb is shown in the same S9 site as Ta. V is shown in grey, Mo in blue, Te in orange, O in red and Ta (and Nb) in green.
and compositional complexity of this system. In this work, combined experimental and computational studies were carried out to elucidate tantalum and niobium locations in the Mo-V-Te-Ta(Nb)-O M1 phases (denoted Ta-M1 and Nb-M1) by high-resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and density functional theory (DFT) calculations.

One unresolved question related to the structure of the Mo-V-Te-Nb-O catalyst is the location of niobium in both the bulk and surface of the M1 phase. Niobium and molybdenum have similar radii, atomic numbers (Z), and charges. Thus they are virtually indistinguishable by X-ray, neutron diffraction and TEM imaging techniques. Desanto et al.[5] proposed that Nb$^{5+}$ substitutes for Mo$^{6+}$ in the pentagonal bipyramidal site (S9) based on the metal-oxygen distances and valence sum calculations. Subsequently, Watanabe and Ueda[7] also proposed that Nb$^{5+}$ occupies the S9 site. Recently, Pyrz et al.[8] applied the HAADF STEM technique to directly image the Mo-V-Te-Nb-O M1 phase. They further investigated the structurally similar Ta-substituted M1 phase[9] (Ta-M1) since Ta can be easily distinguished from Mo by X-ray, neutron diffraction, and TEM imaging techniques due to its much higher atomic number. They found evidence that Ta occupies the S9 and concluded that Nb, being chemically similar to Ta, must also occupy the same site.

Moreover, Pyrz et al.[8] observed segregation of Ta in the Ta-M1 phase into Ta-rich and Ta-poor regions, which may be detrimental to the stability and catalytic behaviour of the M1 phase. One possible explanation for this segregation effect is the presence of mass-transfer limitations during the rapid slurry evaporation (SE) synthesis of the Ta-M1 catalyst employed in their study. Therefore, it is desirable to explore the
synthesis of better-defined M1 phases with uniform chemical compositions by methods that minimize these kinetic limitations in order to elucidate the effects of Ta content and location on the catalytic behaviour of the M1 phase.

We report in this study a better-defined, model Ta-M1 phase obtained by hydrothermal synthesis (HT) that was employed to investigate the Ta locations. The DFT calculations were then performed on cluster models built from truncated \( ab \) planes of the M1 phase to determine the energies of the models with Ta in different lattice sites. The results of these calculations were used to predict the Ta occupancies in various lattice sites by applying methods of statistical thermodynamics. This theoretical methodology was validated against the experimental (HAADF STEM) observations of the Ta-M1 phase, and then applied to predict Nb locations in the bulk of the Nb-M1 phase.

3.2 STEM STUDY OF TA LOCATION IN TA-M1 AND THUS THE INDICATION FOR NB LOCATION IN NB-M1 BY ANALOGY

The representative HAADF STEM images of Ta-M1 (HT) are shown in Figure 2. The HAADF STEM images indicated that the pentagonal sites (S9), highlighted by the red circles in Figure 2a, are much brighter than all other metal sites in the \( ab \) planes. The brightness (i.e., the atomic column intensity) of S9 suggested the presence of Ta as the heaviest atom in this site. No appreciable differences in the intensity of the S9 columns were found between the center region of the Ta-M1 crystal in Figure 2b and its surface region in Figure 2c. This finding suggested that Ta is distributed uniformly throughout the Ta-M1 phase prepared by the hydrothermal synthesis method. The uniform distribution of Ta in Ta-M1 (HT) indicated that the Ta segregation reported previously[8]
is not an intrinsic property of the Ta-M1 phase and can be prevented by adopting an appropriate synthesis method.

A comparison of the normalized intensities of metal sites in the \( ab \) planes found in our study to those obtained in an earlier HAADF STEM study by Pyrz et al.\cite{9} and expected from Rietveld refinement is illustrated in Figure 3. Metal site intensities were normalized to the average intensity of S5 and S8, which were assumed to be 100% Mo \((Z=42)\) sites according to the results of an earlier study\cite{9}. S5 and S8 indeed showed constant intensities for all unit cells examined in this study, whereas S9 had the highest intensity in Ta-M1 (HT). This observation suggested the preference of the heaviest atom, Ta \((Z=73)\), for S9, in agreement with the findings of an earlier study\cite{8}. Lower intensities of S1, S2, S3, S4 and S7 as compared to those of 100% Mo sites S5 and S8 indicated the presence of a lighter atom, V \((Z=23)\). The Ta occupancy of S9 calculated from the normalized intensities in Figure 3 was ca. 49% in Ta-M1 (HT), which is much higher than the Ta occupancy (ca. 23%) at S9 in Ta-M1 (SE) found in a previous study\cite{9}. The increased Ta occupancy in Ta-M1 (HT) and the lack of Ta segregation between the M1 bulk and surface suggested that hydrothermal synthesis conditions are characterized by significantly reduced mass-transfer limitations as compared to slurry evaporation synthesis. Therefore, the analysis of normalized intensities of atomic columns in the HAADF STEM images in Ta-M1 (HT) found evidence of Ta presence only in S9.
Figure 2. The HAADF STEM images of Ta-M1 (HT) viewed down the [001] direction. a) at high magnification; b) the bulk M1 crystal; and c) the surface region. The a and b axis vectors indicate one unit cell in the ab plane. Red circles pointed out by red arrows indicate centers of the pentagonal sites S9.

Figure 3. Normalized atomic column intensities of sites 1-11 taken from the refinement model (expected intensities)[10] and HAADF STEM images of slurry Ta-M1[9] and Ta-M1 (HT) catalyst of this study. Normalization was obtained with reference to the average intensity of S5 and S8, which were assumed to have 100% Mo occupancy.

3.3 THEORETICAL PREDICTION OF NB LOCATION

3.3.1 Computational method and cluster models
Theoretical approaches have shown great promise in recent years as powerful tools to provide new structural insights into multicomponent metal oxides, e.g., Chenoweth et al. [11] study of the Mo$_3$VO$_{x}$ M1 structure and Goddard III et al. [12] investigation of the partial site occupancies in the Mo-V-Te-Nb-O M1 phase by a Monte Carlo reactive dynamics method employing the Reactive Force Field (ReaxFF). In the present study we employed DFT to calculate the energies of various Ta (and Nb) containing cluster models of the M1 phase where these atoms initially located in S9 were exchanged with Mo atoms located in Mo-containing sites. Only exchanges between S9 and Mo-containing sites were examined, because it has been shown experimentally [5, 13, 10] that only Ta and Mo are present in the pentagonal bipyramidal site S9 of Mo-V-Te-O and Mo-V-Te-Ta-O M1 phases.

Following the approaches adopted in our previous studies [14, 15], cluster models were employed that consisted of several truncated $ab$ planes of the M1 phase, containing not only the proposed active center [16] but also the S9, the pentagonal bipyramidal site (Figure 4). A total of ten cluster models were constructed, including the cluster with Ta in S9 and nine models where Ta was exchanged with Mo in Mo-containing sites. Further details can be found in the Methods section.
Figure 4. The top view (a) and side view (b) of the cluster model of M1 phase. V is shown in grey, Mo in blue, Te in orange, O in red and Ta (and Nb) in green. The different cation sites are as labeled.

The energies of Nb-containing cluster models were examined first as a function of the number of truncated \(ab\) planes (Figure 5). Cluster models with up to 5 \(ab\) planes were investigated using reduced parameters (see Methods). The energy of sequentially adding an \(ab\) plane converged at the third layer at -1.60 eV/layer. Cluster models with up to 3 \(ab\) planes were also investigated using the full parameter set, and the energy also converged at the third \(ab\) layer at ca. -1.00 eV/layer. The differences between the energies of the full and reduced parameter set calculations for a three-layer cluster were less than 0.5 eV/layer, which is less than 0.01 eV/Å\(^2\). Therefore, the use of a three-layer cluster model led to sufficiently accurate energies in both the reduced and full parameter set calculations. Accordingly, the cluster models with 3 truncated \(ab\) planes were subsequently employed in this study.

Figure 5. The energy of adding one \(ab\) plane to the Nb-containing cluster model as a function of number of existing \(ab\) planes in the model using the reduced parameter set (red) and the full parameter set (blue).
3.3.2 Ta location in Ta-M1 phase cluster models

The Ta and Nb occupancies of the 10 lattice sites were estimated by statistical models that considered both the internal energy and entropy contributions to the Gibbs energy of the Ta (and Nb) distribution for the entire M1 phase structure. The following assumptions were made to calculate the Ta (and Nb) occupancy of each lattice site investigated: 1) All lattice sites are occupied by Mo, V, or Ta (and Nb); 2) All Mo-containing sites and S9 are equivalent but distinguishable sites; 3) All Mo-containing sites and S9 are only occupied by Ta (and Nb) or Mo; 4) The calculated energy of Ta (or Nb)/Mo atom exchange is related to the site energy and can be used as the relative site energy. The Gibbs energy corresponding to the Ta (and Nb) distribution in the M1 phase can be written as:

\[ G = \sum_j E_j m_j - kT \ln \frac{N!}{(N-M)! \prod_j m_j!} \] (1)

and \[ M = \sum_j m_j \] (2)

where \( E_j \) is the site energy for site \( j \), \( m_j \) is the number of Ta (and Nb) atoms in site \( j \), \( N \) is the total number of Ta (and Nb) lattice sites available, and \( M \) is the total number of Ta (and Nb) atoms.

Since \( N \), \( M \), and \( m_j \) are large numbers, the Stirling’s rule can be applied to equation (1) to obtain the following expression:

\[ G = \sum_j E_j m_j - kT (N \ln N - N) + kT [(N - M) \ln(N - M) - (N - M)] + kT \sum_j (m_j \ln m_j - m_j) \] (3)
To minimize the Gibbs energy $G$ in equation (3) while constraining $M$ according to equation (2), a Lagrange multiplier $\lambda$ and Lagrange function $L$ are introduced. By solving $\partial L / \partial m_j = 0$ and $\partial L / \partial \lambda = 0$, $m_j$ is calculated as:

$$m_j = M \ p_j$$

(4)

where $p_j$ is the probability of finding Ta (and Nb) in site $j$ that can be expressed in terms of relative site energy $\Delta E_j$ as follows:

$$p_j = \frac{e^{-\Delta E_j / kT}}{\sum_j e^{-\Delta E_j / kT}}$$

(5)

where $k$ is the Boltzmann constant, $8.617 \times 10^{-5}$ eV/K.

The Ta (and Nb) occupancy of each lattice site can be expressed as:

$$P_j = \frac{M \ p_j}{N_j}$$

(6)

where $N_j$ is the total number of lattice sites $j$.

However, all $N_j$ are the same since all metal lattice sites of the M1 phase considered here possess the same multiplicity. Moreover, since the chemical composition of the M1 phase$^{[7]}$ corresponds rather closely to $M=N_j$, equation (5) may be simplified further to yield:

$$P_j = \frac{e^{-\Delta E_j / kT}}{\sum_j e^{-\Delta E_j / kT}}$$

(7)

The optimized energies based on the reduced parameter set calculations for the cluster models with Ta in different lattice sites are shown in Table 1. The energy difference per layer ($\Delta E$) for each atom exchange was calculated with respect to the energy of the cluster containing Ta in S9. These results show that the pentagonal bipyramidal site 9 is energetically preferred by Ta. The second (S10) and third (S11) lowest energy sites for Ta are 0.15 and 0.36 eV higher in energy than S9, respectively.
The other sites rank in the following order in terms of decreasing preference: S5 > S6 > S8 > S4 > S7. The predicted Ta occupancies of different lattice sites are shown in Table 1. The S9 was shown as the dominant site for Ta with the occupancy of nearly 1. The second highest site occupancy was ca. 10^{-2}. The predicted Ta location in the M1 phase by the combined DFT/statistical thermodynamics approach is in agreement with our HAADF STEM observations that the S9 is the preferred Ta site in the M1 phase. These findings strongly suggested that the Ta location in the M1 phase is not significantly influenced by the kinetic effects during hydrothermal synthesis of the Ta-M1 phase.
Table 1. Optimized energies for cluster models with Ta (and Nb) in different lattice sites using reduced parameter and full parameter sets.

Energy for exchanging Ta (and Nb) in site S9 with Mo in several other lattice sites ($\Delta E$, in eV). $\Delta E$ is averaged over three layers and calculated with respect to the cluster containing Ta (and Nb) in the pentagonal bipyramidal site S9.

<table>
<thead>
<tr>
<th>Lattice site</th>
<th>$\Delta E_{Ta}^{red}$</th>
<th>Ta</th>
<th>$\Delta E_{Nb}^{red}$</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>S9</td>
<td>0 (0)</td>
<td>0.98</td>
<td>0 (0)</td>
<td>0.98</td>
</tr>
<tr>
<td>S10</td>
<td>0.15 (0.20)</td>
<td>1.9×10^{-2}</td>
<td>0.36 (0.40)</td>
<td>9.55×10^{-5}</td>
</tr>
<tr>
<td>S11</td>
<td>0.36 (0.42)</td>
<td>9.54×10^{-5}</td>
<td>0.16 (0.18)</td>
<td>1.70×10^{-2}</td>
</tr>
<tr>
<td>S5</td>
<td>0.38</td>
<td>5.21×10^{-5}</td>
<td>0.48</td>
<td>3.92×10^{-6}</td>
</tr>
<tr>
<td>S6</td>
<td>0.54</td>
<td>7.58×10^{-7}</td>
<td>0.54</td>
<td>9.02×10^{-7}</td>
</tr>
<tr>
<td>S4*</td>
<td>0.71</td>
<td>1.10×10^{-8}</td>
<td>0.59</td>
<td>1.47×10^{-7}</td>
</tr>
<tr>
<td>S4</td>
<td>0.72</td>
<td>7.16×10^{-9}</td>
<td>0.63</td>
<td>8.04×10^{-8}</td>
</tr>
<tr>
<td>S7*</td>
<td>0.74</td>
<td>4.26×10^{-9}</td>
<td>0.79</td>
<td>1.27×10^{-9}</td>
</tr>
<tr>
<td>S7</td>
<td>1.01</td>
<td>4.65×10^{-12}</td>
<td>0.97</td>
<td>1.20×10^{-11}</td>
</tr>
</tbody>
</table>

The location of each lattice site is shown in Figure 4a. The cluster model contains two sites 4 (4 and 4*) and two sites 7 (7 and 7*) that are equivalent in the bulk M1 structure. For clarity the results for sites 4* and 7* are listed here not discussed in the text. [a] Results calculated using the full parameter set are shown in parentheses. [b] Site occupancies are calculated by equation (7) based on $\Delta E^{red}$. 


3.3.3 Nb location in Nb-M1 phase cluster models

The same computational approaches (reduced parameter set DFT) were applied to investigate the Nb locations in the Nb-M1 phase, since Nb could not be distinguished from Mo by HAADF STEM and other diffraction methods. The optimized energies of atom exchanges between Nb in S9 and Mo in other Mo-containing lattice sites are shown in Table 1. The Nb-containing cluster models showed a similar trend in terms of site preference: S9 > S11 > S10 > S5 > S6 > S8 > S4 > S7. The S9 was also a dominant site for Nb with the occupancy of nearly 1. The second and third highest occupied sites (S11 and S10) were predicted to have occupancies of ca. 10^{-2} and 10^{-5}, respectively.

The three highest occupied lattice sites for Ta and Nb were further examined by DFT calculations using the full parameter set. The results shown in parentheses in Table 1 confirmed the trend for S9, S10, and S11 for Ta and Nb, respectively. The comparison of the results of the full parameter and reduced parameter set calculations indicated the largest error of 0.07 eV/layer or 0.008 eV/Å². Therefore, the site occupancies are not expected to be influenced by somewhat lower accuracy of the reduced set calculations. Moreover, the calculations employing both parameter sets indicated S9 as the preferred site for both Ta and Nb in the M1 phases.

3.4 CONCLUSIONS

In summary, HAADF STEM imaging and DFT calculations were employed to determine the location of Ta in the Mo-V-Te-Ta-O M1 phase. The HAADF STEM images of Ta-M1 prepared by hydrothermal synthesis indicated the location of Ta in the pentagonal bipyramidal site, S9. The results of DFT calculations are in good agreement with experimental results confirming that Ta is predominantly located in the S9 in the bulk M1.
structure. The validated DFT methodologies were then applied to predict the location of Nb in the Mo-V-Te-Nb-O M1 phase. Nb prefers the same pentagonal bipyramidal site S9 in the M1 bulk. Moreover, the analysis of atomic column intensities in the HAADF STEM images of Ta-M1 phases further indicated that the partial occupancy of Ta in S9 depends on synthesis methods, with hydrothermal synthesis providing more equilibrated, less mass-transfer influenced M1 phases.

Experimental Section

The M1 phase catalyst with a molar ratio of Mo/V/Te/Nb(Ta)=1:0.3(0.31):0.17(0.22):0.12(0.12) was prepared by hydrothermal synthesis as previously reported[7]. Ammonium paramolybdate, telluric acid, vanadyl (IV) sulfate, niobium (V) oxalate hexahydrate or tantalum(V) ethoxide were used as precursors. The resulting slurry stirred for 10 min then introduced into the Teflon inner tube of a stainless steel autoclave. Following a 5 min period of nitrogen bubbling to replace the residual air, the autoclave was sealed and heated at 448 K for 48 h. After hydrothermal synthesis, the obtained dark blue slurry was washed, filtered with distilled water and dried overnight at 353 K. Then, the dried powder catalyst was calcined in ultrahigh purity nitrogen (50 ml/min) at 873 K for 2h.

