#### NORTHWESTERN UNIVERSITY

## The Effect of Reducible Metal Oxides on the Structure and Activity of Supported Vanadium

Oxide Catalysts Prepared by Atomic Layer Deposition for Cyclohexane Oxidative

Dehydrogenation

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# Abstract

Supported vanadium oxide materials have been extensively studied for alkane oxidative dehydrogenation (ODH) reactions due to their high activity and selectivity. The catalytic activity of supported VO<sub>x</sub> materials is influenced by the surface coverage of VO<sub>x</sub> sites and hence the distribution of V=O, V-O-V, and V-O-S (S, support) bonds. The impact of the type of V-O-S bonds is often investigated by varying the bulk oxide support and it is known that the activity of these catalysts is highly dependent on the nature of the support material. This dissertation seeks to develop a fundamental understanding of the contribution of reducible supports to the activity of VO<sub>x</sub> species in cyclohexane ODH as a model reaction of ODH of alkanes.

The first part of this thesis focuses on investigating the interactions of VO<sub>x</sub> species with amorphous TiO<sub>2</sub> domains deposited by atomic layer deposition (ALD) on an inert Al<sub>2</sub>O<sub>3</sub> support. A combination of ALD and calcination procedures is shown to influence the surface site distribution. Preferential binding of VO<sub>x</sub> and TiO<sub>2</sub> domains to each other on an Al<sub>2</sub>O<sub>3</sub> support is demonstrated by UV Raman spectroscopy and confirmed by DFT. Varying distributions of V-O-V, V-O-Ti and V-O-Al bonds have an effect on the ease of reducibility of VO<sub>x</sub> sites. The interactions of VO<sub>x</sub> and TiO<sub>2</sub> species are elucidated further under a reducing H<sub>2</sub> environment at elevated temperatures. Reversible migration and aggregation of V and Ti atoms is detected upon heating in H<sub>2</sub>. Changes in the oxidation state of V, but not Ti, are observed by XPS. The elucidation of VO<sub>x</sub> and TiO<sub>2</sub> speciation on the Al<sub>2</sub>O<sub>3</sub> support in their oxidized state and upon reduction facilitates the understanding of the function of individual sites in catalytic reactions relying on a redox mechanism.

The second part of this thesis investigates the catalytic activities of alumina-supported VO<sub>x</sub>-TiO<sub>2</sub> materials in comparison with VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/TiO<sub>2</sub> to determine the role the TiO<sub>2</sub> support plays in the improvement of ODH activity of surface VO<sub>x</sub> sites in comparison to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The ease of reducibility of VO<sub>x</sub> species cannot exhaustively explain the observed variability in ODH activity. The increased activity of VO<sub>x</sub> supported on TiO<sub>2</sub> films above a monolayer TiO<sub>2</sub> coverage is attributed to the formation of oxygen vacancies within the TiO<sub>2</sub> structure. The use of ALD in the synthesis of mixed metal oxide materials enables the distinction between the contribution of V-O-Ti bonds and that of the bulk TiO<sub>2</sub> structure to the catalytic activity of supported VO<sub>x</sub> domains. However, while the catalytic activity is dependent on the composition of the support, the selectivity-conversion trends remain unchanged.

Finally, the study of alumina-supported mixed metal oxides is extended to catalytically active CeO<sub>2</sub>. The individual contributions of VO<sub>x</sub> and CeO<sub>2</sub> sites to the cyclohexane ODH reaction mechanism are evaluated by studying CeO<sub>2</sub>, VO<sub>x</sub>/CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> modified with CeO<sub>2</sub> and VO<sub>x</sub> domains by ALD. The bare ceria support shows the highest activity and favored total oxidation to CO<sub>2</sub>. The catalytic behavior is dependent on the distribution of V-O-S bonds, and small clusters of CeO<sub>2</sub> at low surface densities favor total oxidation similarly to exposed CeO<sub>2</sub> surface sites in  $VO_x/CeO_2$ .

The extensive study of the influence of reducible metal oxide domains on the structure and catalytic activity of supported  $VO_x$  sites and the resulting assignment of specific catalytic functions to individual surface structures can lead to the rational design of alkane ODH catalysts with improved alkene yields.

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# **1** Introduction

#### **1.1 Supported Vanadium Oxide Catalysts**

Vanadium oxide, among other transition metal oxides, was early identified as an oxidation catalyst due to its ability to readily modify its electronic configuration.<sup>1</sup> In the 1920s, V<sub>2</sub>O<sub>5</sub> gained interest for its activity towards the transformation of aromatic hydrocarbons, specifically the conversion of naphthalene to phthalic anhydride and benzene to maleic acid.<sup>2-3</sup> Kinetic studies performed by Mars and van Krevelen in the 1950s revealed that surface oxygen participates in oxidation reactions catalyzed by V<sub>2</sub>O<sub>5</sub>. A relationship between the reaction rate and reactant partial pressures was derived based on oxidation of aromatics, and it was extended to the oxidation of SO<sub>2</sub>.<sup>4</sup> In the 1970s, researchers began to study V<sub>2</sub>O<sub>5</sub> dispersed on high surface area supports in order to improve catalytic activity. Shibata et al. reported that there exists an optimum amount of the surface vanadium oxide active sites in their study of SO<sub>2</sub> oxidation.<sup>5</sup> The concept of monolayer coverage was introduced by Wachs et al. in 1985 for a V2O5/TiO2 catalyst in o-xylene oxidation to phthalic anhydride. In this work, surface vanadium oxide species were distinguished from crystalline V<sub>2</sub>O<sub>5</sub> with the use of Raman spectroscopy. The latter was reported to form above a monolayer coverage and exhibit lower catalytic activity.<sup>6</sup> Vanadium oxide has been since dispersed on a variety of different oxide supports and the catalytic activity of the resulting material has been found to depend on the nature of the supporting oxide.<sup>7-9</sup> On an industrial scale, vanadium oxide catalysts are currently used in the manufacture of chemicals (oxidation of SO<sub>2</sub> to SO<sub>3</sub> in the production of sulfuric acid and naphthalene oxidation to phthalic anhydride) and in the reduction of pollution (selective reduction of NO<sub>x</sub> with NH<sub>3</sub>).<sup>7</sup>

Supported VO<sub>x</sub> species are chemically and electronically distinct from bulk V<sub>2</sub>O<sub>5</sub>. Due to the lower surface free energy of supported vanadium oxide species in comparison to physical mixtures of V<sub>2</sub>O<sub>5</sub> with the support, the former spontaneously form on the surface of oxide supports.<sup>8</sup> The preparation method and post-synthesis treatment can affect the dispersion of surface VO<sub>x</sub> sites. Different amounts of residual V<sub>2</sub>O<sub>5</sub> have been reported on the surface of a titania support following grafting with VOCl<sub>3</sub> and wet impregnation with vanadium oxalate.<sup>10</sup> Impregnation generally offers limited control over the speciation and dispersion of surface VO<sub>x</sub>. Aqueous phase synthesis methods with regulated pH provide control over the speciation of molecular V in solution. However, the pH changes during the drying procedure, which may lead to polymerization of VO<sub>x</sub> sites.<sup>9</sup> Furthermore, the structure of the catalyst is highly dependent on the calcination temperature. Mixed oxide phases can form between vanadium oxide and the oxide support at sufficiently high temperatures.<sup>11</sup> An illustration of the possible binding modes of VO<sub>x</sub> to the surface is shown in Figure 1.1.



**Figure 1.1.** Possible binding modes of  $VO_x$  species to the surface of the support including molecular (A), monodentate (B), bidentate (C), tridentate (D) and polymeric (E) sites.