The Mo-V-Te-Ta-O M1 catalyst was thoroughly ground by mortar and pestle for 10 min, embedded in a resin, and sectioned by microtome as approximately 50 nm slices[17]. These specimens were introduced into a holy-carbon coated Cu grid. The HR-STEM imaging was performed on a FEI Titan S 80-300 operated at 300 kV and equipped with CEOS aberration corrector (probe semi-angle 27 mrad, inner detector angle 80 mrad, probe size ~0.7 Å). The acquisition time used for these images is 6
seconds/1024×1024 pixels. All specimens were plasma cleaned by Fischione plasma cleaner to prevent specimen from contamination during the STEM observation.

**HAADF STEM Image Analysis:** the positions and intensities of atomic columns were determined by center-of-mass fit. In order to interpret the intensity quantitatively in terms of elemental occupancies, the following assumptions were made: (1) the thickness of each unit cell was constant; (2) background was constant through one unit cell; (3) the measured intensity was proportional to $Z^2$ (following the Rutherford scattering relationship)[18]. Based on these assumptions, the observed intensities were analyzed by Digital Microscopy (DM) scripts. The obtained atomic column intensities were normalized to the average intensity of the 100% Mo sites, S5 and S8, followed by subtraction of the background intensity in Fig.3. The error bars in Fig. 3 were obtained by averaging over the same crystallographic sites in multiple unit cells observed in multiple images.

**Theoretical Methods:** Spin-polarized periodic DFT calculations were performed in the generalized gradient approximation (GGA-PBE)[19] using the Vienna *ab initio* Simulation Package (VASP)[20–23]. The core electrons were described by the projector augmented-wave (PAW)[24, 25] method and the Kohn-Sham valence states were expanded in a plane-wave basis set. The Brillouin zone was sampled at the $\Gamma$ point only. Different spin states for each cluster system were checked and the energy of the ground state was used in this study. The cluster models employed in this study consisted of successive truncated M1 *ab* planes (Figure 4) containing the S9 pentagonal sites and surrounding cation sites. The terminating oxygen atoms in each atomic layer in the cluster models were capped with hydrogen atoms and both oxygen and hydrogen atoms
were fixed at bond lengths of 0.96 Å. Each plane contained a total of 67 atoms and the inter-\textit{ab} plane distance was fixed at the experimentally measured distance of 4.016 Å. Each cluster was separated from its neighbouring images by \textasciitilde11 Å in the \( x, y, \) and \( z \) directions. Since the system had a large number of electrons, the reduced parameter set was applied to reduce the computational cost, with omitted semi-core electrons in the PAW potential for Mo(4d5s), V(3d4s), and Ta(5d6s) (others are Te(5s5p), Nb(4p4d5s), O(2s2p), and H(1s)), and 283 eV kinetic energy cutoff. Subsequently, the energetically and electronically converged structures obtained in the reduced parameter set calculations were further modelled using the full parameter set with the PAW potential (including Mo(4p4d5s), Te(5s5p), V(3s3p3d4s), Nb(4p4d5s), Ta(5p5d6s), O(2s2p), and H(1s)) and a 400 eV kinetic energy cutoff. Geometry optimization was converged to 0.05 eV/Å in each degree of freedom for all relaxed atoms.
REFERENCES:


Chapter 4. Propane and sequential C$_3$ intermediates activation through oxidative dehydrogenation

4.1 INTRODUCTION

Acrylonitrile is an important industrial chemical widely used in polymer synthesis that is currently produced via propene ammonoxidation. Direct propane ammonoxidation to acrylonitrile catalyzed by the bulk mixed metal oxides has received significant attention in recent years [1–3]. This process is more environmentally benign and potentially more economical due to the abundance and low cost of propane as compared to propene. Among all mixed metal oxides, the bulk mixed Mo-V-Te-Nb-O system is particularly promising because of its significant activity and selectivity in transforming propane to acrylonitrile [4]. Earlier studies showed the presence of two major crystalline phases, the so-called M1 and M2, in the Mo-V-Te-Nb-O system [5,6]. The M1 phase is solely responsible for propane activation, while the M2 phase improves the yield of acrylonitrile at low propane conversion by converting some propene intermediate into acrylonitrile in synergy with the M1 phase.

Propane ammonoxidation to acrylonitrile over the Mo-V-Te-Nb-O M1 phase was proposed to proceed via a series of elementary reaction steps, including propane oxidative dehydrogenation (ODH), ammonia and dioxygen activation, NH$_3$ insertion into the allyl intermediate, and final ODH of the C-N coupled precursor leading to acrylonitrile [7]. Invoking the concept of site isolation, Grasselli et al. [3] proposed the catalytic role of each metal ion present in surface $ab$ planes of the Mo-V-Te-Nb-O M1 phase in propane ammonoxidation to acrylonitrile. Propane activation was proposed to
occur on a surface V$^{5+}$=O site, while subsequent H abstraction steps leading to allyl intermediate are performed by the Te$^{4+}$=O species. Ammonia was proposed to be activated on a Mo$^{6+}$ site, followed by NH insertion into the allyl intermediate on the same site. All metal cations that were proposed to be responsible for propane transformation to acrylonitrile are arranged within bonding distances of one another in the proposed active center present in the $ab$ plane of the M1 phase (Figure 1) [8,9]. According to this proposed mechanism, the Nb$^{5+}$ pentagonal bipyramidal sites do not participate in this reaction directly. They instead stabilize the M1 structure and isolate the active centers from one another thereby hindering side reactions and improving the selectivity to acrylonitrile. Since the M2 phase was found to contain only V$^{4+}$ in the bulk [9–11], it explains the inability of this phase to activate propane.
Figure 1: The ab plane of the Mo-V-Te-Nb-O M1 phase with the different metal lattice sites labeled. Blue, gray, orange, green, and red spheres represent Mo, V, Te, Nb, and O atoms, respectively. The proposed active center is outlined with dashed lines.

Quantum chemistry-based theoretical approaches are well established as powerful tools for generating mechanistic insights that are otherwise unavailable. So far, only a handful of theoretical studies have been performed to better understand the catalytic behavior of the Mo-V-Te-Nb-O M1 and M2 phases [12–16]. Previously [17,18], we performed density functional theory (DFT) calculations using cluster models of the proposed active surface center of the M1 phase to study the adsorption of H and C₃ species (propane, isopropyl, propene, and allyl), and the initial homolytic H abstraction from propane on the various metal sites. We have found that propane and propene have nearly zero chemisorption energy according to DFT in the generalized gradient approximation (GGA), while isopropyl and allyl radicals bind strongly to V=O and Te=O, and weakly on other sites. Atomic H binds more strongly to Te=O by at least 1 eV than to all the other sites investigated. The activation energy for the oxidative dehydrogenation (ODH) of propane was calculated on different cation sites, and V⁵⁺=O was found to be more active than V⁴⁺=O with an activation barrier that is 0.5 eV lower, consistent with the proposed reaction mechanism for propane activation on the Mo-V-Te-Nb-O M1 phase and the understanding of V⁵⁺ as the active site for alkane activation in general [8,9,19]. In this study, we investigate the H abstraction steps from propane to π-allyl on two different sites, V⁵⁺=O and Mo⁵⁺=O, as part of propane ammoxidation over the cluster models of the Mo-V-Te-Nb-O M1 phase using DFT calculations. We found
V$^{5+}$=O to be the active site for propane activation and that the first H abstraction step is rate-limiting in this process, which is consistent with previous experimental and theoretical work on propane activation on the M1 phase and related vanadium oxide systems.

### 4.2 METHODS

#### 4.2.1 Cluster Models

Our cluster models are based on truncated M1 $ab$ planes containing the proposed active site, which contains V in the S2 lattice site, Mo in the S4 and S7 lattice sites, and Te in the S12 channel sites (Figure 2) [9,20]. In our previous studies [17,18,21], we have shown that three truncated $ab$ planes are adequate to allow the bulk energy and the reactivity of the surface to converge. The inter-planar distance was fixed at the experimentally measured value of 4.016 Å for adjacent $ab$ planes. In the bulk M1 phase, the V and Mo cations are terminated by oxo groups on opposite sides of the bulk $ab$ planes [1,9], but the nature of surface $ab$ plane termination by oxo groups remains a subject of on-going research [13]. In this study, V and Te were capped by oxygen forming vanadyl (V=O) and telluryl (Te=O) oxo moieties, while the molybdyl oxo group (Mo=O) were located on the opposite side of the cluster. The terminating equatorial oxygen atoms in each truncated $ab$ plane were capped with hydrogen atoms and both the O and H atoms are fixed at a bond length of 0.96 Å during optimization, while all other atoms in the cluster models and adsorbates were relaxed. Each cluster was separated from its neighboring images by ~11 Å in the x, y, and z directions.
Figure 2: Top and side views of the four different model clusters used to represent the active centers. Arrow indicates line of sight for the side views. Blue, gray, orange, green, red, and white spheres represent Mo, V, Te, Nb, O, and H atoms, respectively.
In this study, we employ the same four cluster models (Figure 2) as in our previous study [17]. Model A is the original model that represents proposed active centers in the crystal structure of the catalyst M1 phase $ab$ plane. Model A is used to represent the telluryl and molybdyl oxo groups, with the molybdyl oxo being present on the opposite side of the telluryl oxo (the bottom side of the cluster; Figure 2a). Based on Model A, Model B has the oxygen atoms in both surface telluryl oxo groups removed, while Model C has both surface Te=O moieties completely removed. Both Models B and C are used to isolate the effect of vanadyl oxo group. On the other hand, Model D has the surface vanadyl oxo group removed to isolate the effect of telluryl oxo group. Model E is new in this study and contains not only the proposed active sites in Model A but also one of the bipyramidal pentagonal Nb=O centers attached to the active sites and corresponding to Site 9 of the M1 phase according to the findings of our recent structural study [21].

The oxidation states of the cations were estimated using the Bader charge analysis [22] as implemented by Henkelman et al. [23]. The Bader charge analysis confirmed the oxidation state of V in the surface vanadyl group to be +4 in Model A and B, while it was +5 in Model C, in comparison with the average oxidation states of V in bulk VO$_2$ and V$_2$O$_5$ (Table 1). The average oxidation state of Mo in the surface molybdyl oxo groups was found to be +5 in the Model A. The average oxidation state of Te in the Te=O moieties as proposed to exist in the bulk S12 channel sites [7] was found to be far lower than that +4 as in bulk TeO$_2$, and was tentatively assigned to be +2.
Table 1. Bader charges of Mo, V, and Te cations present in the surfaces of the cluster models of the Mo–V–Te–Nb-O M1 phase; the bulk molybdenum, vanadium, and tellurium oxides; and selected molybdenum oxide clusters. The formal oxidation states assigned to each cation are shown in parentheses. The results obtained from the literature are as noted.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>V</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>2.52 (+5)</td>
<td>1.91 (+4)</td>
<td>2.07 (+2)</td>
</tr>
<tr>
<td>Model B</td>
<td>2.48 (+5)</td>
<td>1.90 (+4)</td>
<td>2.07 (+2)</td>
</tr>
<tr>
<td>Model C</td>
<td>2.51 (+5)</td>
<td>2.18 (+5)</td>
<td>-</td>
</tr>
<tr>
<td>Model D</td>
<td>2.51 (+5)</td>
<td>1.97 (+4)</td>
<td>2.08 (+2)</td>
</tr>
<tr>
<td>Mo(=O)(OH)(H2O) [42]</td>
<td>2.47 (+5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo(=O)2(OH)2(H2O) [42]</td>
<td>2.65 (+6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>α-MoO₃ [42]</td>
<td>2.71 (+6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VO₂ [17]</td>
<td>-</td>
<td>2.09 (+4)</td>
<td>-</td>
</tr>
<tr>
<td>V₂O₅ [17]</td>
<td>-</td>
<td>2.22 (+5)</td>
<td>-</td>
</tr>
<tr>
<td>TeO₂</td>
<td>-</td>
<td>-</td>
<td>4.07 (+4)</td>
</tr>
</tbody>
</table>

The Mo cations in the clusters reported here are those with their oxo groups exposed on the surface, i.e., those that are present on the bottom side of each cluster model. The values for the cluster models and bulk oxides are averaged values.
4.2.2 Computational Details

Spin-polarized, periodic DFT calculations were performed using the Vienna \textit{Ab initio} Simulation Package (VASP) [24–26]. The exchange-correlation interaction was described by the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [27]. The core electrons were described by the projector-augmented-wave (PAW) method [28], and the Kohn-Sham valence states (including Mo(4p4d5s), Te(5s5p), V(3s3p3d4s), O(2s2p), and H(1s)) were expanded in plane wave basis sets up to 400 eV. The Brillouin zone was sampled at the \textit{Γ} point only. Spin polarization was considered for all calculations. Different integral spin states for each system were checked and only the lowest-energy results were reported below unless otherwise noted. For the cluster-adsorbate systems employed in this study, the ground energy state occurred in all cases with one of the lowest spins (e.g. singlet or triplet for closed-shell systems) that are usually energetically spaced within 0.1 eV.

Geometry optimization was considered converged when the force in each of the x, y, and z directions on each relaxed atom fell below 0.03 eV/Å. The adsorption energy was defined as \( \Delta E = E_{\text{total}} - E_{\text{cluster}} - E_{\text{adsorbate}} \), where \( E_{\text{total}} \), \( E_{\text{cluster}} \), and \( E_{\text{adsorbate}} \) are the energies of the combined system (adsorbate and cluster), the cluster without the adsorbate, and the adsorbate molecule in a neutral state (closed-shell or radical) in the gas phase, respectively.

The minimum-energy reaction paths and their associated transition states (TSs) for H abstraction from C\(_3\) species on the different metal oxo groups were calculated using the climbing-image nudged elastic band (CI-NEB) and dimer methods [23,29] using 0.03
eV/Å as the convergence criterion. These steps involve homolytic H abstraction on a single oxygen site, which has been shown to be a more facile mechanism for activating propane and propene on vanadia surfaces than heterolytic C-H dissociation on a pair of metal-oxygen sites [30–33]. The hemolytic nature of the H abstraction steps were verified by Bader analysis, which indicated that the dissociating H atom at each TS possesses ~0.6 electrons and not a proton. Each reaction path including the TS was constrained to stay on the same spin state as that of the ground energy state of the initial state. Vibrational frequencies were calculated in the harmonic oscillator approximation by diagonalizing the mass-weighted Hessian matrix, which was built from the calculated two-sided differences of the first derivatives of the total energy due to small geometrical perturbations (0.009 Å in each degree of freedom). All the TSs located in this study were verified to possess one mode of negative curvature with a frequency on the order of 1,000 cm\(^{-1}\) that corresponds to the dissociating C–H bond, and up to two other modes of negative curvature whose frequencies are 50 cm\(^{-1}\) or less that correspond to the transition or rotation of the loosely-bound C\(_3\) species, which could not be removed even after geometry optimization was converged to 0.03 eV/Å.

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Adsorption of H and C\(_3\) species

In our previous studies [17,18], the adsorption of a hydrogen atom and all C\(_3\) species has been examined in detail on different oxygen and metal sites present on the surface of the cluster models. There are three types of O atoms in the cluster models:
terminal oxygen in metal oxo groups, bridging oxygen linking metal atoms on the same plane, and linking oxygen connecting metals in the same column on adjacent \(ab\) planes. Previous studies of the ODH of hydrocarbons on the surfaces of vanadium and molybdenum oxides \([13,30,31,34]\) have shown that terminal oxo groups are more reactive than bridging oxygens and are primarily responsible for hydrocarbon activation. To highlight the different reactivity of the surface metal oxo groups, we briefly recap our findings on the adsorption of H and C\(_3\) species on the metal oxo sites V=O, Te=O, and Mo=O on the small cluster surface, and Nb=O on the big cluster surface. We will only consider the surface metal oxo sites later in the investigation of H abstraction from C\(_3\) species.

Closed-shell C\(_3\) species, i.e., propane and propene, have nearly zero chemisorption energy at the GGA level of DFT. The van der Waals (vdW) adsorption energy for propane has been measured to be -0.38 eV and calculated to be -0.16 eV on surface vanadyl oxo and -0.29 eV over the surface valley on \(V_2O_3\)(0001) \([30,35,36]\). On the other hand, open-shell C\(_3\) species, i.e., isopropyl and \(\pi\)-allyl, prefer surface telluryl and vanadyl with adsorption energies of ca. -2 eV, followed by the molybdyl site (ca. -0.60 eV). Likewise, H atom has a strong preference for the telluryl oxo site (-3.63 eV) followed by the vanadyl oxo site in Model C (-2.59 eV) and the molybdyl oxo site (-2.13 eV) (Table 2). Nb=O present in the Model E which was proposed to be catalytically inactive, shows only moderate affinity to all radical species similar to that observed for the Mo=O site.
Table 2. Adsorption energies (ΔE, in eV) of the C₃Hₓ (propane, isopropyl, propene, and π-allyl) species and atomic H on the various metal oxo groups that are present in the ab plane of the Mo–V–Te–Nb-O M1 phase, forming C-O and H-O bonds.

<table>
<thead>
<tr>
<th>Model</th>
<th>site</th>
<th>Isopropyl (C₃H₇)</th>
<th>π-allyl (C₃H₅)</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>Mo=O</td>
<td>-1.08</td>
<td>-0.34</td>
<td>-2.15</td>
</tr>
<tr>
<td>Model B</td>
<td>V⁴⁺=O</td>
<td>-1.10</td>
<td>-0.49</td>
<td>-2.15</td>
</tr>
<tr>
<td>Model C</td>
<td>V⁵⁺=O</td>
<td>-1.61</td>
<td>-0.81</td>
<td>-2.59</td>
</tr>
<tr>
<td>Model D</td>
<td>Te=O</td>
<td>-2.06</td>
<td>-1.19</td>
<td>-3.22</td>
</tr>
<tr>
<td>Model E</td>
<td>Nb=O</td>
<td>-1.30</td>
<td>-0.55</td>
<td>-2.14</td>
</tr>
</tbody>
</table>

4.3.2 Propane → isopropyl

In our previous study [17], the methylene H abstraction from propane was studied on Te=O (Model A and D), V⁵⁺=O (Model C), and V⁴⁺=O (Model B) sites. Previous experimental and theoretical studies suggest that propane ODH on vanadyl oxides preferentially begins with the dissociation of the secondary C-H bond, not the primary C-H bond [31,33,37]. Therefore we investigated the abstraction of only the methylene H on the different sites. This step,

\[
\text{Propane}_{(g)} + \frac{1}{4} \text{O}_2(g) \rightarrow \text{isopropyl}_{(g)} + \frac{1}{2} \text{H}_2\text{O}_{(g)}
\]

is endothermic (ΔEₕᵥ=+0.79 eV). The transition states (TSs) of this step on the four sites are shown in Figure 3. The activation barriers with respect to gas-phase propane (thus
the same as the adsorption energy of the TSs with respect to gas-phase propane, $\Delta E_{TS}$) are 0.89 eV on Te=O and 2.23 eV on Mo=O in Model A, 2.08 eV on $V^{4+}$=O in Model B, 1.58 eV on $V^{5+}$=O in Model C, and 1.05 eV on Te=O in Model D, without the ZPE or vdw contribution. A linear energy relation was observed between the H adsorption energy ($\Delta E_H$) and the H abstraction activation barrier ($\Delta E_{TS}$), as $BE - \Delta E_{TS} = 1.03 \cdot (-\Delta E_H)$, with $R^2=0.98$, where $BE$ is the bond energy of the secondary C-H bond in propane (calculated to be 4.32 eV). The near-unity slope can be rationalized as reflecting that the TS for H abstraction from propane involves primarily the breaking of the C-H bond and formation of the O-H bond, so the affinity of the oxo group for H (measured by $\Delta E_H$) and the strength of the C-H bond (measured by $BE$) are the predominant factors in the activation barrier for this step. By this relation, the activation energy of H abstraction from propane by a metal oxo site in the $ab$ plane of the Mo-V-Te-Nb-O M1 phase can be estimated from the H adsorption energy at the same site. This energy for the Nb=O site can thus be estimated to be 2.12 eV, by using $\Delta E_H=-2.14$ eV on Nb=O (Table 2).
**Figure 3:** Snapshots of the transition states for the methylene H abstraction from propane on (a) Te=O in Model A, (b) Mo=O in Model A, (c) V$^{4+}$=O in Model B, (d) V$^{5+}$=O in Model C, and (e) Te=O Model D; the transition states for the methyl H abstraction from isopropyl on (f) Model C and (h) Model A (bottom side); and the transition states for the
methyl H abstraction from propene on (g) Model C and (i) Model A (bottom side). Key bond lengths are indicated (in Å).

The $V^{4+}\equiv O$, $Mo\equiv O$, and $Nb\equiv O$ groups are therefore much less active than $V^{5+}\equiv O$ for the initial H abstraction from propane. For the Te=O sites in both Models A and D, the calculated activation barriers are 1.0 eV and lower, indicating that these sites are significantly more active than $V^{5+}\equiv O$. Furthermore, it is expected that the activation barriers for the subsequent H abstraction steps on the Te=O sites would also be lower than those on $V^{5+}\equiv O$. As we pointed out before [17], if the first H abstraction step is rate-limiting, then the activity of the Te=O groups would be inconsistent with the experimentally measured apparent activation energy for propane oxidation on vanadyl oxides and for its ammoxidation over the M1 phase, which are generally reported to be 1.2 eV and higher. The much lower activation barriers on Te=O suggested a much more complex picture of the locations and structure of the surface Te=O sites in a working M1 catalyst, which may not be accurately captured by the present cluster models based on the bulk structure of the M1 phase. Accordingly, this study is instead focused on the catalytic properties of redox $V^{5+}\equiv O$ and Mo=O sites as, respectively, the most and least preferred sites for the H abstraction by surface oxo groups from gas-phase $C_3$ intermediates. The sequential steps of H abstraction from isopropyl and allyl are explored on these two surface metal oxo groups only.

4.3.3 Isopropyl $\rightarrow$ propene

Unlike H abstraction from propane, which is a closed-shell species, the abstraction of a methyl H from the open-shell isopropyl radical to form propene,
isopropyl\textsubscript{(g)} + \frac{1}{4} \text{O}_2\textsubscript{(g)} \rightarrow \text{propene}\textsubscript{(g)} + \frac{1}{2} \text{H}_2\text{O}\textsubscript{(g)}

is exothermic with $\Delta E_{\text{rxn}} = -1.73$ eV. The activation barriers calculated for this step is -0.30 eV on V\textsuperscript{5+}=O and 0.59 eV on Mo=O, respectively, with respect to gas-phase isopropyl. The negative activation barrier on V\textsuperscript{5+}=O is the consequence of the existence of a metastable intermediate state in which isopropyl interacts appreciably with the vanadyl oxo through one of its methyl H atoms, with an O-H distance of 1.98 Å. The activation barrier with respect to this metastable state is 0.18 eV. The C-H and O-H bond lengths in the TS for isopropyl to propene on V\textsuperscript{5+}=O are 1.23 Å and 1.43 Å, respectively (Figure 3f). On Mo=O, the C-H and O-H bond length in the TS are 1.27 Å and 1.38 Å, respectively (Figure 3h).

4.3.4 Propene $\rightarrow$ π-allyl

The calculated energy barriers for the abstraction of an H atom from the remaining methyl group in propene to form π-allyl,

propene\textsubscript{(g)} + \frac{1}{4} \text{O}_2\textsubscript{(g)} \rightarrow \pi\text{-allyl}\textsubscript{(g)} + \frac{1}{2} \text{H}_2\text{O}\textsubscript{(g)}

on the V\textsuperscript{5+}=O and Mo=O sites are 0.99 and 1.94 eV, respectively with respect to gas-phase propene, with V\textsuperscript{5+}=O again being more reactive than Mo=O. Previously, Dai et al. [37] have reported the activation barrier for propene ODH to π-allyl by surface vanadyl oxo groups on V\textsubscript{2}O\textsubscript{5}(001) to be 0.92 eV using periodic DFT calculations. Alexopoulos et al. [30] have reported the same barrier to be 1.01 eV using periodic DFT calculations with dispersion corrections. Therefore, the activation barrier determined in this study for propene ODH to π-allyl on the V\textsuperscript{5+} vanadyl oxo group in the $ab$ plane of bulk M1 phase is
in good agreement with the previous DFT results for the same step on vanadia. Similar to the H abstraction from propane, the H abstraction from propene is endothermic with $\Delta E_{\text{rxn}} = +0.33$ eV and characterized by a high activation barrier. C-H and O-H bond length in the TS for propene transformation to allyl on $V^{5+}=O$ are 1.61 Å and 1.08 Å, respectively (Figure 3g). On Mo=O the C-H and O-H bond length in the TS are 1.69 Å and 1.08 Å, respectively (Figure 3i).

4.3.5 Reaction energy profile for propane ODH to π-allyl

The reaction energy profiles for the three successive H abstraction steps from propane forming isopropyl, propene, and π-allyl on $V^{5+}=O$ and Mo=O are shown in Figure 4. The activation barrier for each of the three steps is lower on $V^{5+}=O$ than Mo=O. Among the three H abstraction steps on $V^{5+}=O$ site, propane activation has the highest activation barrier (1.58 eV), suggesting that the initial H abstraction is rate-limiting, at least in the propane ODH step of the overall propane ammoxidation reaction. The ZPE contribution to the TS energy is $\sim-0.2$ eV [17], so the sum of the vdW and ZPE contributions would total $\sim0.4$ eV, thus lowering the calculated activation barrier for propane activation on the $V^{5+}=O$ site to $\sim1.2$ eV, and bringing it into excellent agreement with the experimental apparent activation energy for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase (1.2 eV [38]). In comparison, the activation barrier for propane ODH to propene over unsupported vanadium oxides is also $\sim1.2$ eV [31,33,37], which suggests that the $V^{5+}=O$ site is likely the common propane activation site on both surfaces. The activation barriers are high ($\sim2$ eV) for the H abstraction steps from propane and propene on Mo=O, but relatively low for the H abstraction from isopropyl (0.59 eV), suggesting that the second H abstraction step may be able to take place on
several different oxo groups and that Mo=O is not involved in the activation of propane beyond this limited role.

**Figure 4:** DFT total energy reaction energy profiles for the H abstraction steps from propane to π-allyl on V$_{5+}^{5+}$=O (green; Model C) and Mo=O (red; Model A bottom side). The zero on the y-axis corresponds to one propane molecule and ¾ of an O$_2$ molecule in the gas phase at infinite separation from each cluster. The dissociated H atom after each step is represented as ½ of a water molecule in the gas phase. The values indicated on the curves are the activation barriers for each H abstraction step.

Dinse et al. [39] have reported that the activation energy for the propene combustion is measured to be lower than that for the ODH of propane by 0.73 eV due to the weaker allylic C-H bond in propene than the secondary C-H bond in propane. We have calculated that the H abstraction from propene has a lower energy barrier than the H abstraction from propane by 0.59 eV on V$_{5+}^{5+}$=O, also in agreement with experiment assuming that each step is the rate-limiting step in the respective process. Propene is a
closed-shell species with a finite probability of escaping without further reaction, which explains its detection as a stable reaction intermediate during propane ammoxidation.

Both isopropyl and π-allyl are unstable radical species. Alexopoulos et al. have calculated that the re-bounding of gas-phase propyl and π-allyl species to different surface oxygen sites on $V_2O_5(0001)$ have low activation barriers that do not exceed 0.1~0.2 eV [30,31]. Isopropyl has the option of transferring one of its H atoms to the surface in order to become a closed-shell species again (propene), which is also a low-barrier process (Figure 4) that competes with re-bounding. On the other hand, the dehydrogenation of π-allyl to form a closed-shell species cannot be accomplished in a single step, and, unlike the situation in isopropyl, the unpaired electron in π-allyl is stabilized by resonance structures. Therefore, π-allyl is expected to have a longer lifetime than isopropyl being more likely to re-bound to the surface than isopropyl, e.g., via NH$_x$ insertion to form a C-N bond leading to acrylonitrile, or via O insertion to form C-O bonds leading to oxidation products. According to this view, the relative surface concentrations of N and O species should play a key role in determining the selectivity for C-N compounds (e.g., acrylonitrile) vs. C-O compounds (e.g., acrolein and acrylic acid).

As mentioned above, a linear energy relation was observed between the H adsorption energy ($\Delta E_H$) and H abstraction energy barrier ($\Delta E_{TS}$) for propane. Here we include the additional TSs from the 3rd H abstraction step (also from a closed-shell species, propene $\rightarrow$ π-allyl) on $V^{5+}=O$ and Mo=O (Figure 5). The linear regression is almost unchanged: $BE-\Delta E_{TS}=1.03 \times (-\Delta E_H)$, with $R^2=0.92$. This linear relation suggests that for the homolytic H abstraction from propane and propene by the metal oxo groups
in the M1 \( ab \) plane, the activation barrier is primarily determined by the sum of the energy cost to break the C-H bond and the energy gain to form the O-H bond. Similar linear relations between the C-H activation barriers for hydrocarbons and the H adsorption energies on oxide surfaces have been reported previously, e.g., by Tyo et al. for propane (as a proxy for cyclohexane) activation on \( \text{Co}_3\text{O}_4(110) \) surfaces \cite{40}. This linear relationship may be of significant utility to future studies of alkane ODH on this and other related metal oxide surfaces.

**Figure 5:** The energies of the TSs of the methylene H abstraction from propane and the methyl H abstraction from propene (\( \Delta E_{TS} \); relative to gas-phase propane or propene) plotted against the H adsorption energy (\( \Delta E_{H} \)). Each point is labeled with the reactant (ppa=propane, ppe=propene), cluster model, and site. The line is the result of linear regression on all six data points (\( \text{BE}-\Delta E_{TS}=1.03 \cdot (\Delta E_{H}), R^2=0.92 \)).
4.4 CONCLUSIONS

We employed DFT theory and cluster models to investigate the mechanism of propane ammoxidation to acrylonitrile on the proposed active center present in the surface ab planes of the Mo-V-Te-Nb-O M1 phase, focusing specifically on three sequential H abstraction steps from propane to \( \pi \)-allyl. The transition states and activation barriers for the methylene H abstraction from propane, methyl H abstraction from isopropyl, and methyl H abstraction from propene on the \( V^{5+}=O \) and Mo=O oxo groups have been determined using a combination of CI-NEB and dimer methods.

\( V^{5+}=O \) was found to be the preferred surface site for all three H abstraction steps investigated. The activation barriers for the H abstraction from propane and propene are calculated to be 1.58 and 0.99 eV, and that for the H abstraction from isopropyl is negligible. On Mo=O, the activation barriers for the H abstraction from propane and propene are both ~2 eV, while that for the H abstraction from isopropyl is 0.59 eV, suggesting that Mo=O does not play a role in propane activation at typical ammoxidation reaction conditions beyond offering limited activity for dehydrogenating isopropyl. The initial H abstraction from propane on \( V^{5+}=O \) was found to be the rate-limiting step with an apparent activation barrier of ~1.2 eV (after ZPE and vdW contributions), which is in excellent agreement with experimental activation energies for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase [38] and supported VO\(_x\) species [31,32,37,41]. These observations suggest that H abstraction from propane is the rate-limiting step for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase and that \( V^{5+}=O \) is the active site for this step.
ACKNOWLEDGMENTS

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REFERENCES


Chapter 5. Ammonia activation and NH insertion

5.1 INTRODUCTION

Acrylonitrile is an important industrial chemical that is currently produced by propene ammoxidation. Direct propane ammoxidation to acrylonitrile catalyzed by the bulk mixed metal oxides has gained considerable attention in recent years [1–3] because it is an environmentally benign and potentially more economical process that relies on the abundant propane feedstock than the current process of propene ammoxidation. Among all mixed metal oxides, the bulk mixed Mo-V-Te-Nb-O system is particularly promising because of its significant activity and selectivity in converting propane to acrylonitrile [4] compared to other Mo-V-O based catalysts. Earlier studies have showed the presence of two major crystalline Mo-V-Te-Nb-O phases, so-called M1 and M2 [5, 6]. The M1 phase is shown to be solely responsible for propane activation, while the M2 phase improves the yield of acrylonitrile at low propane conversion in synergy with the M1 phase by transforming propene intermediate into acrylonitrile.

Propane ammoxidation to acrylonitrile over the Mo-V-Te-Nb-O M1 phase was proposed to consist of a series of elementary reaction steps, including propane oxidative dehydrogenation (ODH), ammonia (NH₃) and dioxygen activation, NHₓ insertion into allyl intermediate, and final ODH of the C-N coupled precursor leading to acrylonitrile [7]. Based on the concept of site isolation and the catalytic properties of relevant binary metal oxides, Grasselli et al. proposed a hypothetical reaction pathway that outlined the catalytic roles of each metal ion present in surface ab planes of the Mo-V-Te-Nb-O M1 phase in propane ammoxidation to acrylonitrile [3]. All metal cations proposed to be
responsible for propane transformation to acrylonitrile are thus arranged within bonding distances of one another in the proposed active center present in the surface \textit{ab} plane of the M1 phase (Figure 1) \cite{8, 9}. Among these metal cations, the Mo\textsuperscript{4+}/Mo\textsuperscript{6+} site was proposed to be responsible for NH\textsubscript{3} activation and C-N bond formation between the \(\pi\)-allyl intermediate and NH\textsubscript{3} species. The subsequent hydrogen abstraction steps from the C-N coupled precursor in this hypothetical reaction pathway \cite{3} were proposed to occur with an aid of adjacent telluryl sites.

\textbf{Figure 1}: The \textit{ab} plane of the Mo-V-Te-Nb-O M1 phase showing labeled metal lattice sites. Blue, grey, orange, green, and red spheres represent Mo, V, Te, Nb, and O atoms, respectively. The proposed active center is outlined by dashed lines.
First-principles density functional theory (DFT) calculations permit the accurate determination of the energetic parameters of elementary reaction steps at the atomic level, and have been accepted as a powerful tool for generating unique mechanistic insights that are difficult to access experimentally. So far, however, only a handful of theoretical studies have been performed to better understand the catalytic behavior of the Mo-V-Te-Nb-O M1 and M2 phases [10–14]. Previously, we have performed DFT calculations using cluster models of the proposed active surface center of the M1 phase to study the hydrogen abstraction steps from propane to \( \pi \)-allyl intermediate on the various metal sites [15–17]. We found that the ODH of propane is the most difficult step in the formation of the \( \pi \)-allyl \((C_3H_5)\) intermediate from propane. Propane ODH is calculated to have an activation barrier \( (E_a) \) of less than \( \sim 1\) eV on Te\(^{4+}\)=O, 1.74 eV on V\(^{5+}\)=O, 2.11 eV on V\(^{4+}\)=O, and 2.10 eV on Mo\(^{5+}\)=O, relative to gas-phase propane. Propane ODH on V\(^{5+}\)=O \( (E_a \sim 1.3\) eV after including zero-point energy and van der Waals (vdW) contributions) as the rate-limiting step is in excellent agreement with the experimental apparent activation energy for this reaction on the Mo-V-Te-Nb-O M1 phase [18]. Moreover, this calculated \( E_a \) is also in good agreement with both measured and calculated activation energies for the ODH of propane and other alkane species on vanadium oxide \([8, 9, 19, 20]\).