Supported VO<sub>x</sub> sites have been studied with a number of different characterization techniques to improve the understanding of their surface speciation. UV-vis and Raman spectroscopy reveal the presence of isolated and oligomeric surface sites and indicate that the fraction of the latter increases with increasing vanadium loading. V<sub>2</sub>O<sub>5</sub> nanoparticles exhibit different catalytic properties than dispersed VO<sub>x</sub> species and can be easily distinguished by the presence of a sharp Raman band at 995 cm<sup>-1</sup>.<sup>8, 12</sup> The number of V-O-V bonds, and hence the average size of VO<sub>x</sub> clusters, has been previously correlated with the edge energy calculated from UV-vis absorption data.<sup>13</sup> Monomeric and oligomeric VO<sub>x</sub> species can be further distinguished from highly polymerized surface structures by applying a multiwavelength excitation approach in Raman spectroscopy. UV Raman enhances the signal from isolated and less polymerized VO<sub>x</sub> species, while visible Raman is more sensitive to highly polymerized VO<sub>x</sub>.<sup>12</sup> It is difficult to distinguish between V-O-V and various V-

O-S (S, Support) bonds. However, IR and Raman spectroscopy studies as well as <sup>18</sup>O labeling experiments have previously indicated that a single terminal V=O bond is present in VO<sub>x</sub> sites.<sup>14-</sup> <sup>15</sup> Additionally, XANES and solid-state <sup>51</sup>V NMR studies demonstrate that, following dehydration,  $VO_x$  species are present in the V<sup>5+</sup> state and a VO<sub>4</sub> coordination.<sup>8, 16-18</sup> Density functional theory (DFT) calculations have been applied to study the structures and relative stability of monomeric and polymeric VO<sub>x</sub> species on oxide supports.<sup>19-20</sup> In-situ reduction experiments under H<sub>2</sub> have been carried out to distinguish the ease of reducibility of different VO<sub>x</sub> species, which is a probe of their reactivity in reactions following a redox mechanism.<sup>21-23</sup> Polyvanadates and V<sub>2</sub>O<sub>5</sub> have been found to be more easily reducible than monovanadate species, and within the latter the following reducibility trend has been reported: bidentate > molecular > tridentate.<sup>24-25</sup> Spectroscopic characterization methods have also been used to study supported vanadium oxide catalysts under reaction conditions, which allows to assign changes at the molecular scale directly to catalytic activity and selectivity.<sup>26-31</sup> Chapter 2 of this thesis describes in detail how information from different spectroscopic techniques and DFT calculations can complement each other to form a comprehensive description of VO<sub>x</sub> surface speciation.

#### **1.2 Atomic Layer Deposition of Supported Metal Oxide Catalysts**

Atomic layer deposition (ALD) offers angstrom-level control during catalyst synthesis, making it possible to achieve well-defined complex structures of oxide catalysts on high surface area supports.<sup>32-36</sup> The ALD process relies on a sequence of self-limiting reactions, the simplest of which can be described as an AB-type, where reaction A involves the discrete pulsing of a high vapor pressure metal precursor whose ligands partially react with surface hydroxyl groups of a support, and reaction B introduces an oxidizing or reducing agent to remove remaining ligands

and regenerate surface active sites.<sup>32, 37-38</sup> An example process of depositing metal oxide species on the surface of an oxide support is depicted in Scheme 1.1. This reaction sequence can be further modified to include multiple precursors and create materials with different functionalities.<sup>39-40</sup>



**Scheme 1.1.** An ALD process involving the deposition of a metal oxide species in a binary AB reaction sequence.

The precise control of oxide film thickness attainable by ALD enables the simultaneous monitoring of structural changes and their corresponding catalytic functions. The distribution of the initial isolated metal oxide species can be controlled by the bulkiness of the precursor ligands, the density of active sites on the support surface and the introduction of blocking agents prior to deposition. The lack of solvent use in the ALD process prevents aggregation of metal oxide sites during deposition. Variations in the number of reaction cycles can further modify the distribution of surface species below a monolayer coverage as well as provide information about the thickness of metal oxide films, which begin to exhibit bulk properties.<sup>32, 41-44</sup>

The use of ALD in the synthesis of supported  $VO_x$  materials has previously enabled the formation of a more homogeneous distribution of catalytically active surface sites. Stronger interactions with the support and more acidic character of  $VO_x$  species grown by ALD in comparison to impregnated materials have been reported both in VO<sub>x</sub> supported on bulk oxides as well as on TiO<sub>2</sub>-modified SiO<sub>2</sub>.<sup>45-47</sup> Additionally, VO<sub>x</sub> species grown by ALD have shown superior catalytic activity in alkane dehydrogenation reactions in comparison with conventionally impregnated catalysts.<sup>45, 48</sup> The enhanced activity of VO<sub>x</sub> supported on anodic aluminum oxide in cyclohexane oxidative dehydrogenation (ODH) has been assigned to the improved dispersion of catalytically active sites achieved by ALD, where V-O-V bonds are not expected to form following a single ALD cycle.<sup>48-49</sup> Additionally, ALD synthesis of well-defined VO<sub>x</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> has enabled the elucidation of the reaction mechanism of methanol oxidation to formate.<sup>29</sup> This thesis aims to show how ALD can be used to create mixed metal oxide catalysts with varying distributions of surface sites in an atomically precise manner and, as a result, enable the differentiation between the catalytic contribution of the bonds VO<sub>x</sub> domains form with an oxide support and the support itself.

#### **1.3 Alkane Oxidative Dehydrogenation**

Oxidative dehydrogenation is a thermodynamically favorable route from alkanes to alkenes. It requires lower temperatures than steam cracking or dehydrogenation, which limits the formation of coke. The reaction is exothermic and hence does not require an external heat supply. The presence of oxygen in the feed stream can prevent catalyst deactivation. However, the reaction mixture is flammable and the thermodynamically favored products are CO<sub>2</sub> and CO.<sup>50</sup> Studies of propane ODH have been motivated by a growing gap between the demand for propene and its supply from steam cracking.<sup>51</sup> Propene is an important intermediate in a number of chemical processes including the manufacture of polymers such as polypropylene and polyurethane and other materials including acrylonitrile, propene oxide and isopropanol.<sup>52</sup> One of the industrial processes for the on-purpose production of propene is propane (non-oxidative) dehydrogenation.

The technologies with the most installations worldwide are Catofin (Lummus) and Oleflex (UOP). The Catofin process utilizes an alumina-supported  $CrO_x$  catalyst, which is regenerated by combustion of coke, and the regeneration process provides part of the heat required for the dehydrogenation reactors operating in parallel. The Oleflex process uses a Pt-Sn-based catalyst on alumina in a fluidized bed reactor, where the gases are preheated prior to being in contact with the catalyst. The catalyst is regenerated by combustion of coke and redispersion of Pt by a chlorine-air mixture. The lifetime of the catalytic materials in both processes is up to three years.<sup>53</sup> While the introduction of oxygen to the feed stream could prevent catalyst deactivation and lower the required energy use, the alkene yields from ODH reactions are not yet sufficient to be economically profitable.<sup>9</sup> This provides an opportunity for the rational design of catalysts that limit the undesirable consecutive and parallel total oxidation reactions.

The alkane ODH reaction mechanism has been reviewed for reactants including ethane, propane, butane, isobutane and cyclohexane.<sup>9, 54-55</sup> It is generally accepted that the reaction follows a mechanism described by Mars and van Krevelen, where the reactive oxygen is supplied by the catalyst surface lattice and the catalyst is reoxidized by gas-phase O<sub>2</sub>.<sup>4</sup> The rate limiting step has been identified as C-H bond breaking. This is supported by the fact that the reaction is first order with respect to the alkane partial pressure and zero order with respect to oxygen partial pressure, as well as kinetic isotope exchange experiments.<sup>9, 54-56</sup> The lower energy of secondary C-H bonds in comparison to primary ones leads to the higher reactivity of butane and cyclohexane in comparison with lighter alkanes due to the increased probability of a secondary carbon adsorbing to the catalyst surface.<sup>54</sup> The energy of an allylic C-H bond is significantly lower than either the primary or secondary C-H, which means the resulting alkene is more reactive than the initial

alkane, leading to undesired over-oxidation reactions.<sup>54</sup> CO<sub>x</sub> products can form directly from the alkane or through consecutive reaction pathways. In light alkane ODH reactions, the formation of CO<sub>x</sub> species is a result of breaking multiple C-H bonds. In contrast, the reaction network of cyclohexane ODH is more diverse, as shown in Scheme 1.2. Benzene is formed by breaking multiple C-H bonds, but the formation of CO<sub>x</sub> requires breaking multiple C-H bonds on a single methylene group, C-C scission, O insertion or a radical pathway.<sup>48</sup> The C-H bond strength of benzene is significantly higher than those in cyclohexane or cyclohexene, which results in the termination of consecutive over-oxidation at the aromatic.<sup>57</sup>



Scheme 1.2. Cyclohexane ODH reaction network.