Another other aspect in the proposed reaction mechanism is \( \text{NH}_3 \) activation and formation of surface \( \text{NH}_x \) group followed by C-N bond formation via NH insertion into the surface allyl species. In this study, we performed DFT calculations and investigated the adsorption of \( \text{NH}_x \) \((x = 0\)-3\) species, the initial H abstraction from \( \text{NH}_3 \), and the
subsequent insertion of the surface NH group into π-allyl species employing cluster models of the M1 phase containing various surface cation sites.

5.2 METHODS

5.2.1 Cluster Models

The cluster models were based on the truncated $ab$ plane of the M1 phase containing the proposed active center, which consisted of one V cation in the S2 lattice site, four Mo cations in the S4 and S7 lattice sites, and two Te cations in the S12 channel sites (Figure 1) [9, 21]. We have shown previously that three truncated $ab$ planes were sufficient to allow the bulk energy per layer and surface reactivity to converge [15]. Accordingly, the cluster models used in this study each consisted of three truncated $ab$ planes. The distance between adjacent $ab$ planes was fixed at the experimentally measured distance of 4.016 Å. Each cluster was separated from its neighboring images by ~11 Å in the x, y, and z directions. In the bulk M1 phase, the V and Mo cations are capped by oxo groups on opposite sides of the bulk $ab$ planes [1, 9], whereas the nature of the surface $ab$ plane termination by oxo groups remains a subject of on-going research [11]. The eight equatorial oxygen atoms in each truncated $ab$ plane were terminated with hydrogen atoms and both the O and H atoms were fixed at a bond length of 0.96 Å during geometry optimization, while all of the other atoms in the cluster models and all the atoms in the adsorbates were allowed to relaxed.
Three different cluster models were employed in this study (Figure 2). Model A (with a formal composition of $\text{Mo}_{12}\text{Te}_6\text{V}_3\text{O}_{63}\text{H}_{24}$) contained the proposed active centers in the bulk $ab$ plane of the M1 phase, where the vanadyl and telluryl oxo ($\text{V}=$O and $\text{Te}=$O) groups were present on one side of the $ab$ plane, while the molybdyl oxo ($\text{Mo}=$O) groups were present on the opposite side. This model has been used in our previous studies [15–17]. For the $\text{NH}_3$ activation and NH insertion studies, the direction of the $\text{Te}=$O groups was reversed so that the $\text{Te}=$O and $\text{Mo}=$O groups were present on the same side of the $ab$ plane and adjacent to each other, as suggested by the reaction mechanism proposed by Grasselli [8, 9, 19]. Moreover, the oxygen atom in one of the four $\text{Mo}=$O groups was removed to form a reduced Mo site in order to accommodate the $\text{NH}_3$ species resulting in Model A’ (with a formal composition of $\text{Mo}_{12}\text{Te}_6\text{V}_3\text{O}_{62}\text{H}_{24}$). The direction of the $\text{Te}=$O groups in the original Model C used in our previous studies [14] was also reversed to create Model C’ (with a formal composition of $\text{Mo}_{12}\text{Te}_4\text{V}_3\text{O}_{61}\text{H}_{24}$), in order to generate a surface $\text{V}^{5+}$ site.

![Diagram of cluster models A, A', and C']
Figure 2: Top (top panels) and side (bottom panels) views of the three different cluster models used in this study. Arrow indicates line of sight for the side views. Blue, grey, orange, red, and white spheres represent Mo, V, Te, O, and H atoms, respectively.

5.2.2 Computational Details

Spin-polarized, periodic DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP). The exchange-correlation interaction was described by the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [23]. The core electrons were described by the projector-augmented-wave (PAW) method [24–26], and the Kohn-Sham valence states (including Mo(4p4d5s), Te(5s5p), V(3s3p3d4s), O(2s2p), N(2s2p) and H(1s)) were expanded in plane wave basis sets up to 400 eV. The Brillouin zone was sampled at the Γ point only. Spin polarization was considered for all calculations. Different integral spin states for each system have been checked and only the lowest-energy states are reported below unless otherwise noted. For the cluster-adsorbate systems in this study, the ground energy state occurred in all cases with one of the lowest spins (e.g. singlet or triplet for closed-shell systems), which were usually energetically separated by no more than 0.1~0.2 eV.

Adsorbates were placed on one side of the cluster only. The adsorption energy of an adsorbate was defined as $\Delta E = E_{\text{total}} - E_{\text{cluster}} - E_{\text{adsorbate}}$, where $E_{\text{total}}$, $E_{\text{cluster}}$, and $E_{\text{adsorbate}}$ are the energies of the combined system (adsorbate and cluster), the clean cluster without the adsorbate, and the adsorbate atom/molecule in a neutral state (closed-shell or radical)
in the gas phase. Geometry optimization was considered to have converged when the force in each of the x, y, and z directions on each relaxed atom fell below 0.05 eV/Å.

Minimum-energy reaction paths and corresponding transition states (TSs) were calculated using climbing-image nudged elastic band (CI-NEB) and dimer methods [27, 28] using 0.03 eV/Å as the convergence criterion. Each reaction path was constrained to stay on the same spin state as determined by the ground energy spin state of the initial states. Vibrational frequencies were calculated in the harmonic oscillator approximation by diagonalizing the mass-weighted Hessian matrix, which was built from the calculated two-sided differences of the first derivatives of the total energy due to small geometrical perturbations (0.009 Å in each degree of freedom). Each calculated TS reported in this study was verified to possess one main mode of negative curvature in the direction of the bond in transition. As we have reported previously for the TS’s for dehydrogenation of the C₃ species [17], the TS found for the NH insertion step also possesses an additional mode of negative curvature, which has an imaginary frequency of 34 cm⁻¹ and corresponds to the translation of the loosely-bound C₃ moiety at the TS, which could not be removed even after geometry optimization converged to 0.01 eV/Å. vdW interactions were not included in the TS calculations. Their effects on TSs were expected to be negligible for the activation of a small species like NH₃, but of a similar extent to propane (which lowered the energy by ~0.2 eV vs. gas-phase species) for allyl coupling to nitrogen.

The oxidation states of surface cations were estimated using the Bader charge analysis as implemented by Henkelman et al. [29] and compared with bulk and molecular
reference systems. Our analysis suggested that the oxidation state of the surface V cation was +4 in Models A and A’, and +5 in Model C’, and that the surface Mo cations were in the +5 oxidation state in the Models A, A’, and C’ (Table 1). Te was tentatively assigned the +4 oxidation state by comparison with bulk tellurium oxide [17].

Table 1. Bader charges of Mo and V cations present in the surfaces of the cluster models of the Mo–V–Te–Nb-O M1 phase; the bulk molybdenum and vanadium oxides; and selected molybdenum oxide clusters. The formal oxidation state assigned to each cation is shown in parenthesis. The results taken from the literature are as noted.

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>+2.52 (+5)</td>
<td>+1.91 (+4)</td>
</tr>
<tr>
<td>Model A’</td>
<td>+2.51 (+5)</td>
<td>+2.00 (+4)</td>
</tr>
<tr>
<td>Model C’</td>
<td>+2.53 (+5)</td>
<td>+2.11 (+5)</td>
</tr>
<tr>
<td>Mo(=O)(OH)₃(H₂O)[32]</td>
<td>+2.47 (+5)</td>
<td>-</td>
</tr>
<tr>
<td>Mo(=O)₂(OH)₂(H₂O)[32]</td>
<td>+2.65 (+6)</td>
<td>-</td>
</tr>
<tr>
<td>α-MoO₃[32]</td>
<td>+2.71 (+6)</td>
<td>-</td>
</tr>
<tr>
<td>VO₂[15]</td>
<td>-</td>
<td>+1.94 (+4)</td>
</tr>
<tr>
<td>V₂O₅[15]</td>
<td>-</td>
<td>+2.09 (+5)</td>
</tr>
</tbody>
</table>
5.3 RESULTS AND DISCUSSION

5.3.1 Adsorption of NH$_x$ species

First, the adsorption of NH$_x$ ($x = 0, 1, 2, 3$) species was investigated on different metal sites. Each surface cation site can be in one of three states: 1) oxidized, as capped by a terminal oxo group; 2) empty, as on the opposite side of metal oxo groups; 3) reduced, with the oxo group removed. In our previous studies on the adsorption of radical C$_3$ (isopropyl and π-allyl) and H species on the M1 cluster models [16], terminal oxo sites were shown to be generally more reactive than bridging oxygen sites, so the latter are not considered in this portion of our study.

The adsorption energies of the NH$_x$ species on the surface terminal oxo (M=O$^*$), empty ((O=)M$^*$), and reduced (M$^*$) Mo, V, Te sites in Model A, and on the terminal oxo and reduced V$^{5+}$ site in Model C', are reported in Table 2. NH$_3$ has a lone pair of electrons on the N atom and, therefore, strongly prefers to bond to open coordination sites on metal cations (including reduced sites and the opposite side of an oxo group), compared to bonding to the terminal oxo group on the same cation. Apart from the Te sites, the adsorption energies of NH$_3$ on the reduced V sites are in agreement with the reported adsorption energies of $-0.86$ eV for NH$_3$ on the V sites. These values are similar to those found by Rojas et al. [30] for ammonia adsorption on the V sites coordinated to four bridging oxygens in VSbO$_4$(001) which have the same configuration as reduced V sites in our cluster models and the value of $-0.74$ eV for ammonia adsorption on the empty V site in V$_2$O$_5$(001) reported by Yao et al. [31], both calculated using periodic DFT. Overall, the NH and N species (relative to a gas-phase N atom) are much more strongly adsorbed than NH$_2$ and NH$_3$. Atomic N, however, is quite unstable with respect
to gas-phase N₂ on all surface sites considered here except the reduced Te site, suggesting that the M1 ab plane possesses active sites for recombinative N₂ desorption. Indeed, N₂ is often observed experimentally as a major reaction product [18]. Gruber et al. [32] have studied NHₓ adsorption on cluster models of V₂O₅(010) using the RPBE functional and contracted Gaussian basis sets, and reported that NH₃ does not adsorb on a terminal oxo group and adsorbs weakly on an empty V site (-0.25 eV), but adsorbs more strongly at the oxo vacancy (-0.87 eV). Our findings for NH₃ adsorption on the vanadyl oxo, empty vanadium, and reduced vanadium sites (+0.59, -0.05, and -0.78 eV respectively) are in line with the findings of Gruber et al. (Table 2). Gruber et al. [32] further reported the adsorption energies for NH₂, NH, and N on the vanadyl oxo, empty vanadium, and reduced vanadium sites to be -0.46, -0.12, and -2.25 eV for NH₂; -0.95, no adsorption, and -3.16 eV for NH; and -1.54, no adsorption, and -2.17 eV for N (with respect to N). That NH₂, NH, and N prefer the reduced vanadium site most, followed by the vanadyl oxo site, and then the empty vanadium site, is also qualitatively consistent with what we find for the adsorption of these species on the V⁴⁺ and V⁵⁺ sites in the M1 ab plane (Table 2).
Table 2. Adsorption energies ($\Delta E$, in eV) of NH$_x$ ($x = 0, 1, 2, 3$) on different surface sites in the $ab$ plane of Mo-V-Te-Nb-O M1 phase modeled by clusters Models A and C'.

$M=O^*$ denotes a terminal oxo site on a metal cation; $M^*$ indicates a reduced metal site with the oxo group removed; $(O=)M^*$ is an empty metal site that is present on the opposite side of an oxo group.

<table>
<thead>
<tr>
<th>NH$_x$ species</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo=O</td>
</tr>
<tr>
<td>N</td>
<td>3.45</td>
</tr>
<tr>
<td>NH</td>
<td>-1.14</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>-0.07</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>1.96</td>
</tr>
</tbody>
</table>

a) $\Delta E$ of atomic N is calculated with respect to $\frac{1}{2}$ of the energy of a gas-phase N$_2$ molecule. The calculated bond energy of a gas-phase N$_2$ molecule is 10.38 eV.

By far the most stable metal site for the NH$_x$ ($x = 0, 1, 2, 3$) species is a Te center with open coordination (reduced or empty). The high reactivity of the Te center toward NH$_x$ is consistent with our previous findings that the radical C$_3$ and H species adsorb most strongly at Te=O [15]. However, the high reactivity of the Te center toward C$_3$ radical and H adsorption and propane activation [15, 17] is not consistent with the experimentally measured apparent activation barrier for propane conversion on the M1 phase (~1.3 eV [18]) or with the fact that tellurium oxides are not known to activate C-H bonds in alkanes [33]. We speculate that the state or location of the Te species on the
surface of a working M1 catalyst is different from those in the proposed bulk structure of the M1 phase. This may be due to the high volatility of tellurium and tellurium oxide species. Another possibility is that the Te centers are predominantly in a nitrided state instead of an oxo-terminated state under propane ammoxidation conditions, thus making active Te=O species for propane activation unavailable. Incidentally the reactivity of tellurium toward nitrogen has been noted before [34], while tellurium oxide is effective for propene ammoxidation [35].

To further examine NH$_3$ dehydrogenation on the surface of the $ab$ plane in the Mo-V-Te-Nb-O M1 phase, the reaction energy profiles of the sequential dehydrogenation of NH$_3$ on the different surface Mo and V sites are calculated (Figure 3; for brevity those on the Te sites are omitted). The O$_2$ molecule was used as the final H acceptor to form water. The sum of the total energies of one gas-phase NH$_3$ molecule and 3/4 O$_2$ molecule and the clean cluster was set to zero on the energy axis. The results showed that the empty Mo and V sites can adsorb NH$_3$ but all the dehydrogenation steps up to N are endothermic. For instance, it is endothermic by 1.5~2 eV to transform adsorbed NH$_3$ to NH on the empty Mo and V sites. Trapping NH$_3$ on the terminal oxo sites is also expected to be unfavorable because NH$_3$ adsorption is endothermic, particularly on Mo=O. On the other hand, the reduced metal sites showed much more favorable energetics for successively dehydrogenating NH$_3$. In particular, NH$_3$ dehydrogenation has an entirely exothermic energy profile on the reduced Mo site. This suggests that the reduced metal sites, particularly the reduced Mo site, are the preferred sites for generating NH$_x$ intermediates. The formation of NH$_x$ species on Mo sites is good agreement with the hypothetical reaction mechanism proposed by Grasselli et al. [8, 9, 16].
Figure 3: Reaction energy profiles for NH$_3$ dehydrogenation on various surface Mo and V sites in the $ab$ plane of Mo-V-Te-Nb-O M1 phase, represented by cluster Model A. Each dissociated H is represented as $\frac{1}{2}$ water molecule. Star denotes an adsorbed species. M=O$^*$ denotes a terminal oxo group on a metal cation; M$^*$ denotes a reduced metal site with the oxo group removed; (O=)M$^*$ indicates an empty metal site that is present on the opposite side of an oxo group.

5.3.2 Initial H abstraction from NH$_3$

Our previous studies have shown that Te=O and V$^{5+}$=O are the first and second most effective H abstraction sites in the proposed active center because they both show strong affinity for the H atom. Therefore, we investigated two scenarios for the initial H abstraction from NH$_3$, with 1) reduced Mo site as the NH$_3$ adsorption site and an adjacent
Te=O as the H abstraction site (Model A’); 2) empty Mo site as the NH₃ adsorption site and an adjacent V⁵⁺=O as the H abstraction site (Model C’).

According to the first scenario, the reaction is slightly exothermic (-0.04 eV) and the activation barrier is 0.27 eV. The TS in the NH₃ activation study possesses a single negative vibrational mode, with an imaginary frequency of 379 cm⁻¹ that corresponds to the dissociating N–H bond. In the second scenario, the reaction energy alone is +1.10 eV, which implies the greater activation barrier for activating NH₃ by surface V⁵⁺=O species (1.85 eV). Thus NH₃ activation can occur on the reduced Mo site, but the nature of the H abstraction site strongly affects the activation barrier for NH₃ activation. We note that in the proposed mechanism [8, 9, 16], H abstraction from NH₃ is accomplished by an oxo group on the same Mo center to which NH₃ is coordinated [7], whereas in our cluster Model A’ the Mo center is already highly coordinated and cannot accommodate both NH₃ and an oxo group simultaneously. H abstraction from gas-phase NH₃ is a possibility, akin to the propane and propene activation mechanism on the M1 phase proposed in our previous studies [14]. However, the first N-H bond in NH₃ is stronger than the secondary C-H bond in propane (calculated values are 4.88 vs. 4.32 eV). If we assume that $E_a$ for the gas-phase NH₃ activation mechanism is equal to the N-H bond energy minus the H adsorption energy to the acceptor site, as is shown to be the case for propane activation on the M1 ab plane [15, 17], then the $E_a$ for initial hydrogen abstraction from NH₃ would be equal to 2.22 eV on V⁵⁺=O (where $\Delta E_{H}$ is -2.66 eV). Even if H is abstracted by Te=O, where $\Delta E_{H}$ is -3.25 eV [17], the $E_a$ would still be 1.63 eV, which is much higher than when NH₃ is adsorbed on a reduced Mo site as reported above. Therefore, unlike propane
and propene, which do not strongly interact with the surface, NH$_3$ activation is significantly promoted when the nitrogen is directly stabilized on an open metal site.