Supported vanadium oxide catalysts have been extensively studied for alkane ODH reactions due to their high activity and selectivity. The contribution of individual VO<sub>x</sub> surface structures to the reaction mechanism has been under debate. A number of studies suggest that the relative amount of monomeric and polymeric vanadium oxide surface species does not affect ODH activity.<sup>9, 58-61</sup> However, reports of both decreasing and increasing alkane ODH activity as a function of V loading have also been published.<sup>48, 62-63</sup> It has been postulated that, at similar V loadings, the alkane

consumption rate is dependent on the method of catalyst preparation. Enhanced catalytic activity has been reported for VO<sub>x</sub>/SiO<sub>2</sub> prepared with the use of surface organometallic chemistry in comparison to incipient wetness impregnation due to differences in the chemical environment of VO<sub>x</sub> sites.<sup>18</sup> However, at similar edge energies calculated from UV-vis absorption spectra, equivalent conversions were reported for VO<sub>x</sub> prepared by ALD and wetness impregnation. In this study, the reaction rate changed significantly from a material prepared by a single ALD cycle of VO<sub>x</sub> to one prepared with 4 ALD cycles, but remained constant between 4 and 12 cycles.<sup>48</sup> The rate dependence on preparation method and the precursor used during catalyst synthesis has been previously assigned to the possibility of forming V<sub>2</sub>O<sub>5</sub> nanoparticles. It was postulated that changes in ODH activity are only observed for materials synthesized with precursors that can lead to the formation of V<sub>2</sub>O<sub>5</sub>, whereas in the absence of V<sub>2</sub>O<sub>5</sub> the rates are independent of VO<sub>x</sub> domain size.<sup>61</sup> In addition, the ease of reducibility of  $VO_x$  has been reported to depend on the structure of a VO<sub>x</sub> monomer, which indicates that different monomeric species could potentially exhibit varying ODH activity.<sup>25</sup> Based on this lack of agreement within the literature, it is difficult to assign the specific catalytic function of V=O and V-O-V bonds, especially because the existence of the latter cannot be definitively excluded even in low V loading materials.

The role of specific bonding motifs for supported vanadia catalysts in reaction mechanisms where the rate determining step is the activation of a C-H bond has been studied by DFT. In a model system of a VO<sub>x</sub> monomer on a silica support, the first H abstraction was reported to occur on the V=O group both in propane ODH and methanol oxidation.<sup>64-65</sup> The second hydrogen abstraction in propane ODH, however, can also occur at the bridging V-O-Si sites. Additionally, it was found that higher activity can be achieved if the second H abstraction occurs at a different VO<sub>x</sub> monomer,

which did not previously participate in the reaction.<sup>64</sup> The ODH reaction rate was found to increase with increasing  $VO_x$  domain size on a silica support. However, the differences in activation barriers were within uncertainty limits. Additionally, it was shown that the size distribution of  $VO_x$ species at sub-monolayer coverage on silica is statistical with a limited number of oligomers, which was considered to be consistent with experimental results on the lack of variation in reaction rate with VO<sub>x</sub> domain size.<sup>20</sup> In contrast, studies of methanol oxidation on VO<sub>x</sub>/CeO<sub>2</sub> indicate that, on monomeric  $VO_x$  sites, C-H bond activation occurs at the V-O-Ce site and that the reactivity decreases with increasing VO<sub>x</sub> domain size, based on higher oxygen defect formation energies.<sup>66-</sup> <sup>67</sup> Furthermore, it has been postulated that the increased ODH activity of VO<sub>x</sub>/CeO<sub>2</sub> is due to a synergy between the oxide support and the supported oxide, where two electrons are accommodated in the Ce f states, resulting in the reduction of the support during the reaction mechanism and the monomeric VO<sub>x</sub> species remain fully oxidized.<sup>68-69</sup> Similarly, in anatasesupported vanadium oxide, dissociative adsorption of methanol was reported to occur on the V-O-Ti bonds and the rate limiting step involved the transfer of an H atom to the O atom in a Ti-O-Ti bond adjacent to the VO<sub>x</sub> monomer. The two electrons are transferred into subsurface Ti d states, implying the participation of the reducible support surface in the reaction mechanism.<sup>70-71</sup>

Experimentally, an improved understanding of the contribution of different V-O-S bonds to a reaction mechanism can be achieved by studying ternary metal oxide systems. Catalytic materials where VO<sub>x</sub> species are deposited on titania-modified silica supports have been previously investigated for ODH reactions.<sup>72-75</sup> The dispersion of VO<sub>x</sub> species is known to improve in the presence of sub-monolayer domains of an oxide less reducible than vanadia, but more reducible than the support.<sup>72, 76</sup> Dai *et al.* hypothesized that the deposition of MoO<sub>x</sub> domains on alumina

prior to that of VO<sub>x</sub> species introduces V-O-Mo bonds in place of V-O-Al ones, improving the reducibility and, as a result, the propane ODH activity of surface VO<sub>x</sub> species.<sup>76</sup> Further, Hamilton *et al.* have shown that the ODH activity of VO<sub>x</sub> supported on silica modified with sub-monolayer TiO<sub>2</sub> domains does not differ significantly from that of VO<sub>x</sub>/SiO<sub>2</sub>, but increases with increasing amounts of TiO<sub>2</sub>. In this study, V-O-V and V-O-Ti bonds have been postulated to contribute equally to the reaction mechanism.<sup>72</sup> Similarly, methanol oxidation activity has been reported to increase for VO<sub>x</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> materials with an increasing TiO<sub>2</sub> content.<sup>74</sup> Interestingly, Vining *et al.* have found that while introducing sub-monolayer TiO<sub>2</sub>, ZrO<sub>2</sub> or CeO<sub>2</sub> domains to a silica-supported VO<sub>x</sub> system can significantly improve the resulting methanol oxidation activity, there is no difference in the apparent rate constant between the three different metal oxide modifiers.<sup>77</sup> The study of supported mixed metal oxide catalysts synthesized by ALD discussed in this thesis will further elucidate the influence of reducible metal oxide supports on the activity of VO<sub>x</sub> species in alkane ODH reactions.

#### **1.4 Research Objectives**

The overarching goal of this dissertation is to improve the understanding of the contribution of the support material to the activity of  $VO_x$  species in alkane ODH reactions. While it is known that the reactivity of surface  $VO_x$  sites changes depending on the identity of the support, it is difficult to distinguish between the role of V-O-S bonds and that of the exposed support surface. Differentiating between these two effects becomes particularly relevant when the support material is reducible and itself catalytically active. In this work, we systematically modify an inert alumina support with domains of a reducible metal oxide of varying thickness. This approach allows us to compare amorphous oxide domains, which are chemically and electronically distinct from the

bulk, with a bulk oxide support. By introducing sub-monolayer domains of a reducible oxide, we can include V-O-S bonds without creating extended networks of the oxide of interest, eliminating its catalytic contributions. By systematically growing films of increased thickness by ALD, we can further learn at which point and in what capacity the oxide structure impacts the ODH activity of VO<sub>x</sub> sites.