![Figure 4](image)

**Figure 4:** Top (top panels) and side (bottom panels) of a) the TS of H abstraction from NH$_3$ adsorbed on a reduced Mo site by an adjacent Te=O group; b) the TS of NH adsorbed on a reduced Mo site inserting into a gas-phase π-allyl intermediate. Both processes are investigated on Model A’. Key bond lengths are given in units of Å.

5.3.3 NH insertion into π-allyl

Taking NH formed on the reduced Mo site as an example, we further explored NH insertion into π-allyl. The calculated activation barrier to form a C-N bond between the methylene C in a gas-phase π-allyl radical and N in the imido group adsorbed on the reduced Mo site is 0.03 eV with respect to gas-phase π-allyl. The TS for this step
possesses a main negative vibrational mode with an imaginary frequency of 111 cm\(^{-1}\) that corresponds to the C–N bond formation. This is consistent with the negligible activation barriers generally found for the re-bounding of gas-phase radical species to oxide surfaces, such as reported by Alexopoulos et al. in their DFT study of the ODH of propane and propene on V\(_2\)O\(_5\)(001) [31]. The small barrier suggests that the selective formation of allyl-imido intermediate (via C-N coupling) vs. undesired oxidation products (C-O coupling, i.e. oxo-insertion) may depend considerably on the probability of \(\pi\)-allyl finding surface imido and other nitrogen groups as opposed to oxygen groups.

5.4 CONCLUSIONS

NH\(_x\) (\(x=0, 1, 2, 3\)) adsorption, NH\(_3\) activation by H abstraction, and subsequent NH insertion to form allyl-imido intermediate have been investigated on cluster models using DFT calculations as part of an overall mechanism of propane ammoxidation to acrylonitrile over the Mo-V-Te-Nb-O M1 phase. Transition states and activation barriers for NH\(_3\) activation by different H abstraction sites (Te=O and V\(^{5+}\)=O) and subsequent C-N bond formation between surface NH group and gas-phase allyl have been determined using the CI-NEB and dimer methods.

NH\(_x\) prefers bonding directly to metal sites with open coordination (e.g., those where the terminal oxo group was removed, or vacant sites on the opposite side of the oxo group) rather than to the terminal oxo sites. Open Te sites bind NH\(_x\) species very strongly, followed by open Mo sites, while NH adsorbs more strongly than NH\(_2\) and NH\(_3\). Atomic N is not stable on most sites on this surface with respect to gas-phase N\(_2\). Initial H abstraction from NH\(_3\) and NH insertion into \(\pi\)-allyl gas-phase intermediate was
explored for the NH$_3$ species adsorbed on open Mo sites. The activation barrier for H abstraction from NH$_3$ was found to be 0.28 eV and the reaction energy was -2.36 eV. The NH insertion into the allyl species is characterized by a negligible activation barrier of 0.03 eV. These results suggested that Mo functions as the active site for the activation and reaction of the nitrogen species during propane ammoxidation on the $ab$ plane of the Mo-V-Te-Nb-O M1 phase, which is in good agreement with the hypothetical reaction mechanism proposed previously by Grasselli et al. [8, 9, 16].

5.5 ACKNOWLEDGMENTS

This study was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy, under Grant #DE-FG02-04ER15604. Part of the DFT studies were performed at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory (ORNL) by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The resources of the National Energy Research Scientific Computing Center, supported by DOE Office of Science under Contract DE-AC02-05CH11231, are gratefully acknowledged.
REFERENCES


Chapter 6. Acrylonitrile formation and combustion

6.1 INTRODUCTION

In the mechanism proposed by Grasselli et al.[1,2], the final formation of acrylonitrile is completed via three hydrogen abstractions by telluryl after the step of NH insertion into allyl intermediate occurring on molybdyl surface site. This step is then followed by the release of acrylonitrile into the gas phase and the surface restoration by the release of water molecules and the reoxidation of oxo-depleted surface metal oxo sites. Based on our previous studies, ammonia is activated by the empty Mo site with oxo depleted and form the imido group NH on the same site via two hydrogen abstractions. Thus the next step NH insertion into allyl to form the acrylonitrile precursor occurs on the same empty Mo site. Based on previous studies of H abstractions from C₃ species [3], the nearby metal oxo sites around the C₃ species act as the active H abstraction centers. As it has been shown before, the activation energy of H abstraction from C₃ species by surface oxo site is proportional to the corresponding H atom adsorption energy on the same site. The stronger the H is bonded to the abstraction center, the lower the activation energy of H abstraction step is. There are three different types of metal oxo sites on Mo-V-Te-Nb-O M1 phase ab plane surface. Based on the previous studies of the reactivity of surface sites in the active center, V⁵⁺=O site shows the strongest capability of binding H atom from CHₓ groups, therefore lowest energy barriers for the H abstraction reaction steps. Whereas Mo=O site shows the weakest capability of abstracting H atom from CHₓ group, thus the highest energy barriers.
Therefore in the studies of modeling following H abstraction steps, Mo=O site is chosen as the H abstraction site while acrylonitrile precursor allyl-imido is adsorbed on the nearby empty Mo site. The calculated energy barrier for each H abstraction from allyl-imido by Mo=O site is then the predicted upper limit of energy barrier for each step occurring on the surface of Mo-V-Te-O M1 ab plane.

6.2 Computational Modeling and Methods

6.2.1 Computational Methods Details

Spin-polarized, periodic DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP). The exchange-correlation interaction was described by the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [4]. The core electrons were described by the projector-augmented-wave (PAW) method [5–7], and the Kohn-Sham valence states (including Mo(4p4d5s), Te(5s5p), V(3s3p3d4s), O(2s2p), N(2s2p) and H(1s)) were expanded in plane wave basis sets up to 400 eV. The Brillouin zone was sampled at the Γ point only. Spin polarization was considered for all calculations. Different integral spin states for each system have been checked and only the lowest-energy states are reported below unless otherwise noted. For the cluster-adsorbate systems in this study, the ground energy state occurred in all cases with one of the lowest spins (e.g. singlet or triplet for closed-shell systems), which were usually energetically separated by no more than 0.1~0.2 eV.

Adsorbates were placed on one side of the cluster only. The adsorption energy of an adsorbate was defined as \( \Delta E = E_{\text{total}} - E_{\text{cluster}} - E_{\text{adsorbate}} \), where \( E_{\text{total}} \), \( E_{\text{cluster}} \), and \( E_{\text{adsorbate}} \) are...
are the energies of the combined system (adsorbate and cluster), the clean cluster without the adsorbate, and the adsorbate atom/molecule in a neutral state (closed-shell or radical) in the gas phase. Geometry optimization was considered to have converged when the force in each of the x, y, and z directions on each relaxed atom fell below 0.05 eV/Å.

Minimum-energy reaction paths and corresponding transition states (TSs) were calculated using climbing-image nudged elastic band (CI-NEB) and dimer methods [8,9] using 0.03 eV/Å as the convergence criterion. Each reaction path was constrained to stay on the same spin state as determined by the ground energy spin state of the initial states. Vibrational frequencies were calculated in the harmonic oscillator approximation by diagonalizing the mass-weighted Hessian matrix, which was built from the calculated two-sided differences of the first derivatives of the total energy due to small geometrical perturbations (0.009 Å in each degree of freedom). Each calculated TS reported in this study was verified to possess one main mode of negative curvature in the direction of the bond in transition. As we have reported previously for the TS’s for dehydrogenation of the C₃ species [3], the TS found for the step of H abstraction from CH group leading to the final formation of acrylonitrile also possesses an additional mode of negative curvature, which has an imaginary frequency of 54 cm⁻¹ and corresponds to the translation of the loosely-bound C₃ moiety at the TS, which could not be removed even after geometry optimization converged to 0.01 eV/Å. vdW interactions were not included in the TS calculations. Their effects on TSs were expected to be of a similar extent to propane (which lowered the energy by ~0.2 eV vs. gas-phase species) for allyl coupling to nitrogen.
6.2.2 Cluster Model

We have shown previously [10–12] that cluster models built from three truncated \( ab \) planes containing the proposed active center with one V cation in the lattice site S2, four Mo cations in the S4 and S7 lattice sites, and two Te cations in the S12 channel sites (Figure 1) are sufficient for accurate modeling of the bulk energy and surface reactivity. In this study, we employed cluster model (Figure 1) reported in our previous studies [10,12]. The model is made up of the proposed active centers based on bulk \( ab \) planes of the M1 phase where vanadyl oxygens are present on one side of the \( ab \) plane, while molybdyl and telluryl oxygens are located on the opposite side. Based on this model, one oxygen atom on molybdyl site was removed to form a reduced Mo site for the allyl-imido precursor formation. The interplanar distance was fixed at the experimentally observed d-spacing of 4.016 Å for adjacent \( ab \) planes, and the neighboring images were separated by \( \sim 11 \) Å in the x, y, and z directions.

The oxidation states of surface cations were estimated using the Bader charge analysis as implemented by Henkelman et al. [13] before exploring the reactivity of

Figure 1. Side (left) and top (right) views of the cluster model deployed in the study.
surface metal sites. The Bader charge analysis confirmed the oxidation state of V to be 4+. Mo was found to be 5+. Te was in 4+.

6.3 RESULTS AND DISCUSSION

6.3.1 First H abstraction from allyl-imido

Unlike H abstraction from propane and propene before, which is a closed-shell species, the abstraction of H from imido group in the acrylonitrile precursor which is the open-shell radical to form next intermediate:

\[
\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_{\text{(surface)}} \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2-\text{N}_{\text{(surface)}} + \text{HO}_{\text{(surface)}},
\]

The first H abstraction from imido in acrylonitrile precursor by nearby Mo=O is overall exothermic with \( \Delta E_{\text{rxn}} = -0.90 \text{ eV} \). The reaction shows negative energy barrier based on the NEB calculation, which means this step is thermodynamically barrierless. This is due to the weakened N-H bond after the formation of acrylonitrile precursor on the surface Mo site in \( ab \) plane of Mo-V-Te-Nb-O M1 phase.
Figure 2. DFT total energy reaction energy profiles for the H abstraction steps from allyl-imido surface intermediate to acrylonitrile on Mo=O. The zero on the y-axis corresponds to one allyl-imido surface intermediate anchored on empty Mo in the cluster. The dissociated H atom after each step is represented as absorbed on nearby Mo=O site. The labels on the lines are the activation barriers for each of the H abstraction steps.
6.3.2 Second H abstraction

Second abstraction of H from methylene group:

\[
\text{CH}_2=\text{CH}-\text{CH}_2\text{-N}_{\text{(surface)}} \rightarrow \text{CH}_2=\text{CH}=\text{N}_{\text{(surface)}} + \text{HO}_{\text{(surface)}}
\]

is endothermic with \(\Delta E_{\text{rxn}}=+0.52\) eV and characterized by high activation barriers as 1.26 eV (Figure 2). In our previous studies, H abstraction from methylene group propane to form isopropyl in gas phase has the activation barrier as 2.10 eV on the same Mo=O site. The lowered the energy barrier can be attributed to the adjacent C-N bond which
withdraws electrons. C-H and O-H bond length in the TS for H abstraction from methylene group by Mo=O are 1.47 and 1.18 Å respectively (Figure 3a).

6.3.3 Third H abstraction and formation of acrylonitrile

Third abstraction of H from methine group:

\[
\text{CH}_2=\text{CH-CH=N}_{\text{(surface)}} \rightarrow \text{CH}_2=\text{CH-C=N}_{\text{(surface)}} + \text{HO}_{\text{(surface)}}
\]

is slightly endothermic with \( \Delta E_{\text{rxn}} = +0.39 \text{ eV} \), however characterized by a higher activation barriers as 1.62 eV (Figure 2). The possible explanation is that the open-shell intermediate from the previous step \( \text{CH}_2=\text{CH-CH=N} \) is stabilized by the anchored at surface empty Mo site. Therefore a further H abstraction from the methyl group in the middle requires more energy than the previous H abstraction from the C atom. Furthermore, previous studies show that a similar case where H abstraction from methyl group in gas phase propene to \( \pi \)-allyl by the same Mo=O site is also characterized by a high activation barrier as 1.94 eV. C-H and O-H bond length in the TS for H abstraction from methylene group by Mo=O are 1.71 and 1.06 Å respectively (Figure 3b).

6.3.4 Formation of acrylonitrile from allyl-imido intermediate

The final formation of acrylonitrile is completed through three H abstraction from NH group and CH₂ group respectively. The study here focuses on the Mo=O site as the abstraction center which can provide with the upper limit for energy barriers for these steps based on the conclusion from the previous studies that Mo=O as the least favored H adsorption site is also the site with the highest activation energy for H abstraction from
C₃ species. The first H abstraction from imido group is exothermic and barrierless. The second and third H abstractions from methylene and methine respectively are both endothermic with 1.26 and 1.62 eV activation energies respectively. Hence the overall reaction of allyl-imido transferred to acrylonitrile occurring on surface in \(ab\) plane of Mo-V-Nb-Te-O M1 phase requires at most 1.62 eV activation energy. As reported before, the highest energy barrier for overall propane converted to allyl and NH insertion in allyl is 2.10 eV for initial H abstraction from propane by Mo=O while 1.94 eV for H abstraction from propene [3]. Therefore the formation of acrylonitrile from allyl-imido precursor is not the rate-limiting step thermodynamically by compared the activation energy to the one for the previous steps. The previous conclusion still stands that initial propane activation in gas phase through H abstraction from methylene group is the rate-limiting step and the activation center for this step is \(V^{5+}=O\).

Previously we also reported a linear energy relation between the H adsorption energy (\(\Delta E_{\text{H}}\)) and the H abstraction activation barrier (\(\Delta E_{\text{TS}}\)), as \(\Delta E_{\text{TS}}=0.980\cdot(\text{BE}+\Delta E_{\text{H}})\) with \(R^2=0.995\), where BE is the bond energy in the gas phase. The relationship is derived from the H abstraction reactions from gas phase C3 species by surface metal oxo groups. The predicted energy barrier by using the above equation can give predicted activation energy for the similar H abstraction reaction from surface reactant adsorbed on the catalyst surface active site. If applying the same equation to the three H abstraction steps here, the calculated energy barriers are -0.66, 1.70, and -0.69 eV respectively for the Mo=O as the H abstraction center. Both first and second energies are in consistent with the calculated activation energies by CI-NEB and dimer method and are higher than the
calculated value. The off for the third energy might be attributed to the special stabilization effect on the open-shell reactant by the surface empty Mo site.

6.4 CONCLUSION

We have employed DFT theory and cluster models to investigate the mechanism of propane ammoxidation to acrylonitrile on the proposed active center in the $ab$ plane of the Mo-V-Te-Nb-O M1 phase, focusing specifically on three sequential H abstraction steps from allyl-imido surface intermediate to acrylonitrile. The transition states and activation barriers for the H abstraction from imido, methyl H abstraction, and methine H abstraction from the allyl on the Mo=O oxo groups have been determined using a combination of CI-NEB and dimer methods.

Since Mo=O is found to be the least preferred surface site for H abstraction steps investigated in C3 species before, the results for activation barriers on Mo=O can provide the upper limit for the highest energy required to completes the series of reactions. The activation barriers for the H abstraction from methyl and methine group are calculated to be 1.26 and 1.62 eV, and that for the H abstraction from imido is negligible. Both are lower than the activation energies for initial H abstraction from propane and propene on the same Mo=O site. Therefore the final formation of acrylonitrile by H abstraction is not the rate-limiting step for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase.
REFERENCES

Chapter 7. Microkinetic model of propane ammoxidation over surface \textit{ab} planes of Mo-V-Te-Nb-O M1 phase

7.1 MECHANISM OF PROPANE AMMOXIDATION

Acrylonitrile (ACN) is an important industrial intermediate which is produced industrially by propene ammoxidation in the SOHIO process \cite{1}. Recently, significant global efforts were dedicated to the development of a new catalytic process of acrylonitrile production through selective ammoxidation of propane because propane is a more abundant resource due to the increased production of natural gas \cite{2,3}. The Mo-V-Te-Nb-O mixed metal oxide is among the most active and selective catalysts investigated in propane ammoxidation being characterized by the 62 mol. \% ACN yield \cite{4-7}. Earlier studies showed that this catalyst contains two major crystalline phases, so-called M1 and M2 phases \cite{8-12}. The M1 phase is solely responsible for propane activation and mostly responsible for the subsequent activation of the propene reaction intermediate \cite{13}. The proposed mechanism of propane ammoxidation over the M1 phase is described by a series of elementary reaction steps, including propane oxidative dehydrogenation (ODH), ammonia and dioxygen activation, NH$_x$ insertion into the \textit{\Pi}-allyl intermediate, and final ODH of the C-N coupled precursor leading to acrylonitrile \cite{4}.

In our previous studies, density functional theory (DFT) calculations have been performed to elucidate elementary steps of propane activation in a series of three sequential H abstraction steps from propane to \textit{\Pi}-allyl \cite{14-16}. The initial H abstraction from propane on V$^{5+}$=O was found to be the rate-limiting step with an apparent activation barrier of \textasciitilde1.3 eV (including ZPE and vdW contributions), which is in good agreement
with experimental activation energies for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase \(^7\) and supported VO\(_x\) species \(^{17-20}\). These observations suggested that H abstraction from propane is the rate-limiting step for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase and that V\(^{5+}\)=O is the active site for this step. The energetics of ammonia activation and surface imido formation in the proposed active center in the \(ab\) plane of the M1 phase have been investigated by DFT calculations \(^{21}\). The activation barrier for the initial H abstraction from ammonia was found to depend strongly on the surface sites that stabilize H and NH\(_2\), and is as low as 0.28 eV when NH\(_2\) is stabilized by the reduced Mo site and H is abstracted by the telluryl oxo group. The subsequent step of surface NH insertion into a \(\pi\)-allyl gas intermediate was also found to have a low activation energy barrier of 0.03 eV on the reduced Mo site.