The first objective of this thesis is to elucidate the interactions of  $VO_x$  species with amorphous  $TiO_2$  domains deposited by ALD on an alumina support. Here, we vary the amount of  $TiO_2$  species as well as the order of deposition of the two metal oxides. We investigate how we can influence the surface metal oxide speciation by applying a sequence of ALD and calcination procedures. We combine spectroscopic characterization techniques with DFT calculations to determine the surface distribution of  $VO_x$  species in their oxidized state as well as during a redox cycle. This leads to an improved understanding of the distribution of V=O, V-O-V and V-O-S bonds in these mixed metal oxide catalysts, which can aid in the assignment of specific catalytic functions to individual bonding motifs.

The second objective of this thesis is to determine the role the TiO<sub>2</sub> support plays in the improvement of ODH activity of surface VO<sub>x</sub> sites in comparison to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. This is accomplished by evaluating the activity of alumina-supported mixed VO<sub>x</sub>-TiO<sub>2</sub> materials in cyclohexane ODH and comparing it to the reactivity of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/TiO<sub>2</sub>. The catalytic activity is related to the ease of reducibility of VO<sub>x</sub> species determined by H<sub>2</sub> consumption in temperature programmed reduction experiments. The contribution of V-O-V and V-O-Ti bonds to the catalytic activity is isolated in low metal loading materials, and the impact of TiO<sub>2</sub> is evaluated

in  $VO_x/TiO_2/Al_2O_3$  catalysts with varying  $TiO_2$  film thickness. Selectivity-conversion trends are also discussed.

The third objective of this thesis is to investigate interactions of  $VO_x$  domains with a support that is not only reducible, but also a known oxidation catalyst. Here, we compare the cyclohexane ODH activity of bare CeO<sub>2</sub> with VO<sub>x</sub> species deposited on CeO<sub>2</sub> by ALD and evaluate materials synthesized with single ALD cycles of VO<sub>x</sub> and CeO<sub>2</sub> on alumina to improve the understanding of how various surface sites contribute to the overall catalytic behavior. We use spectroscopic characterization to determine how the two ALD precursors react with existing surface sites, as well as how the order of deposition of the two metal oxides impacts the resulting surface site distribution.

Overall, the work presented here investigates the influence of reducible metal oxides on the ODH activity of supported VO<sub>x</sub> catalysts, which has not been previously probed in catalysts synthesized with a method enabling angstrom scale precision. The combination of atomically precise synthesis, extensive spectroscopic characterization and gas-phase reaction studies enables the assignment of specific catalytic functions to individual surface structures and can lead to the rational design of alkane ODH catalysts with improved alkene yields.

# 2 Interactions of VO<sub>x</sub> Species with Amorphous TiO<sub>2</sub> Domains on ALD-Derived Alumina-Supported Materials

#### A collaboration between

Izabela A. Samek, N. Scott Bobbitt, Randall Q. Snurr and Peter C. Stair

This chapter presents a modified version of the work published in *The Journal of Physical Chemistry C*.<sup>78</sup> Density functional theory calculations were performed by N. Scott Bobbitt. All other experiments and analysis were done by Izabela Samek.

#### **2.1 Introduction**

Supported vanadium oxide materials have been widely applied in heterogeneous catalytic oxidation reactions.<sup>8, 79-80</sup> They have been extensively studied for alkane oxidative dehydrogenation (ODH) reactions due to their high activity and selectivity.<sup>21-22, 48, 80-82</sup> The favorable reducibility of surface VO<sub>x</sub> species and the ease of transition between different oxidation states are often considered as the main contributors to their catalytic activity.<sup>9, 83</sup> The initial oxidized state of vanadium is generally V<sup>5+.9</sup> However, the extent of reduction of vanadium depends on a number of factors such as the reducing environment, VO<sub>x</sub> surface coverage and the nature of the support material.<sup>80</sup> The variety of surface VO<sub>x</sub> species, the distribution of vanadium-oxygen bonds as well as the surface acidity of the support can also affect the reactivity of supported VO<sub>x</sub> catalysts in alkane ODH reactions.<sup>21</sup>

Surface vanadium oxide species can take the form of isolated monovanadates, polyvanadate domains or  $V_2O_5$  crystallites depending on the surface coverage and method of preparation. Vanadium oxide is known to form two-dimensional surface layers on oxide supports prior to the

formation of crystalline  $V_2O_5$ .<sup>8</sup> This is due to the mobility of  $VO_x$  species on the surface as well as the lower surface free energy of  $V_2O_5$  in comparison to that of oxide supports such as  $Al_2O_3$  or TiO<sub>2</sub>.<sup>8</sup> An enhanced mobility of surface  $VO_x$  species has been observed under reaction conditions at elevated temperatures.<sup>84-86</sup>

Varying the surface coverage of VO<sub>x</sub> sites can impact the distribution of V=O, V-O-V and V-O-S (S, support) bonds.<sup>12</sup> All three of these bonding motifs have been postulated to have an impact on the catalytic activity of supported VO<sub>x</sub> materials. Density functional theory (DFT) calculations have been previously applied to study the propane ODH reaction mechanism. For monomeric  $VO_x/SiO_2$  species, it was found that both V=O and V-O-Si play a role in the reaction mechanism, but only V=O bonds are involved in the rate-determining step.<sup>64</sup> There exist conflicting reports in the literature regarding the impact of the ratio of monomeric to polymeric VO<sub>x</sub> surface species on the rates of alkane ODH reactions. The catalytic turnover frequency (TOF) for propane ODH has been previously described as independent of the extent of polymerization of surface VO<sub>x</sub> species.<sup>60-61</sup> However, several studies have established a positive correlation between the ODH reaction rate and  $VO_x$  surface density, implying that polyvanadates are more active than monovanadate species.<sup>48, 58, 63, 81</sup> The activation barriers of the rate-determining H-abstraction step have been calculated by DFT and found to decrease from monomeric to dimeric to oligomeric vanadia species on the surface of silica. However, the absolute differences were reported to be within experimental error.<sup>20</sup> The opposite was found for ceria-supported VO<sub>x</sub>, where monomeric species are the most active.<sup>67</sup>

Ternary oxide systems have been investigated as a strategy to influence the activity and selectivity of supported vanadium oxide in ODH reactions. Dai *et al.* have shown that  $VO_x$  dispersed on  $Al_2O_3$ 

coated with MoO<sub>x</sub> exhibits an increased activity in propane ODH, and they attributed this effect to the substitution of V-O-Al bonds with V-O-Mo, which enhances the reducibility of the surface VO<sub>x</sub> species.<sup>76</sup> The deposition of VO<sub>x</sub> on small domains of an oxide less reducible than vanadia but more reducible than the support is expected to improve the dispersion of surface VO<sub>x</sub> species.<sup>76</sup> Similarly, sub-monolayer titania improved the dispersion of vanadium oxide on SiO<sub>2</sub> compared to bulk titania.<sup>72, 75, 87</sup> Hamilton *et al.* synthesized a series of mixed (VO<sub>x</sub>)<sub>n</sub>-(TiO<sub>x</sub>)<sub>m</sub>/SBA-15 materials in order to combine the beneficial characteristics of the two metal oxides. While titania-supported vanadium oxide has the highest TOF for propane ODH, VO<sub>x</sub> on a silica support is reported to be more selective towards propene. A maximum productivity was assigned to a material where the total metal loading approached one monolayer.<sup>72-73</sup> Lapina *et al.* investigated VO<sub>x</sub> and TiO<sub>2</sub> surface structures in silica-supported VO<sub>x</sub>-TiO<sub>2</sub> as a function of the order of deposition of the two metal oxides on the support.<sup>88</sup> They postulated that complexes with different geometries can be deposited on the surface depending on the synthesis sequence. However, the implications of these variations on catalytic activity were not examined.<sup>88</sup>

The distribution of VO<sub>x</sub> active sites on the surface is highly dependent on the method used to prepare the material.<sup>9</sup> Catalysts synthesized in a well-defined manner can aid in determining the role of individual VO<sub>x</sub> structures. Atomic layer deposition (ALD) enables the synthesis of heterogeneous catalysts with Ångstrom-level control over the resulting surface species. In a typical ALD process, a film of a desired thickness is grown via a sequence of two self-limiting reactions. The first reaction introduces a metal precursor, which reacts with all available surface hydroxyl groups. In the second reaction, an oxidant or a reducing agent removes the remaining ligands on the metal precursor and regenerates of the hydroxyl groups.<sup>32, 37</sup> Supported VO<sub>x</sub> materials

In this chapter, we deposit VO<sub>x</sub> and TiO<sub>2</sub> domains on an alumina support by ALD with control over the amount as well as the order of the deposition of the two metal oxides. We study the interactions of VO<sub>x</sub> species with amorphous polymeric domains of TiO<sub>2</sub>, which are chemically and electronically distinct from bulk TiO<sub>2</sub>, and compare these materials with vanadia on bulk alumina and titania. Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were specifically chosen based on their contrasting contribution to the catalytic activity of supported VO<sub>x</sub> species in alkane ODH reactions.<sup>9</sup> Additionally, the  $Al_2O_3$  support does not exhibit intense Raman bands, which facilitates the assignment of observed features to VO<sub>x</sub> and TiO<sub>2</sub> surface structures.<sup>12</sup> We carefully characterize the catalysts with a range of spectroscopic techniques. The surface structures of the catalyst materials are probed by diffuse reflectance UV-vis (DRUV-vis) spectroscopy, UV (244 nm) and visible (488 nm) laser-excited Raman spectroscopy, and X-ray absorption near-edge spectroscopy (XANES). The Raman spectra are supplemented by DFT calculations aimed at understanding the atomic and electronic structure of V=O as a function the distribution of V-O-Al and V-O-Ti bonds. The reducibility of these materials is evaluated by  $H_2$  Temperature Programmed Reduction ( $H_2$ TPR), and the reduction behavior of  $VO_x$  and  $TiO_2$  sites is further probed by in-situ H<sub>2</sub> reduction Raman spectroscopy experiments and X-ray photoelectron spectroscopy (XPS) measurements of reduced samples. The combination of an atomically-precise synthesis method and surfacesensitive characterization techniques enables us to identify surface structures in alumina-supported  $VO_x$ -TiO<sub>2</sub> materials as well as probe the structural changes of the two oxides upon reduction. A
better understanding of the surface  $VO_x$  speciation within these inhomogeneous materials will enable the development of structure-function relationships for these catalysts.

# 2.2 Methods

#### 2.2.1 Sample Preparation

VO<sub>x</sub> films were grown via ALD on Al<sub>2</sub>O<sub>3</sub> (32-40 m<sup>2</sup>/g; 70%  $\delta$  phase, 30%  $\gamma$  phase; 99.5% purity, Alfa Aesar NanoArc) and TiO<sub>2</sub> (45 m<sup>2</sup>/g; anatase phase; 99.9% purity, Alfa Aesar NanoArc) at 100 °C with vanadyl triisopropoxide (VOTP, Sigma-Aldrich) and water in a viscous flow reactor described previously.<sup>89</sup> The VOTP bubbler was heated to 45 °C and the water bubbler was at room temperature (RT). 300 s dose times were followed by 450 s nitrogen purge times for the metal precursor and water alike. The total N<sub>2</sub> flow during deposition was 160 sccm. The amount of  $VO_x$ was kept constant at a single ALD cycle in all samples. VOx domains were also deposited on TiO2modifed alumina supports prepared by the deposition of titanium tetraisopropoxide (TTIP, Sigma-Alrich) and water in an Arradiance Gemstar-6 ALD system at 150 °C. The TTIP bubbler was heated to 80 °C and the water bubbler was at RT. A 5 s dose of TTIP was followed by a 180 s hold and 60 s nitrogen purge. Water was dosed for 5 s, held for 5 s and purged with nitrogen for 60 s. The alumina support was modified with varying amounts of  $TiO_2$  (denoted as xcTiO<sub>2</sub>, where x represents the number of ALD cycles). In some cases, TiO<sub>2</sub> was deposited on previously calcined VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. Samples were calcined in air at 450 °C for 4 hours at a heating rate of 5 °C/min. The order of deposition is denoted as follows: VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> represents a sample where the alumina support was first modified with one cycle of TiO<sub>2</sub> ALD, followed by one cycle of VO<sub>x</sub> ALD.

## 2.2.2 Catalyst Characterization

The metal content in selected samples was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo iCAP 7600 instrument calibrated with V and Ti standards of known concentration. The remaining samples were analyzed by Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry measured with an Oxford ED2000. A calibration curve established between known ICP-OES and EDXRF concentrations was used to confirm reproducible ALD deposition of V and Ti.

DRUV-vis spectra were collected with a Shimadzu UV-3600 spectrophotometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. The baseline white standard used was polytetrafluoroethylene (Sigma-Aldrich). The reflectance data were transformed to pseudo-absorbance using the Kubelka-Munk function  $F(R_{\infty})$ , with the alumina support as a reference. Absorption edge energies were estimated from the x-intercept of a linear fit to the increasing absorption edge in a plot of  $(F(R_{\infty})hv)^{1/n}$  vs. edge energy. n=1/2 was chosen in order to enable a comparison between the data collected as part of this work and the correlation between the number of covalent V-O-V bonds in the coordination sphere of central V<sup>5+</sup> cations and edge energies established by Gao and Wachs.<sup>13</sup>

UV (244 nm) and visible (488 nm) laser excited Raman spectra of the alumina-supported  $VO_x$ -TiO<sub>2</sub> materials were collected using a custom-built Raman instrument. The 244 nm excitation comes from a Lexel 95 SHG (second harmonic generation) laser equipped with an intracavity nonlinear crystal, BBO (BaB<sub>2</sub>O<sub>4</sub>), which frequency doubles visible radiation into the midultraviolet region.<sup>12, 90-91</sup> The Raman spectra were collected under a controlled atmosphere with the use of a fluidized bed reactor developed by Chua and Stair to minimize the adverse effects of UV radiation.<sup>92</sup> The catalysts were heated in flowing  $O_2$  at 450 °C for 30 min to remove any absorbed moisture prior to taking measurements. The spectra were collected at RT in flowing  $O_2$ . The visible laser power at the sample position was approximately 50 mW and that of the UV laser was 5 mW into a spot size of ca. 200  $\mu$ m.<sup>93</sup> The spectral collection time was 40 min. The Raman shift was calibrated by measuring cyclohexane as a standard prior to every experiment.

V and Ti K-edge XANES was performed at Sector 5 of the Advanced Photon Source, Argonne National Laboratory, on the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) bending magnet D beamline. The beam energy was controlled by a Si(111) monochromator with a resolution of  $10^{-4}$  eV. Incident and transmitted intensities were measured with Canberra ionization chambers. Fluorescence measurements were measured using a four-channel SII Vortex-ME4 detector. Energies were calibrated in transmission mode against V and Ti foils, setting the first inflection points at the known V and Ti energies of 5465 eV and 4966 eV, respectively. Spectra of samples in pellet form positioned at  $45\pm5^{\circ}$  with respect to the beam and the fluorescence detector were collected in fluorescence mode. The samples were dried at 120 °C in air prior to the collection of spectra. VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> standards were brushed onto Kapton tape and spectra collected in transmission mode in ambient conditions. The spectra were analyzed using the Athena package. The Ti K pre-edge region was fitted to four Gaussian peaks after normalization, labeled A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, and B in increasing energy according to a previously described procedure.<sup>94</sup>

XPS measurements were carried out on a Thermo Scientific ESCALAB 250Xi instrument (Thermo Scientific) equipped with an Al K $\alpha$  X-ray source (hv = 1486.6 eV). The binding energies were referenced to the O1s peak at 531.1 eV for Al<sub>2</sub>O<sub>3</sub> and 530 eV for TiO<sub>2</sub>.