Microkinetic modeling (MKM) based on DFT calculations has emerged as a powerful tool to analyze the heterogeneously catalyzed reactions based on the elementary steps involving the adsorbed reactants, products, and intermediates on surface active sites \(^{22,23}\). This method makes no assumptions about the rate-limiting step or the surface coverage and relates thermochemical and kinetic parameters to the molecular-level descriptors derived from DFT calculations, which allows more flexible and systematic investigation of the reaction network and provides fundamental insights into surface chemistry during a catalytic reaction. MKM can predict the catalytic activity and selectivity towards product species in complex reactions involving a number of parallel elementary steps as a function of reaction conditions, e.g., temperature, partial pressures of reactant species, and their flow rates.
The MKM calculations typically involve solving a set of non-linear differential equations to determine the reaction rate for each elementary step. Therefore, the construction of a microkinetic model requires a set of thermodynamic and kinetic parameters, including the reaction rate constants \((k)\) and reaction equilibrium constants \((K)\). The unique advantage of DFT calculations lies in the ability to provide many required parameters, e.g., heats of reaction \((\Delta E)\), entropies of reaction \((\Delta S)\), activation energies \((E_a)\), and pre-exponential factors \((A_0)\) entirely by computation. Not surprisingly, DFT-based microkinetic models have been found to display good predictive capability for the catalytic activity and selectivity and have become increasingly popular in recent years.

DFT-based microkinetic modeling was first reported by Dumesic \(^{24}\). Schumacher et al. have reported a microkinetic model based on a redox mechanism to study low-temperature water–gas shift reactivity (WGSR) trends on copper and other transition metals \(^{25}\). Their model was able to predict the WGS activity trends for transition metals, but failed to quantitatively describe the experimental data, probably because it assumed that the redox mechanism was dominant for all transition metal catalysts and neglected adsorbate interactions, which play an important role at high coverage. The model predicted that the WGS activity of copper can be improved by increasing the surface bond energies for carbon monoxide and oxygen, thereby suggesting some new possibilities for improving the Cu catalysts for low-temperature WGSR.

Singh et al. combined a comprehensive mean-field microkinetic model with reaction kinetics experiments and scanning transmission electron microscopy (STEM) imaging to study the reaction mechanism and provide insights into the nature of active
sites for formic acid (HCOOH) decomposition on Au/SiC catalysts. The parameters in the comprehensive mean-field microkinetic model were derived from density functional theory calculations on Au(111), Au(100), and Au(211) and subsequently adjusted to describe the experimental HCOOH decomposition rate and selectivity data. It was shown that the HCOOH decomposition follows the formate (HCOO) mediated path, with 100% selectivity toward the dehydrogenation products (CO₂+H₂) under a wide range of reaction conditions. They also proposed an improved model for the Au surface where the coordination number less than 4 is required for the surface active Au sites for HCOOH decomposition based on the analysis of the kinetic parameters.

Recently, the MKM method has also been applied to model reactions catalyzed by metal/metal oxide and pure metal oxide surfaces. Aranifard et al. have conducted microkinetic modeling based on density functional theory calculations to investigate the mechanism of WGS reaction at the three-phase boundary of Pt/CeO₂ catalysts to better understand the importance of metal–oxide interfacial sites in heterogeneous catalysis. The reaction order, apparent activation energy, and turnover frequency under different reaction conditions from MKM were compared to experimental data for the ‘‘redox pathway’’ and the ‘‘associative carboxyl pathway with redox regeneration’’. Their study suggested that both pathways could operate on Pt/CeO₂ catalysts. The high activity of interfacial Pt/CeO₂ sites originates from a significantly enhanced water activation and dissociation at interfacial oxygen vacancies. Christiansen et al. have investigated the γ-Al₂O₃-catalyzed production of ethylene and diethyl ether from ethanol in a combined density functional theory (DFT) and microkinetic modeling study. DFT calculations performed for the c-Al₂O₃(111) surface facet demonstrated that
the energetically favorable pathway for ethylene formation is an $E_2$ mechanism ($E_a = 28$ kcal/mol), while ether formation takes place via a bimolecular ($SN_2$) mechanism ($E_a = 32$ kcal/mol). The DFT-parameterized two-site mean-field microkinetic model successfully captured trends in experimentally measured reaction orders. Microkinetic analysis indicated that the $SN_2$ and $E_2$ elementary steps control the overall rate. The analytical rate expressions were derived from the full microkinetic model and fit to experimental data, capturing reaction order trends with similar success as the full model. The outcome of the fitting suggested that an additional active site may be responsible for some ethanol conversion.

However, DFT-driven microkinetic models for multi-metal oxides have not been reported to date. This study reports for the very first time a simple equilibrium microkinetic model for propane ammoxidation, which predicts the reaction rate, product selectivity, and coverages of surface intermediates for a pair of metal cation sites ($Mo^{5+}$ and $V^{5+}$) present in the surface $ab$ planes of the Mo-V-Te-Nb-O M1 phase. The MK model developed in this study is a simplified model that solves for the reaction rate calculated at the equilibrium conditions without the consideration of mass balance in a reactor model. Thermodynamic and kinetic parameters related to surface species in the MKM were calculated from the results obtained in previous DFT calculations as described below.
7.2 MICROKINETIC MODELING OF PROPANE AMMOXIDATION OVER M1 PHASE

7.2.1 Reaction mechanism

Surface active site preference

Watanabe and Ueda \(^7\) investigated the essential roles of Mo and V sites in the mechanism of propane ammoxidation over Mo-V-O based M1 phase catalysts, which included Mo-V-O, Mo-V-Te-O, Mo-V-Te-Nb-O, Mo-V-Sb-O, and Mo-V-Sb-Nb-O compositions. The reaction was conducted at 683 K with a fixed gas composition of \(\text{NH}_3:O_2=8.6:17.1\) (%). Both Mo and V were indicated to be responsible for selective oxidation of propane to the propene intermediate, which was suggested by the slight difference in both propane oxidation rate and propane conversion despite of the fundamental difference in the catalyst composition. Also, the ammonia consumption rate and conversion were unaffected by the additional metal cation species, indicating that only Mo and V are possible active sites for ammonia activation. The experimental reaction rates and activation energy indicated that the propane activation is the rate-limiting step and the corresponding activation energy values for different catalysts were similar, ranging from 105 kJ/mol to 131 kJ/mol. Also in the previous studies, DFT calculations have been performed to study the oxidative dehydrogenation (ODH) of \(C_3\) species and ammonia on different surface active sites on \(ab\) plane surface of Mo-V-Te-Nb-O M1 phase\(^{15,16,21}\). It was found that \(V^{5+}=O\) is responsible for propane activation and sequential ODH to form the intermediate \(\pi\)-allyl. The ammonia oxidative activation and the subsequent step \(\text{NH}_x\) insertion occur on the surface Mo site. The Te=O species was found to be much more reactive than both Mo=O and \(V^{5+}=O\) for the H abstraction from
propane. Its role in the reaction mechanism needs to be elucidated further as it appears to be different from that of the α-hydrogen extraction site proposed earlier. Therefore, in this study, the MKM has been developed for the Mo$^{5+}$ and V$^{5+}$ as the active sites to investigate the overall reaction mechanism of propane ammoxidation over surface ab planes of the Mo-V-Te-Nb-O M1 phase.

**Proposed reaction network**

The starting point for the development of a microkinetic model is the construction of the detailed reaction mechanism containing all key elementary steps. Based on the results of previous studies, the overall mechanism consisting of total eight elementary steps shown in Table 1 was adopted in this study.

**Table 1.** Propane ammoxidation mechanism employed in the present microkinetic model. Mo denotes the surface Mo$^{5+}$ sites and V denotes the surface V$^{5+}$ sites.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NH$_3$(g) + *Mo ⇌ NH$_3$*Mo</td>
</tr>
<tr>
<td>2.</td>
<td>NH$_3$(g) + *V ⇌ NH$_3$*V</td>
</tr>
<tr>
<td>3.</td>
<td>O$_2$(g) + 2<em>Mo ⇌ 2O</em>Mo</td>
</tr>
<tr>
<td>4.</td>
<td>O$_2$(g) + 2<em>V ⇌ 2O</em>V</td>
</tr>
<tr>
<td>5.</td>
<td>NH$_3$<em>Mo + 2O</em>V ⇌ NH<em>Mo + 2 OH</em>V</td>
</tr>
<tr>
<td>6.</td>
<td>2 OH<em>V → H$_2$O(g) + O</em>V + *V</td>
</tr>
<tr>
<td>7.</td>
<td>CH$_3$CH$_2$CH$_3$(g)+2O<em>V ⇌ CH$_3$CHCH$_2$(g) + 2OH</em>V</td>
</tr>
<tr>
<td>8.</td>
<td>CH$_3$CHCH$_2$ (g)+O<em>V ⇌ CH$_2$CHCH$_2$ (g) + OH</em>V</td>
</tr>
</tbody>
</table>
Step 1 is the adsorption of gas phase ammonia at the active surface Mo\(^{5+}\) site. Mo\(^ {5+}\) site was selected for ammonia adsorption and activation as it was indicated by our previous study 21. Step 2 is the physisorption of gas phase ammonia at the surface active V\(^ {5+}\) site. Step 3 is the physisorption of gas phase dioxygen at the surface active Mo\(^{5+}\) site. Step 4 is the adsorption of gas phase dioxygen at the surface active V\(^ {5+}\) site. Vanadyl oxo is responsible for oxidation of C\(_3\) surface intermediates. It was assumed that the adsorption steps are fast with zero energy barriers. Therefore, the adsorption was considered to be thermodynamically controlled, where the equilibrium state was rapidly attained.

Step 5 is the ammonia activation and formation of surface imido species. As shown in our previous studies of ammonia activation over Mo-V-Te-Nb-O M1 phase, the imido NH is the most thermodynamically stable species among all NH\(_x\) species 21. The first H abstraction from NH\(_3\) is considered to be the highest energy barrier step among all steps of ammonia dehydrogenation. Therefore, this step represents the formation of surface imido species via two sequential hydrogen abstractions from the ammonia molecule adsorbed at Mo\(^{5+}\) site by the vanadyl oxo, with the activation barrier of the first abstraction being the activation energy for the overall reaction.

Step 6 is the elimination of hydroxyl groups from the surface V\(^ {5+}\) sites through the formation of water molecule in gas phase. This step of water formation is generally considered to be a rapid process with a zero energy barrier.

Step 7 is the activation of propane and propene formation. As shown in our previous extensive studies of C\(_3\) species activation over the M1 phase surface, the isopropyl species is not stable at the surface, whereas the formation of propene by H
abstraction from surface isopropyl is almost barrierless and exothermic\textsuperscript{16}. Therefore, the first two H abstractions from propane are grouped into one step characterized by the activation energy corresponding to the initial H abstraction step.

Step 8 is the formation of $\pi$-allyl intermediate by H abstraction from propene. The reactions that follows branch into two pathways: (1) imido insertion into $\pi$-allyl that triggers the selective pathway leading to acrylonitrile, whereas (2) surface O insertion into $\pi$-allyl species initiates the unselective pathway leading to the combustion of C\textsubscript{3} species. The initial NH and O insertion steps are both rapid steps with small activation energies and low reaction energies. Moreover, the concentrations of surface NH and O species are in equilibrium according to step 5 and steps 3 and 4, respectively. Combined with the fact that $\pi$-allyl is an unstable intermediate, which is not detected experimentally, it can be assumed that $\pi$-allyl is fully converted to acrylonitrile and CO\textsubscript{x} once it is formed on the surface. Therefore, it was assumed in this study that the selectivity to acrylonitrile is defined by the relative concentrations of surface NH and O species. In the present microkinetic model, the overall mechanism includes all eight steps described above and the selectivity to acrylonitrile is calculated by the ratio of surface coverages of ammonia and imido at the Mo\textsuperscript{5+} sites with respect to the combined surface coverage of ammonia and imido species at the Mo\textsuperscript{5+} sites and surface oxygen species at V\textsuperscript{5+} sites. This theoretical selectivity was compared to the experimental selectivity to acrylonitrile observed during propane ammoxidation over the Mo-V-Te-Nb-O M1 phase.
7.2.2 DFT - based microkinetic modeling

Our microkinetic model employed the binding energies, reaction energies, and activation energies calculated by DFT and reported in our previous studies \(^{14-16,21}\). The following section discusses the details of DFT calculations and their applications in microkinetic modeling.

**DFT method**

Spin-polarized, periodic DFT calculations have been performed using the Vienna *Ab initio* Simulation Package (VASP) \(^{31-33}\). The exchange-correlation interaction is described by the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) \(^{34}\). The core electrons are described by the projector-augmented-wave (PAW) method \(^{35}\), and the Kohn-Sham valence states (including Mo(4p4d5s), Te(5s5p), V(3s3p3d4s), O(2s2p), and H(1s)) are expanded in plane wave basis sets up to 400 eV. The Brillouin zone is sampled at the Γ point only. Different integral spin states for each system are checked and only the lowest-energy results are reported below unless otherwise noted. For the cluster-adsorbate systems employed in this study, the ground energy state occurs in all cases with one of the lowest spins (e.g. singlet or triplet for closed-shell systems), which are usually energetically spaced within 0.1 eV.

Geometry optimization is considered converged when the force in each of the x, y, and z directions on each relaxed atom falls below 0.03 eV/Å. The adsorption energy is defined as \(\Delta E_{ads} = E_{total} - E_{cluster} - E_{adsorbate}\), where \(E_{total}\), \(E_{cluster}\), and \(E_{adsorbate}\) are the energies of the combined system (adsorbate and cluster), the cluster without the adsorbate,
and the adsorbate molecule in a neutral state (closed-shell or radical) in the gas phase, respectively.

The minimum-energy reaction paths and associated transition states are calculated using the climbing-image nudged elastic band (CI-NEB) and dimer methods. Each reaction path including the TS is constrained to stay on the same spin state as that of the ground energy state of the initial state. Vibrational frequencies are calculated in the harmonic oscillator approximation by diagonalizing the mass-weighted Hessian matrix, which is built from the calculated two-sided differences of the first derivatives of the total energy due to small geometrical perturbations (0.009 Å in each degree of freedom).

**Equilibrium constants K**

For elementary reaction

\[ A^* + B^* \rightarrow C^* + D^* \]

where * denotes a surface species, the equilibrium constant can be written as:

\[
K = e^{-\Delta G^o} = e^{-\Delta H^o + T \Delta S^o \over k_B T}
\]  

(1)

where \( k_B \) is the Boltzmann constant, \( T \) is the reaction temperature. \( \Delta G^o, \Delta H^o, \) and \( \Delta S^o \) are the standard state Gibbs energy, enthalpy, and entropy changes, respectively.

The enthalpy change can be calculated from the adsorption energies of reactants and products by DFT:

\[
\Delta H = \sum E_{ads(products)} - \sum E_{ads(reactants)} + \Delta H_{gas}
\]

(2)

where \( \Delta H_{gas} \) is the heat of reaction in the gas phase.
The standard entropy consists of three contributions, vibrational $S_{\text{vib}}$, transitional $S_{\text{trans}}$, and rotational $S_{\text{rot}}$. The vibrational contribution is calculated as:

$$S_{\text{vib}} = k_B \sum_i \left( \frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right)$$  (3)

where $x_i$ is determined for each vibrational mode using the formula:

$$x_i = \frac{h\nu_i}{k_B T}$$  (4)

where $h$ is the Planck’s constant.

For a gaseous species, the remaining entropy contributions from transitional and rotational modes can be calculated as:

$$S_{\text{trans,3D}} = k_B \left( \ln \left( \frac{(2\pi m k_B T)^{3/2}}{h^3} \right) + \ln \left( \frac{V}{N_g} \right) + \frac{5}{2} \right)$$  (5)

$$S_{\text{rot}} = k_B \left( \ln \left( \frac{8\pi^2 \sqrt{I_{x1} I_{x2} I_{x3}} (k_B T)^{3/2}}{\sigma_r h^3} \right) + 1.5 \right)$$  (6)

where $m$ is the mass of the molecule, and $V/N_g$ is the volume per molecule in the standard state. $I_{x1}, I_{x2}, I_{x3}$ are three moments of inertia about the principal axes, and $\sigma_r$ is the rotational symmetry number. For a strongly adsorbed species, the transitional and rotational modes can be replaced with vibrational modes corresponding to frustrated translation and rotation on the surface using equation (3) and (4). For a loosely adsorbed species and transition state species, it is assumed that they behave like a two-dimensional gas molecule with full rotational and vibrational modes of a three-dimensional gas molecule. Thus the translational entropy from the surface mobility can be written as:

$$S_{\text{trans,2D}} = k_B \left( \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \ln \frac{1}{c_{\text{site}}} + 2 \right)$$  (7)
**Rate constants r**

The reaction rate constants can be calculated using two different methods. The reactions involving bond breaking and formation are usually described by transition state theory, while the adsorption and desorption process can be described by collision theory.

For an elementary step represented by the transition state theory:

\[
A^* + B^* \xrightarrow{k_{for}^*} AB^* \xrightarrow{k_{rev}^*} C^* + D^* \]

where * denotes a absorbed species and ≠ denotes the transition state species.