## 2.2.3 Catalyst Reducibility

 $H_2$  TPR experiments were performed on an Altamira AMI-200 chemisorption instrument in the CleanCat Core user facility at Northwestern University. The materials were pretreated in flowing 10% O<sub>2</sub>/He at 450 °C for 1 hr. The experiments were carried out in 10%  $H_2/N_2$  from 100 to 600 °C at a 30 °C/min ramp rate. Temperature Programmed Oxidation (TPO) was carried out in 10% O<sub>2</sub>/He in the same temperature range. A thermal conductivity detector (TCD) was used to determine the  $H_2$  and  $O_2$  content of the outlet gas. A sequence of TPR and TPO experiments were conducted to determine the reversibility of the applied treatments.

In-situ reduction measurements were carried out with UV-excited Raman spectroscopy. The samples were reduced at a desired temperature between 450 and 600 °C in flowing 10% H<sub>2</sub>/N<sub>2</sub> for 1 hour and cooled down to RT in nitrogen. Additionally, the catalysts were re-oxidized in flowing O<sub>2</sub> at 450 °C. The spectra were collected at RT in flowing N<sub>2</sub>.

In order to study the oxidation state of V and Ti under reducing conditions with XPS, the samples were treated with flowing 10%H<sub>2</sub>/N<sub>2</sub> in a quartz plug flow reactor for 1 hour at 450 or 550 °C and subsequently moved to a glovebox without exposure to air. A transfer vessel compatible with the ESCALAB 250Xi instrument was used to transfer reduced samples from the glovebox to the instrument.

### 2.2.4 Theoretical Methods

Density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP 5.4.1)<sup>95-98</sup> with the PBE exchange-correlation functional<sup>99</sup> with DFT-D3(BJ) van der Waals corrections<sup>100-101</sup> and the standard PAW-PBE potentials provided in VASP.<sup>102-103</sup> Spin-

polarization was used for calculations containing Ti or V. The energy cutoff used was 520 eV, with an SCF convergence criterion of  $10^{-6}$  ( $10^{-8}$  for frequency calculations) and a k-point mesh of [1,2,1] for a unit cell. This is sufficient to converge the total energy of the system within 0.005 eV. Geometry optimizations for all structures were performed until the largest force on any atom was below 0.02 eV/Å. The Hessian matrix was obtained for frequency calculations using central differencing with a step size of 0.01 Å. Additional computational details are provided in Appendix B.

# 2.3 Results and Discussion

## 2.3.1 VO<sub>x</sub> and TiO<sub>2</sub> Surface Speciation

The V and Ti loading in each material was quantified by ICP-OES. The surface density of vanadium was in the range of 1-2 V/nm<sup>2</sup> for all of the investigated materials. This is below monolayer coverage, which is achieved at 7.3 V/nm<sup>2</sup> on alumina and at 7.9 V/nm<sup>2</sup> for titania supports.<sup>104</sup> The titania films were deposited at a rate of 0.1 Å/cycle. This value was calculated based on the deposition of 100 ALD cycles of TiO<sub>2</sub> on the alumina support and is consistent with previous reports in the literature under similar experimental conditions.<sup>105-106</sup> The surface density of Ti atoms is shown in Figure 2.1. Monolayer coverage is expected at 6-8 Ti/nm<sup>2</sup>.<sup>72</sup> All samples produced by a single ALD cycle of TiO<sub>2</sub> exhibit the same Ti surface density, which is significantly below monolayer coverage. The Ti surface density in materials synthesized with 16 ALD cycles of TiO<sub>2</sub> is sufficient to completely cover the alumina support in these materials. The average surface speciation of vanadia is correlated to the edge energy (E<sub>g</sub>) determined from absorption data obtained with DRUV-vis. The TiO<sub>2</sub> support strongly absorbs in the UV-vis region, which typically prevents exact characterization of VO<sub>x</sub> surface sites in VO<sub>x</sub>/TiO<sub>2</sub>.<sup>13</sup> However, sub-monolayer TiO<sub>2</sub>

on alumina absorbs at lower wavelengths and exhibits higher absorption edge energies than  $VO_x/Al_2O_3$ , which enables the assignment of  $E_g$  values to  $VO_x$  species in alumina-supported  $VO_x$  catalysts with low TiO<sub>2</sub> loadings. The measured edge energies for a range of materials synthesized by ALD and the corresponding DRUV-vis spectra are shown in Figure 2.1. The absorbance edge energy values determined for supported  $VO_x$  sites are consistent with isolated tetrahedrally coordinated  $VO_4$  species according to the correlation established by Gao and Wachs.<sup>13</sup> This result emphasizes the control over the dispersion of metal oxide species that can be achieved with ALD. However, the correlation does not distinguish between individual  $VO_x$  sites on the support surface.



**Figure 2.1.** Ti surface density (bars) in samples prepared by ALD and corresponding absorbance edge energies (■) (A) and the corresponding DRUV-vis spectra (B).

We further studied these materials using Raman spectroscopy by taking the multiwavelength excitation approach, which allows identification of isolated VO<sub>x</sub> sites, polyvanadates and V<sub>2</sub>O<sub>5</sub> crystallites. This differentiation is possible due to the selective resonance enhancement, which results in higher sensitivity of UV Raman to isolated and less polymerized VO<sub>x</sub> species and visible Raman towards highly polymerized VO<sub>x</sub> species and crystalline V<sub>2</sub>O<sub>5</sub>.<sup>12</sup> The Raman spectra of supported VO<sub>x</sub> materials are shown in Figure 2.2.



**Figure 2.2.** UV (A,B) and visible (C) excitation wavelength Raman spectra of supported  $VO_x$  materials. An expanded view of the V=O band marked by the dotted rectangle in A is shown in B.

The band above 1000 cm<sup>-1</sup>, magnified in Figure 2.2B, can be assigned to the V=O stretching mode of VO<sub>x</sub> species. As shown in Figures 2.2B and 2.2C, a shift of this vibration is observed as a function of excitation wavelength, but also upon the addition of TiO<sub>2</sub> domains in aluminasupported VO<sub>x</sub> materials. The former shift can be explained by the presence of a variety of surface VO<sub>x</sub> species, which are excited at different excitation wavelengths, as was previously shown for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>.<sup>12</sup> VO<sub>x</sub> sites supported on bulk titania cannot typically be investigated by UV Raman, due to the strong absorption of UV light by the support. However, thin TiO<sub>2</sub> films grown by ALD do not obscure the V=O stretching band and enable the detection of isolated VO<sub>x</sub> surface sites. VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> shows a broad feature centered at 1010 cm<sup>-1</sup> associated with the V=O stretching vibration in the UV Raman spectrum (Figure 2.2B). A shift and narrowing of this feature to higher wavenumbers is observed upon the addition of TiO<sub>2</sub> domains. Similar shifts have been previously reported in association with increasing vanadia surface coverage as well as with the identity of the oxide support.<sup>12, 104, 107</sup> Since the V surface density of the materials synthesized in this work does not vary significantly, we assign the shift in the V=O band to the formation of V-O-Ti bonds. This assignment implies VO<sub>x</sub> binds preferentially to TiO<sub>2</sub> domains, as confirmed by DFT calculations below. We attribute the larger, broad V=O feature in VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> to the presence of a variety of surface VO<sub>x</sub> structures. The reduction of the V=O band width in alumina-supported materials modified with TiO<sub>2</sub> domains implies the presence of a narrower distribution of VO<sub>x</sub> sites. The broad feature at ~900 cm<sup>-1</sup> in VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> has been previously ascribed to interfacial V-O-Al