The reaction constant \( r \) for this step can be written as:

\[
r = r_{for} - r_{rev} = k_{for} \theta_{AB^*} - k_{rev} \theta_c \theta_D \quad (8)
\]

where \( r_{for} \) and \( r_{rev} \) are forward and reverse reaction rate respectively; \( \theta \) is the surface coverage of the corresponding species. The rate constants \( k_{for} \) and \( k_{rev} \) can be related to the equilibrium constant \( K \) as:

\[
K = \frac{k_{for}}{k_{rev}} \quad (9)
\]

The forward rate constant \( k_{for} \) can be expressed as:

\[
k_{for} = A_0 e^{\frac{-E_f}{k_B T}} \quad (10)
\]

where the activation energy of forward reaction \( E_f \) can be calculated from DFT-based simulations. The frequency factor \( A_0 \) can be written as:
\[ A_0 = \frac{k_B T}{\hbar} e^{\frac{\Delta S_{for}^{\circ}}{k_B}} \]  

(11)

where \( \Delta S_{for}^{\circ} \), the standard entropy change for the formation of the transition state \( AB^\circ \) can be calculated as:

\[ \Delta S_{for}^{\circ} = S^\circ - (S_A^\circ + S_B^\circ) \]  

(12)

For the adsorption and desorption processes, the reaction rate can be calculated by collision theory as:

\[ r_f = \frac{\sigma^*(T, \theta) P_A}{\sqrt{2\pi m_A k_B T}} e^{-\frac{E_f}{k_B T}} \]  

(13)

where \( r_f \) is the rate of adsorption process. \( P_A \) is the partial pressure of the adsorbing species in the gas phase, and \( m_A \) is the molecular weight of the species. \( \sigma^*(T, \theta) \) is the sticking probability as a function of temperature \( T \) and coverage \( \theta \). Usually the adsorption processes are non-activated. Thus the activation energy term \( E_f \) is zero. The rate is in units of molecules per unit surface area per time. The surface area of an active site is calculated as 8.08x10^{-19} m^2 based on the lattice parameters of the M1 phase with \( Pba2 \) symmetry as \( a = 21.134 \) Å, \( b = 26.647 \) Å, and \( c = 4.014 \) Å and the \( ab \) plane compositions of the M1 phase as \{TeO\}_{0.86}Mo_{7.48}V_{1.52}NbO_{28}.^38

7.3 RESULTS AND DISCUSSION

The overall reaction of propane ammoxidation is described as:

\[ C_3H_8 + 2O_2 + NH_3 \rightarrow CH_2CHCN + 4H_2O \]

Therefore, the ratio of ammonia to oxygen in the feed is expected to be highly important for the conversion of propane and selectivity to acrylonitrile. The catalytic performance
of the Mo-V-Te-Nb-O M1 phase in propane ammoxidation to acrylonitrile under different experimental conditions has been reported by several groups using a plug flow reactor\textsuperscript{5,7,9,39}. Holmberg \textit{et al.} \textsuperscript{39} have investigated the catalytic behavior of the M1 phase at different reaction temperatures and ammonia/oxygen ratios in the feed. They also reported a typical selectivity to ACN as 62 mol. % reached with the as-synthesized Mo-V-Te-Nb-O catalyst\textsuperscript{5}. Grasselli \textit{et al.} \textsuperscript{40} have also reported an expected maximum value of selectivity of 59 mol. % at complete propane conversion by assuming the complete conversion of desorbed propene intermediate to acrylonitrile, which should be the upper limit of the selectivity (and yield) to acrylonitrile over the Mo-V-Te-Nb-O M1 catalyst. Also, Holmberg \textit{et al.} \textsuperscript{39} found that the selectivity to acrylonitrile passed through a maximum when the partial pressure of ammonia was increased, while the selectivity to propene increased steadily for the range of ammonia partial pressures investigated. An increase in the partial pressure of oxygen led to increasing propane conversion, while the selectivity to propene decreased. The optimal selectivity to acrylonitrile was achieved when the ratio of ammonia to oxygen was around 1:2.5, while the selectivity to combustion products (CO\textsubscript{x}) steadily increased. These results indicated that an optimal ammonia/oxygen ratio is needed to maximize the selectivity to acrylonitrile. Excess ammonia impedes the further conversion of the propene intermediate into acrylonitrile, while excess oxygen leads to unselective (combustion) products.

7.3.1 MKM parameters derived from DFT calculations

In this study, all the gas phase related parameters including entropy and enthalpy of gas phase molecules (NH\textsubscript{3}, O\textsubscript{2}, propane, propene, \pi-allyl, and H\textsubscript{2}O) were taken from NIST database\textsuperscript{41} (details can be found in Supporting Information). The ratio of Mo\textsuperscript{5+}:.
V$^{5+}$ active sites of 6.5 was based on the composition of the M1 phase {TeO}$^{0.86}$Mo$_{0.74}$V$_{1.52}$NbO$_{28}$. The results of DFT calculations (Table 3) were applied to estimate parameters for surface-adsorbed and transition-state species for the elementary steps that involve bond breaking and formation. According to the reaction conditions reported by Watanabe and Ueda $^{7}$ and our group $^{6,13,42-46}$, the reaction temperature was set at 683K and the total pressure was 1 atm. The inlet gas composition was NH$_3$:O$_2$:propane = 8.6:17.1:5.7 (balance He). These studies also reported propane conversion of 52.7% and the selectivity to propene as 15.8 mol. % under the above reaction conditions. The ratio of each gas species shown in Table 2 was calculated as the average of the each gas composition in the inlet and outlet as present in the experiment $^{7}$. The partial pressure of water vapor, which was not present in the feed (inlet gas) was calculated to be 0.00807 atm at the outlet based on the experimental oxygen conversion (57.7%). Assuming that propane is completely converted to propene and then π–allyl, followed by its conversion to acrylonitrile and CO$_x$, the selectivities to propene and π–allyl were 15.8% and 84.2%, respectively. Since the rebonding of π-allyl to surface sites was found to be nearly barrierless in our previous study $^{14,21}$, the surface bond formation between C atom in the π-allyl intermediate and the surface active site is determined entirely by the nature of the surface active site. Therefore, the selectivities to acrylonitrile and CO$_x$ were assumed to be dependent on the surface NH$_x$ and O species coverages. Therefore, the selectivity to ACN can be expressed as:

$$\text{Selectivity to ACN} = \frac{\theta_{\text{NH-M}}}{\theta_{\text{NH-M}} + \theta_{\text{O-M}} + \theta_{\text{O-V}}}$$

(14)
Table 2. The partial pressures of gas species (atm) shown was calculated as the average of the inlet and outlet pressures for each gas species in the experiment \(^7\). The total pressure is 1 atm.

<table>
<thead>
<tr>
<th></th>
<th>(\text{NH}_3)</th>
<th>(\text{O}_2)</th>
<th>(\text{Propane})</th>
<th>(\text{Propene})</th>
<th>(\text{H}_2\text{O})</th>
<th>(\pi)-allyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{atm}</td>
<td>0.070</td>
<td>0.140</td>
<td>0.049</td>
<td>0.0018</td>
<td>0.080</td>
<td>0.0052</td>
</tr>
</tbody>
</table>

The calculated forward reaction rate constants \(k_{\text{for}}\) for ammonia adsorption using collision theory \(^24\) (Table 3) was \(1.72 \times 10^9\). The reaction equilibrium constants \(K\) for this step was 7 orders of magnitude smaller than the reaction rate constants \(k_{\text{for}}\), indicating that the even a small change in the surface ammonia coverage can lead to a large change in the reaction rate. The dioxygen adsorption steps were characterized by large reaction rate constants and even larger reaction equilibrium constants indicating that this elementary step is almost irreversible and can quickly proceed to equilibrium. The formation of gas-phase water from the surface hydroxyls was a facile step displaying both zero energy barrier and exothermicity indicated by both a large forward reaction rate constant of ca. \(10^{16}\) s\(^{-1}\) and a large reaction equilibrium constant \(K\) of ca. \(10^{14}\). Moreover, it was observed in the DFT calculations that the water molecule could be quickly released once formed on the active site. Among other elementary steps involving chemical reactions, propane activation and conversion to propene were characterized by the highest activation energy and the smallest reaction rate constant. This observation is in agreement with the experimental finding that the rate-limiting step is propane conversion to propene \(^7\).
**Table 3.** Thermodynamic and kinetic parameters of DFT-based microkinetic model of propane ammoxidation over Mo-Te-Nb-O M1 phase.*

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>$k_{for}$ (s$^{-1}$)</th>
<th>$A_0$ (s$^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$(g) + *M ⇌ NH$_3$*M</td>
<td>1.72×10$^7$</td>
<td>--------</td>
<td>0</td>
<td>1.53×10$^2$</td>
</tr>
<tr>
<td>NH$_3$(g) + *V ⇌ NH$_3$*V</td>
<td>1.72×10$^7$</td>
<td>--------</td>
<td>0</td>
<td>16.8</td>
</tr>
<tr>
<td>O$_2$(g) + 2* M ⇌ 2O* M</td>
<td>2.50×10$^9$</td>
<td>--------</td>
<td>0</td>
<td>1.04×10$^{16}$</td>
</tr>
<tr>
<td>O$_2$(g) + 2* V ⇌ 2O*V</td>
<td>2.50×10$^9$</td>
<td>--------</td>
<td>0</td>
<td>1.02×10$^{12}$</td>
</tr>
<tr>
<td>NH$_3$<em>M + 2O</em>V ⇌ NH<em>M + 2OH</em>V</td>
<td>1.24×10$^4$</td>
<td>1.24×10$^4$</td>
<td>0</td>
<td>1.53×10$^3$</td>
</tr>
<tr>
<td>2OH*V →</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O(g) + O*V + *V</td>
<td>4.19×10$^{16}$</td>
<td>4.19×10$^{16}$</td>
<td>0</td>
<td>4.41×10$^{14}$</td>
</tr>
<tr>
<td>propane(g) + 2O<em>V ⇌ propene(g) + 2OH</em>V</td>
<td>7.34×10$^{-5}$</td>
<td>5.86×10$^5$</td>
<td>1.34</td>
<td>2.41×10$^3$</td>
</tr>
<tr>
<td>propene(g) + O<em>V ⇌ π-allyl(g) + OH</em>V</td>
<td>7.21</td>
<td>5.02×10$^4$</td>
<td>0.52</td>
<td>3.47×10$^{-7}$</td>
</tr>
</tbody>
</table>

* additional details are located in Supporting Information.

7.3.2 Surface species coverage

In the present microkinetic model, the coverages of surface intermediates (NH, OH, O, and NH$_3$) were calculated using the parameters and reaction network as described above. These results (Table 4) showed that the dominant species on the surface was NH*M with the coverage of 0.48 and followed by O*M with the coverage of 0.38. The
steady-state analysis of NH$_3$ at both Mo$^{5+}$ and V$^{5+}$ sites showed residuals as small as 0.9 due to their extreme sensitivity to the surface coverage of ammonia as mentioned above. Since the dioxygen adsorption is a quickly equilibrated step as compared to ammonia adsorption, oxygen can occupy all the surface V$^{5+}$ sites in competition with ammonia. Furthermore, the absence of the surface OH species indicated that water is formed and released rapidly from the surface once the surface OH species are in proximity to each other. The model output showed that NH is the most abundant surface species after ammonia activation and propane conversion to π-allyl on the surface of Mo-V-Te-Nb-O M1 phase.

Based on the assumption that the selectivity to acrylonitrile and CO$_x$ byproduct is solely dependent on the coverage of surface nitrogen and oxygen species, these results indicated that the maximum selectivity to acrylonitrile during propane ammoxidation over the Mo-V-Te-Nb-O M1 phase was estimated by equation 14 to be 49% which is close to the maximum selectivity predicted by the hypothetical probability models based on the distribution of metal cations in the multi-element active centers $^{47}$. It should be noted that the present microkinetic model is a simple model that included only the Mo$^{5+}$ and V$^{5+}$ surface active sites without considering the impact of the surface Te and Nb cations on the catalytic performance of the M1 phase in selective propane ammoxidation.
Table 4. The steady-state surface coverages of each surface species including empty Mo$^{5+}$ and V$^{5+}$ sites. *Mo denotes Mo$^{5+}$ site and *V denotes V$^{5+}$ site.

<table>
<thead>
<tr>
<th></th>
<th>V$^{5+}$</th>
<th>NH$_3$ *Mo</th>
<th>NH$_3$ *V</th>
<th>NH *Mo</th>
<th>O*Mo</th>
<th>O*V</th>
<th>OH*V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.00090</td>
<td>0.0</td>
<td>0.010</td>
<td>0.00</td>
<td>0.48</td>
<td>0.38</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.4 CONCLUSIONS

The microkinetic model based on the results of DFT calculations was constructed here to investigate the surface species coverages on Mo-V-Te-Nb-O M1 phase catalyst during propane ammoxidation and their impact on the selectivity to acrylonitrile. This model is based on a reaction mechanism consisting of 8 steps starting from the adsorption of gas-phase ammonia and oxygen on surface active site to the formation of the $\pi$-allyl intermediate. The selectivity to acrylonitrile and CO$_x$ is determined by the ratio of surface coverages of NH$_x$ to O species. The calculated reaction rate and equilibrium constants indicated that: 1) oxygen can compete with ammonia in occupying the surface active sites; 2) the formation of water from surface hydroxyls and its release are rapid steps characterized by exothermicity and a high reaction rate constant. The calculated surface species coverages supported these observations: the dominant surface species is surface imido NH at the Mo$^{5+}$ site with 0.48 coverage followed by the surface oxygen at Mo$^{5+}$ site. Therefore, acrylonitrile represents 49% of products from propane ammoxidation, which is in a reasonable agreement with experiment. Further improvements in predictive capability for propane ammoxidation over Mo-V-Te-Nb-O M1 phase are possible for more comprehensive microkinetic models that include the
surface Te and Nb sites together with the cooperation effects between different surface active sites.
REFERENCES


Chapter 8. Summary and Future work

8.1 THE MECHANISM OF PROPANE AMMOXIDATION OVER MO-V-TE-NB-O OXIDE M1 PHASE

Acrylonitrile (ACN) is an important industrial intermediate which is produced by propene ammoxidation in the SOHIO process. Recently, significant global efforts were dedicated to the development of a new catalytic process of acrylonitrile production through selective ammoxidation of propane because propane is a more abundant resource due to the increased production of natural gas. The Mo-V-Te-Nb-O mixed metal oxide displaying the 62 mol. % ACN yield is among the most active and selective catalysts investigated in propane ammoxidation. Earlier studies showed that this catalyst contains two major crystalline phases, so-called M1 and M2 phases. The M1 phase is solely responsible for propane activation and mostly responsible for the subsequent activation of the propene reaction intermediate. The proposed mechanism of propane ammoxidation over the M1 phase is described by a series of elementary reaction steps, including propane oxidative dehydrogenation (ODH), ammonia and dioxygen activation, NH₂ insertion into the π-allyl intermediate, and final ODH of the C-N coupled precursor leading to acrylonitrile. However, the current yield of ACN during propane ammoxidation over the Mo-V-Te-Nb-O catalyst needs to be improved further in order for this novel catalytic process to replace the SOHIO process. This required improvement may be realized by gaining fundamental understanding of the surface molecular structure-reactivity relationship and the mechanism of propane ammoxidation to ACN over this mixed metal oxide system, which was the major objective of this PhD thesis.
In this thesis, the locations of Nb and chemically similar Ta in the Mo-V-Te-Nb(Ta)-O M1 phase were predicted using the density functional theory (DFT) and validated experimentally for the Mo-V-Te-Ta-O M1 phase using HAADF STEM imaging \(^{14}\). Niobium and molybdenum have similar radii, atomic numbers (Z), and charges and are virtually indistinguishable by X-ray, neutron diffraction and TEM imaging techniques. Ta in the structurally similar Ta-substituted M1 phase can be easily distinguished from Mo by these techniques due to its much higher atomic number. Therefore the Ta locations in the M1 phase were first investigated by DFT to validate this theoretical methodology against the experimental (HAADF STEM) observations of Ta locations. This study demonstrated that Nb and Ta strongly preferred the pentagonal bipyramidal site S9 in the M1 phase lattice.

Density functional theory (DFT) calculations were performed to investigate the overall propane ammoxidation pathway employing the cluster models of the proposed selective and active sites present in the surface \(ab\) plane of the Mo-V-Te-Nb-O M1 phase \(^{15-17}\). The activation energies for the ODH of propane and sequentially formed intermediates (isopropyl, propene, and \(\pi\)-allyl) were calculated for different surface cation sites. Propane activation on the surface \(V^{5+}=\text{O}\) site was found to be the rate-limiting step \((E_a = 1.2 \text{ eV})\), consistent with the current proposed reaction mechanism for propane activation on the bulk mixed Mo-V-Te-Nb oxides and the current understanding of \(V^{5+}\) as the active site for alkane activation present in V-based mixed oxides.

Furthermore, a linear relationship \(^{15}\) was established between the H adsorption energy and the activation energy for H abstraction from various C3 intermediates, which is highly useful for predicting the energy barriers of H abstraction from C3 species based
solely on H adsorption energy. The energy barriers for ammonia activation on different surface sites and NH insertion into the $\pi$-allyl species were investigated and discussed in terms of the hypothetical reaction pathway reported in the literature $^{18}$. These elementary reaction steps were indicated to be nearly energetically barrier-less. As reported in Chapter 6, the formation of acrylonitrile by sequential H abstraction steps from the surface imido-allyl precursor on empty Mo sites was not found to be the rate-limiting step for propane ammoxidation over the Mo-V-Te-Nb-O M1 phase due to its lower activation energy as compared to those for propane and propene activation on the same surface Mo site.