bonds.<sup>12</sup> We observe a broadening of this band in materials modified with sub-monolayer TiO<sub>2</sub> domains, which may correspond to the co-existence of V-O-Al and V-O-Ti bonds. We expect that V-O-Al bonds are no longer present in  $VO_x/16cTiO_2/Al_2O_3$  and the broad band centered at 820 cm<sup>-1</sup> is a combination of V-O-Ti and Ti-O-Ti vibrations. The UV Raman spectrum of 1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> shown in Figure 2.2A reveals bands at 710 and 840 cm<sup>-1</sup>, which have been previously assigned to Ti-O-Ti bonds in a polymeric TiO<sub>2</sub> structure on alumina.<sup>107</sup> The presence of these bands is indicative of Ti-O-Ti bond formation in TiO<sub>2</sub>-modified alumina. VO<sub>x</sub>-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with sub-monolayer amounts of TiO<sub>2</sub> do not exhibit these features suggesting that the presence of VO<sub>x</sub> sites increases the dispersion of TiO<sub>2</sub> in these materials. The formation of Ti-O-Ti bonds is anticipated in VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> due to the increased surface coverage of TiO<sub>2</sub>, but the structure remains amorphous, as indicated by the lack of crystalline TiO<sub>2</sub> features within the Raman spectra. Raman bands have been previously reported for the anatase phase at 147, 198, 398, 515 and 640 cm<sup>-1</sup> and for the rutile phase at 144, 448, 612 and 827 cm<sup>-1</sup>.<sup>108</sup> The visible Raman spectra shown in Figure 2.2C reveal a V=O stretching band above 1020 cm<sup>-1</sup> in all of the examined materials with the exception of  $VO_x/2cTiO_2/Al_2O_3$ . This material is representative of  $VO_x$  supported on  $Al_2O_3$ . modified with sub-monolayer amounts of TiO<sub>2</sub>. Based on the absence of a V=O band associated with polymerized VO<sub>x</sub>, we infer that the presence of low coverage TiO<sub>2</sub> on alumina improves the dispersion of VO<sub>x</sub> sites, which is in agreement with previously published work on the effect of combining TiO<sub>2</sub> and VO<sub>x</sub> domains on SiO<sub>2</sub>.<sup>72, 75, 87</sup>

DFT calculations were performed to further investigate the binding modes of VO<sub>4</sub> and TiO<sub>4</sub>H on the alumina support. We chose to represent the support with a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> model. The surface of the mixed phase support is expected to exhibit the properties of  $\gamma$ -alumina.<sup>109</sup> The structure of  $\gamma$ - alumina is a defective spinel.<sup>110</sup> The ideal cubic spinel unit cell contains 32 O sites on an *fcc* lattice and 24 cation sites divided between <sup>1</sup>/<sub>3</sub> tetrahedral and <sup>2</sup>/<sub>3</sub> octahedral positions. However, to preserve the Al<sub>2</sub>O<sub>3</sub> stoichiometry,  $\gamma$ -alumina has 2 <sup>2</sup>/<sub>3</sub> vacancies on Al sites, making the unit cell formula  $\Theta_2$ 2/<sub>3</sub>Al<sub>21 1/3</sub>O<sub>32</sub> (where  $\Theta$  = Al vacancy). In order to run DFT simulations with an integer number of Al atoms, we used an expanded unit cell with 64 Al atoms, 96 O atoms, and 8 vacancies. The vacancies were randomly dispersed throughout the cell and occupied a mixture of tetrahedral and octahedral Al sites. The precise distribution of the vacancies is the subject of ongoing debate in the literature.<sup>110-118</sup> However, the general agreement is that octahedral sites are preferred while 25-33% of the vacancies occur on tetrahedral sites.<sup>119-120</sup>

The surface of  $\gamma$ -alumina is difficult to characterize due to the presence of the random vacancies. In a unit cell with 72 Al sites, there exist over 10<sup>14</sup> unique arrangements of 8 vacant sites, so identifying one crystal structure as the most stable is untenable. In order to find a reasonable structure for this study, we cleaved four surfaces: two [001] and two [111] surfaces, which are the two most stable faces of  $\gamma$ -alumina.<sup>111, 114</sup> The [001] and [111] surfaces were each cleaved at two different planes of Al atoms (i.e. the octahedral layer and the tetrahedral layer). We then generated 40 unique distributions of vacancies for each surface, resulting in 160 surfaces, and performed DFT optimizations using the level of theory described above. In generating the vacant sites, we constrained the number of tetrahedral sites to 3 or less out of 8, which is approximately the expected proportion. The two lowest energy surfaces were both [001] facets, which agrees with other theoretical calculations about the most stable face of  $\gamma$ -alumina.<sup>111, 114</sup> The most stable face of 1 tetrahedral vacancies and 1 tetrahedral vacancies. The

coordinates for these two structures are provided in Appendix B. The Al atoms on the surface were passivated with -OH groups.

The surface of  $\gamma$ -alumina is highly variable due to the mixture of tetrahedral, octahedral, and vacant Al sites. In order to find the most favorable binding sites for V and Ti, we tested six different binding positions on each surface. The same sites were used for both Ti and V. During the geometry optimization, tetrahedral Al atoms at the surface move into octahedral configurations which results in a flat rectangular binding site between the transformed atom and two neighboring octahedral Al atoms, as shown in Figure B.1. We found that these new sites were the most favorable binding sites for both Ti and V atoms, and we used them for the vibrational calculations presented in this work.

Figure 2.3 shows some structures that were investigated to elucidate the impact of the formation of V-O-Ti bonds on the V=O bond length and the V=O stretching frequency in Raman measurements.



**Figure 2.3.** Visualization of model catalyst structures on [001]  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. O atoms are marked in red, Al atoms are tan, V atoms are blue, and Ti atoms are green. The structures include a top view of a VO<sub>4</sub> site (A), a top view of VO<sub>4</sub> site bound to a TiO<sub>4</sub>H site (B), and a side view of VO<sub>4</sub> site bound to a TiO<sub>4</sub>H site (C).

Structure	V-O[-Al] [Å]	V=0 [Å]	V=O* [cm <sup>-1</sup> ]	$\Delta^*$ [cm <sup>-1</sup> ]	V=O <sup>**</sup> [cm <sup>-1</sup> ]	$\Delta^{**}$ [cm <sup>-1</sup> ]						
А	1.756	1.636	959	12	1010	7						
В	1.837	1.633	971	12	1017	,						

**Table 2.1.** Bond lengths and frequencies associated with VO<sub>4</sub> surface sites calculated from DFT. Structures A and B correspond to those in Figure 2.3.

\*DFT result \*\*Experimental result

Characteristic bonds lengths and V=O stretching frequencies for structures A and B from Figure 2.3 are listed in Table 2.1. The assignments of Raman features associated with V-O-Al, V-O-Ti and Ti-O-Ti vibrations can be found in Figure B.4. In agreement with experimental results, a shift to a higher wavenumber of the V=O stretching mode is reported upon the addition of a V-O-Ti bond. The calculated magnitude of the shift (12 cm<sup>-1</sup>) was similar to the experimentally observed shift (7 cm<sup>-1</sup>), confirming the earlier hypothesis of preferential binding of  $VO_x$  and  $TiO_2$  sites to each other. We used Bader charge analysis<sup>121</sup> to understand changes to the electronic structure of the V=O bond induced by the presence of Ti in the structure shown in Figure 2.3. When Ti atoms are not present, there are about 2.4 valence electrons resting on V and 6.9 valence electrons on the vanadyl oxygen. Upon addition of Ti, the O gains about 1.1 electrons, for a total of 8.0, while there is no change to the density on the V. Bader charge analysis indicates there are 1.4 valence electrons on the Ti atom. This change in the charge distribution suggests that the Ti atom donates some electron density to the bridging O atom (Ti-O-V), which in turn donates more electron density to the V=O bond. This extra electron density strengthens the V=O bond and causes it to contract slightly, resulting in the observed blue shift in the stretching frequency. The V=O bond also contracts slightly from 1.636 to 1.633 Å, while the V-O(-Al) bonds lengthen about 0.08 Å.