Lastly, the overall reaction pathway was explored using a simplified microkinetic model (MKM) to predict the selectivity of propane ammoxidation to acrylonitrile on the Mo-V-Te-Nb-O M1 phase. The coverages of surface intermediates on Mo$^{5+}$ and V$^{5+}$ active sites calculated from the microkinetic model indicated that the NH species located at Mo$^{5+}$ site is the dominant species present on the surface as compared to surface O species at Mo$^{5+}$ or V$^{5+}$ site, which may explain why the M1 phase is so selective in transforming the gas-phase $\pi$-allyl intermediate into acrylonitrile as opposed to combustion products. The predicted selectivity to ACN by the simplified MKM was 49 mol. %, which is comparable to the highest ACN yield of ca. 62 mol. % observed experimentally.

This thesis represents the very first systematic theoretical study of a complete mechanism of propane ammoxidation over surface $ab$ planes of bulk mixed Mo-V-Te-Nb-O M1 phase. Improved understanding of the surface molecular structure – reactivity
relationships for propane ammoniation to acrylonitrile over this model mixed metal oxide system gained in this research may offer a possibility of not only molecular engineering of such mixed metal oxide catalysts for propane (amm)oxidation, but also fundamentally advancing the field of selective alkane (amm)oxidation over bulk mixed metal oxides.

8.2 FURTHER IMPROVEMENT OF V-BASED MIXED METAL OXIDE CATALYSTS

8.2.1 Improvement of MKM model

The microkinetic model employed in this thesis to study the entire reaction pathway of propane ammoniation over the Mo-V-Te-Nb-O M1 phase was a simplified model involving only Mo and V surface sites. It was showed in the earlier studies \(^7,19\) that introducing both Te and Nb into the Mo-V-O M1 phase can simultaneously increase the selectivity to ACN and retard decomposition of ammonia into dinitrogen, although Nb may not be directly involved in propane ammoniation and instead stabilize the M1 structure that is active in propane ammoniation \(^5,11,19\). It has also been suggested \(^20\) that the addition of Te and Nb into this catalytic system can stabilize the structure and partition the surface Mo\(^{6+}\)/Mo\(^{5+}\) and V\(^{5+}\)/V\(^{4+}\) which may explain the high activity and selectivity of the Mo-V-Te-Nb-O M1 phase as compared to the Mo-V-O M1 phase \(^7,21\). Moreover, it was shown that the presence of surface V\(^{5+}\) is essential for propane activation, while excessively high concentration of V\(^{5+}\) on the surface may lead to overoxidation of propane predicted by the elemental distribution analysis based on so-called probability models \(^22\). Therefore, including the effect of the addition of both Te and Nb surface sites on modifying the partition of surface V and Mo sites in future
microkinetic models is expected to yield improved predictive models of the ACN selectivity and provide new useful insights for the molecular engineering of Mo-V-Te-Nb-O mixed metal oxides by optimizing the surface V$^{5+}$ concentration in order to achieve higher ACN yield.

The MKM model described in this thesis was based on a simplified reaction network which explicitly included all elementary steps up to the formation of π-allyl intermediate, where it was further assumed that the final distribution of selective (ACN) and unselective products (CO$_x$) was determined by the ratio of the surface coverage of NH and O species. Future, more accurate model may include also the elementary steps that follow the formation of π-allyl on the surface, i.e., imido insertion into the π-allyl followed by the sequential H abstraction from the imido-allyl precursor to the final formation of can, and oxygen insertion into π-allyl followed by the sequential oxidative dehydrogenation of the π-allyl leading to the unselective products (CO$_x$). These improve models are also expected to provide new insights into the role of the unselective pathway that involves ACN combustion.

8.2.2 Role of M2 phase in propane ammoxidation over Mo-V-Te-Nb-O oxides

As mentioned earlier, the bulk Mo-V-Te-Nb-O oxides also contain another major phase, so-called pseudo-hexagonal M2$^{23,24}$. The M2 phase is an orthorhombically distorted hexagonal tungsten bronze (HTB) type structure with an overall composition of Mo$_{4.31}$V$_{1.36}$Nb$_{0.33}$Te$_{1.81}$O$_{10.81}$$^{12,23,24}$ (Figure 1). Recent studies of the M2 phase employing high resolution STEM (scanning transmission electron microscopy), synchrotron X-ray, and powder neutron diffraction methods, have shown that V, Mo, and Te are present in the 4+, 5+/6+ and 4+ oxidation states, respectively$^{25}$. 
Previously, a synergy effect between M1 and M2 phases during propane ammoxidation over the Mo-V-Te-Nb-O catalysts has been proposed \(^{23}\) by showing that a mixture of M1 and M2 phases can increase the activity and selectivity of these catalysts. However, recent studies \(^{11,13}\) suggested the absence of the synergy effect between the M1 and M2 phases indicating that the M1 phase is alone active and selective in propane ammoxidation to ACN. The lack of \(V^{5+}\) sites in the M2 phase was proposed to be responsible for the lack of its ability to activate propane. Therefore, future theoretical studies of surface reactivity should focus on establishing the role played by the M2 phase in the propane ammoxidation over Mo-V-Te-Nb-O catalysts guided by the insights gained in this thesis about the roles of various surface cation sites present in the M1 phase.

8.2.3 Propane oxidation to acrylic acid over Mo-V-Te-Nb-O catalysts

The Mo-V-Te-Nb-O catalysts have been shown not only to be capable of propane ammoxidation to acrylonitrile, but also selective propane oxidation to acrylic acid. The proposed mechanism is similar to that for propane ammoxidation with the same active
centers of the M1 phase except that after the formation of π-allyl from the ODH of propane, surface O is inserted into the π-allyl intermediate instead of surface NH$_4$. The acrolein intermediate formed in this step can be either desorbed as a byproduct or become further oxidized by the surface O sites into acrylic acid. Therefore, the fundamental insights obtained in this thesis about the catalytic roles played by various metal cations and the ODH steps involving the C3 species provide a robust reference frame for future theoretical studies of propane oxidation to acrylic acid over the Mo-V-Te-Nb-O catalysts.
REFERENCE

(1) American Chemical Society National Historic Chemical Landmarks. Sohio Acrylonitrile Process


### SUPPLEMENTAL MATERIALS FOR CHAPTER 7

Table S.1. Vibrational frequencies for surface transition state (TS) species on surface Mo and V$^{5+}$ sites based on DFT calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Mo site</th>
<th>V$^{5+}$ site</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ (TS)</td>
<td>3479.81982, 3388.49432, 1508.57827, 1399.74376, 1273.87755, 904.449466, 833.338128, 760.338454, 728.201395, 441.722222, 392.673261, 207.190602, 202.95146</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane (TS)</td>
<td>3053.29209, 3046.75344, 3033.4064, 2995.5, 2993.44, 2902.07, 2898.4, 1439.3, 1429.36, 1423.57, 1416.71, 1350.42, 1349.01, 1319.14, 1162.72, 1144.99, 1122.84, 1016.51, 949.216, 904.575, 895.278, 876.52, 772.355, 684.194, 400.882, 317.321, 261.327, 225.95, 175.582, 166.339, 104.623, 78.9158, 47.103, 36.7778</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S.2. Adsorption energy $\Delta E_{ad}$ (eV) for each surface species at Mo (denoted by *M) and $V^{5+}$ site (denoted by *V) over Mo-Te-Nb-O M1 phase based on the DFT calculations.

<table>
<thead>
<tr>
<th>NH$_3$*M</th>
<th>NH$_3$*V</th>
<th>NH$_2$*M</th>
<th>NH*M</th>
<th>O*M</th>
<th>O*V</th>
<th>OH*V</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.97</td>
<td>-0.84</td>
<td>-1.52</td>
<td>-4.03</td>
<td>-2.59</td>
<td>-2.05</td>
<td>-0.682</td>
</tr>
</tbody>
</table>
Table S.3. Entropy and gas phase formation enthalpy of each surface species over Mo-Te-Nb-O M1 phase at reaction temperature $T = 683K$ derived from the DFT calculations.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>$S^\circ$ (J/K/mol)$^b$</th>
<th>$\Delta H^\circ_f$ (kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NH_3^*M$</td>
<td>131.1</td>
<td>-29.9</td>
</tr>
<tr>
<td>$NH_3^*V$</td>
<td>131.1</td>
<td></td>
</tr>
<tr>
<td>$NH^*M$</td>
<td>116.4</td>
<td>50.4</td>
</tr>
<tr>
<td>$O^*M$</td>
<td>85.3</td>
<td>249</td>
</tr>
<tr>
<td>$O^*V$</td>
<td>85.3</td>
<td></td>
</tr>
<tr>
<td>$OH^*V$</td>
<td>118.3</td>
<td>50.4</td>
</tr>
<tr>
<td>$C_3H_7-H-O^*V$ (TS)</td>
<td>300.1</td>
<td></td>
</tr>
<tr>
<td>$C_3H_6-H-O^*V$ (TS)</td>
<td>264.5</td>
<td></td>
</tr>
<tr>
<td>$M^*NH_2-H-O^*V$ (TS)</td>
<td>104.7</td>
<td></td>
</tr>
<tr>
<td>$H_2O$ (g)</td>
<td></td>
<td>-228</td>
</tr>
<tr>
<td>propane (g)</td>
<td></td>
<td>-105</td>
</tr>
<tr>
<td>propene (g)</td>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td>$\pi$-allyl (g)</td>
<td></td>
<td>171</td>
</tr>
</tbody>
</table>

a. The thermodynamic parameters for gas phase species are from NIST database.

b. Entropy of surface stable species is calculated using the empirical relationship from Campbell et al. [1] as $S_{ads} = 0.7 S_{gas} - 3.3 R$ where $R$ is the gas constant.
Table S.4. Kinetic parameters used in MKM for propane ammoxidation over Mo-Te-Nb-O M1 phase at reaction temperature T = 683K derived from the DFT calculations.

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>$k_{fo}(s^{-1})$</th>
<th>$\Delta S^\circ$ (J/K/mol)</th>
<th>$E_a$ (eV)</th>
<th>$A_0$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$(g) + *M $\rightleftharpoons$ NH$_3$*M</td>
<td>1.72×10$^9$</td>
<td>---------------------</td>
<td>0</td>
<td>-----------------</td>
</tr>
<tr>
<td>NH$_3$(g) + *V $\rightleftharpoons$ NH$_3$*V</td>
<td>1.72×10$^9$</td>
<td>---------------------</td>
<td>0</td>
<td>-----------------</td>
</tr>
<tr>
<td>O$_2$(g) + 2* M $\rightleftharpoons$ 20*M</td>
<td>2.50×10$^9$</td>
<td>---------------------</td>
<td>0</td>
<td>-----------------</td>
</tr>
<tr>
<td>O$_2$(g) + 2* V $\rightleftharpoons$ 2O*V</td>
<td>2.50×10$^9$</td>
<td>---------------------</td>
<td>0</td>
<td>-----------------</td>
</tr>
<tr>
<td>NH$_3$<em>M + 2O</em>V $\rightleftharpoons$ NH<em>M + 2OH</em>V</td>
<td>1.24×10$^4$</td>
<td>-173.5</td>
<td>0</td>
<td>1.24×10$^4$</td>
</tr>
<tr>
<td>$2OH<em>V \rightleftharpoons$ H$_2$O(g) + O</em>V + *V</td>
<td>4.19×10$^{16}$</td>
<td>---------------------</td>
<td>0</td>
<td>4.19×10$^{16}$</td>
</tr>
<tr>
<td>propane(g) + 2O<em>V $\rightleftharpoons$ propene(g) + 2OH</em>V</td>
<td>7.34×10$^{-5}$</td>
<td>-141.5</td>
<td>1.34</td>
<td>5.86×10$^5$</td>
</tr>
<tr>
<td>propene(g) + O<em>V $\rightleftharpoons$ $\pi$-allyl(g) + OH</em>V</td>
<td>7.21</td>
<td>-162.0</td>
<td>0.52</td>
<td>5.02×10$^4$</td>
</tr>
</tbody>
</table>
Table S.5. Thermodynamic parameters used in MKM for propane ammoxidation over Mo-Te-Nb-O M1 phase at reaction temperature T = 683K derived from the DFT calculations.

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>$\Delta S^\circ$ (J/K/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3(g) + <em>M \rightleftharpoons \text{NH}_3</em>M$</td>
<td>-95.4</td>
<td>-93.6</td>
<td>$1.53 \times 10^2$</td>
</tr>
<tr>
<td>$\text{NH}_3(g) + <em>V \rightleftharpoons \text{NH}_3</em>V$</td>
<td>-95.4</td>
<td>-81.0</td>
<td>16.8</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 2* M \rightleftharpoons 2\text{O}^*M$</td>
<td>-60.0</td>
<td>-250.0</td>
<td>$1.04 \times 10^{16}$</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 2* V \rightleftharpoons 2\text{O}^*V$</td>
<td>-60.0</td>
<td>-197.7</td>
<td>$1.02 \times 10^{12}$</td>
</tr>
<tr>
<td>$\text{NH}_3*M + 2\text{O}^*V \rightleftharpoons \text{NH}^*M + 2\text{OH}^*V$</td>
<td>-44.2</td>
<td>-11.5</td>
<td>$1.53 \times 10^3$</td>
</tr>
<tr>
<td>$2\text{OH}^*V \rightleftharpoons \text{H}_2\text{O}(g) + \text{O}^*V + *V$</td>
<td>66.4</td>
<td>-145.9</td>
<td>$4.41 \times 10^{14}$</td>
</tr>
<tr>
<td>$\text{propane}(g) + 2\text{O}^*V \rightleftharpoons \text{propene}(g) + 2\text{OH}^*V$</td>
<td>50.8</td>
<td>-9.52</td>
<td>$2.41 \times 10^3$</td>
</tr>
<tr>
<td>$\text{propene}(g) + \text{O}^*V \rightleftharpoons \pi\text{-allyl}(g) + \text{OH}^*V$</td>
<td>23.9</td>
<td>84.3</td>
<td>$3.47 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Appendix A1
Matlab code for solving steady-state differential equations:

**main.m:**
%main solver
clear all;
aeq = [1 -6.5 1 -6.5 1 1 -6.5 -6.5; 1 1 1 1 1 1 1 1];
bq = [0:1];
ub=[1 1 1 1 1 1 1 1 ];
lb = [0 0 0.01 0 0.01 0 0 0];
% output: x: 1theta*M,2theta*V, 3theta_NH3*M,4theta_NH3*V,
% 5theta_NH*M,6theta_O*M,7theta_O*V, 8theta_OH*V,

fvalBest = 5000;
xBest = 0;
outputBest = 0;

options = optimset('MaxFunEvals',1e10,...
  'Maxiter', 1000,...
  'TolX', 1e-11,...
  'TolCon', 1e-11,...
  'Algorithm','trust-region-reflective');
% 'Algorithm', 'interior-point')

warning('off','all')
for itr = 1:5000
    x0 = rand(1,8);
    x0(3) = 0.3;
    x0(5) = 0.3;
    x0 = x0 / sum(x0);

    [x,fval,EXITFLAG,output,LAMBDA,GRAD,HESSIAN]=fmincon(@rate,x0,[],[],aeq,bq,lb,ub,[],options);
    if(fval < fvalBest)
        disp('Found Best solution!')
        disp(fval)
        disp(x)
        fvalBest = fval
        xBest = x;
        outputBest = output;
        figure(1);
        bar(xBest)
        title(fvalBest)
    end
end
%
figure(1);
bar(xBest)
title(fvalBest)

%-------------

rate.m:
function F = rate(x)
% #a = c(1:8) # k_i
ak = [1.72E9,1.72E9,2.50E9,2.50E9,1.24E4,4.19E16,7.34E-5,7.21];
% #b = c(1:8) #K_i
bk = [1.53E2,1.68E1,1.04E16,1.02E12,1.53E3,4.14E14,2.411E3,3.47E-7];
% #c = c(1:7) #P: 1NH3, 2O2, 3P0, 4propane, 5propene,6 H2O,7allyl
cgas = [0.07,0.14,1,0.0488,0.00183,0.08,0.0052];

% # real model
rate = 1:8;
rate(1) = ak(1) * (cgas(1) / cgas(3)) * x(1) - (ak(1) / bk(1)) * x(3);
r(2) = ak(2) * (cgas(1) / cgas(3)) * x(2) - (ak(2) / bk(2)) * x(4);
r(3) = ak(3) * (cgas(2) / cgas(3)) * x(1)^2 - (ak(3) / bk(3)) * x(6)^2;
r(4) = ak(4) * (cgas(2) / cgas(3)) * x(2)^2 - (ak(4) / bk(4)) * x(7)^2;
r(5) = ak(5) * x(3) * x(7)^2 - (ak(5) / bk(5)) * x(5) * (x(8))^2;
r(6) = ak(6) * x(8)^2 - (ak(6) / bk(6)) * (cgas(6) / cgas(3)) * x(2) * x(8);
r(7) = ak(7) * (cgas(4) / cgas(3)) * x(7)^2 - (ak(7) / bk(7)) * (cgas(5) / cgas(3)) * x(8)^2;
r(8) = ak(8) * (cgas(5) / cgas(3)) * x(7) - (ak(8)/bk(8)) * (cgas(7) / cgas(3)) * x(8);

f1 = rate(2); % dx[4] NH3*V
f2 = rate(1)-rate(5); % dx[3] NH3*M
f3 = rate(5); % dx[5] NH*M
f4 = rate(3); % dx[6] O*M
f5 = 2*rate(4) - 2*rate(5) + rate(6) - 2*rate(7)-rate(8); % dx[7] O*V
f6 = 2*rate(5) - 2*rate(6) + 2*rate(7) + rate(8); % dx[8] OH*V
fvec = [f1,f2,f3,f4,f5,f6];
F = sum(abs(fvec));
end