The shift in the V=O stretching band associated with the presence of Ti atoms on the surface suggests  $VO_x$  and  $TiO_2$  sites preferentially bind to the alumina support in proximity to each other. To further support this hypothesis, we compared the energies for surfaces with V and Ti adjacent or far removed from one another. We used a 2x1x1 supercell of Surface 2 so that the most favorable site on Surface 2 is replicated in the supercell. Since the 160-atom cell is repeated, these two sites are equivalent. We then placed a VO<sub>4</sub> moiety on one site and a TiO<sub>4</sub>H on the equivalent site as shown in Figure 2.4. In a separate calculation, the TiO<sub>4</sub>H was placed next to the VO<sub>4</sub>. An extra H atom was added to an -OH group far removed from the catalytic site to preserve the stoichiometry. We found that configurations with V and Ti in adjacent sites are the most favorable, in part due to the hydrogen bond formed between the -OH group on Ti and the V=O structure. By freezing all other atoms and rotating the -OH group, we estimate this hydrogen bond contributes a stabilization in the range of 18-30 kJ/mol.



**Figure 2.4.** Top-down view of [001] surface of  $\gamma$ -alumina (2x1 supercell, Surface 2) with V (blue) and Ti (green) atoms on the surface in various configurations: V occupies the most favorable site with Ti adjacent to it (A), Ti and V are swapped from A so that Ti occupies the most favorable site with V adjacent to it (B), Ti and V occupy equivalent sites in separate unit cells (C). An additional H atom (purple) is added to an -OH group far from the V and Ti atoms to preserve the stoichiometry. A structure equivalent to A with the –OH group on Ti rotated away from the vanadyl oxygen to break the hydrogen bond is shown in D. The differences in total electronic

energy from the most favorable position A are noted below the configurations. For example, D is 29.5 kJ/mol less favorable than A.

XANES studies were performed on VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, 1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> to probe any changes in geometry and oxidation state of V and Ti upon varying deposition conditions. The relevant spectra can be found in Figure 2.5. Based on the similar positons of the pre-edge features and the absorption edges in the materials synthesized by ALD and the V<sub>2</sub>O<sub>5</sub> standard, we conclude that the V in the samples investigated in this work is in the 5+ oxidation state and tetrahedral geometry.<sup>122-123</sup> Ti with an average coordination of 4.4 was present on the support surface of catalysts synthesized with 1 ALD cycle of TiO<sub>2</sub>.<sup>94</sup> No differences in oxidation state or geometry were observed between materials where only one of the metal oxides was present in comparison to mixed VO<sub>x</sub>-TiO<sub>2</sub> catalysts, implying that the ALD synthesis sequence does not impact the preferred surface coordination of VO<sub>x</sub> and TiO<sub>2</sub>.



**Figure 2.5.** V K-edge XANES spectra of supported VO<sub>x</sub> materials and VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> standards (A). The inset marks the pre-edge features. Ti K-edge XANES spectra of materials modified with a single ALD cycle of TiO<sub>2</sub> (B). The inset shows a deconvolution of the pre-edge feature for  $1cTiO_2/Al_2O_3$ . The pre-edge region was deconvoluted into four Gaussian peaks labeled in order of increasing energy A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and B. The ratio of (A<sub>A2</sub>+A<sub>A3</sub>)/A<sub>Atotal</sub> of 0.89 corresponds to an average coordination number of 4.4.<sup>94</sup> The spectra are offset for clarity.

Based on spectroscopic evidence complemented with DFT calculation results, we postulate the presence of VO<sub>x</sub> and TiO<sub>2</sub> structures on the support surface as shown in the schematic representations in Figure 2.6. A mixture of isolated and polymerized VO<sub>x</sub> sites is expected on a bare alumina support due to the fact that the V=O stretching mode was observed in both UV- and visible-excited Raman spectra (Figure 2.6A). The modification of alumina with sub-monolayer TiO<sub>2</sub> domains prior to the deposition of VO<sub>x</sub> species increases the dispersion of both metal oxides and induces preferential binding of VO<sub>x</sub> to TiO<sub>2</sub> domains (Figure 2.6B). 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> materials are characterized by well-dispersed TiO<sub>2</sub> species accompanied by a mixture of VO<sub>x</sub> surface structures (Figure 2.6C), which tend to agglomerate upon calcination performed prior to the deposition of TiO<sub>2</sub>, i.e. the surface is similar to A) prior to titania deposition. Finally, VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, having more than a monolayer coverage of amorphous TiO<sub>2</sub> also includes a range of VO<sub>x</sub> surface structures (Figure 2.6D), as observed in the Raman spectra.



**Figure 2.6.** Proposed surface structures of  $VO_x/Al_2O_3$  (A),  $VO_x/1cTiO_2/Al_2O_3$  (B),  $1cTiO_2/VO_x/Al_2O_3$  (C) and  $VO_x/16cTiO_2/Al_2O_3$  (D). V atoms are shown in blue and Ti atoms are shown in green.

# 2.3.2 VO<sub>x</sub> and TiO<sub>2</sub> Surface Species Formed upon Reduction

The reducibility of VO<sub>x</sub> surface species was probed with H<sub>2</sub> TPR. Figure 2.7 shows the H<sub>2</sub> TPR profiles for supported VO<sub>x</sub> materials. The temperatures of the peak maxima for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/TiO<sub>2</sub> are consistent with previous reports in the literature.<sup>21, 124</sup> Trends of varying VO<sub>x</sub> reducibility as a function of the oxide support have been formerly established based on shifts in these temperatures on the order of 10 °C.<sup>124</sup> The enhanced reducibility of VO<sub>x</sub>/TiO<sub>2</sub> has been attributed to the improved reactivity of surface oxygen in TiO<sub>2</sub>.<sup>124</sup> VO<sub>x</sub> supported on alumina modified with sub-monolayer amounts of TiO<sub>2</sub> (green) is equivalent in reducibility to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, whereas TiO<sub>2</sub> coverages above a monolayer grown on an alumina support (orange) lead to increased VO<sub>x</sub> reducibility, resembling that of VO<sub>x</sub>/TiO<sub>2</sub>. Notably, a reversal of the order of deposition of the two metal oxides, where TiO<sub>2</sub> species are grown on VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (purple), also results in the shift of the peak maximum to a lower temperature. The dispersion and surface

structure distribution of supported VO<sub>x</sub> species have been previously postulated to change upon exposure to several redox cycles.<sup>125</sup> A sequence of TPR/TPO experiments was performed, and the resulting TPR profiles are shown in Figure 2.8. The similarity of consecutive TPR scans demonstrates that structural changes within the surface species induced upon reduction in H<sub>2</sub> are reversible. This observation is consistent with the lack of permanent structural changes reported for supported VO<sub>x</sub> materials in redox cycles performed below 600 °C.<sup>124</sup> A decrease in the intensity of the H<sub>2</sub> consumption peak with consecutive TPR scans for VO<sub>x</sub>/TiO<sub>2</sub> can be associated with the incorporation of V<sup>4+</sup> cations into the TiO<sub>2</sub> crystal lattice.<sup>126</sup>



Figure 2.7. H<sub>2</sub> TPR profiles of supported VO<sub>x</sub> materials.



**Figure 2.8.** H<sub>2</sub> TPR profiles of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (A), VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (B), 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (C), VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (D) and VO<sub>x</sub>/TiO<sub>2</sub> (E) resulting from a sequence of TPR/TPO experiments in the 100 - 600 °C range.

The transformation of VO<sub>x</sub> surface structures during hydrogen reduction was further probed with in-situ UV Raman measurements to gain an improved understanding of the interplay of VO<sub>x</sub> and TiO<sub>2</sub> domains during a redox cycle. Figure 2.9 shows the UV Raman spectra from in-situ reduction experiments performed between 450 and 600 °C. The bands associated with Ti-O-Ti bond vibrations in  $1cTiO_2/Al_2O_3$  shown in Figure 2.9A do not change significantly in hydrogen at elevated temperatures, suggesting that titania species do not reduce or migrate on the surface of the alumina support in the absence of VO<sub>x</sub> species. This is consistent with the absence of clustering or migration previously observed for TiO<sub>2</sub>/SiO<sub>2</sub> during high temperature reduction and

reoxidation.<sup>127</sup> Figure 2.9B presents the reduction profile of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The most substantial difference within this series of Raman spectra occurs between 550 and 600 °C, where we observe a decrease in the intensity of the two bands associated with V=O (1010 cm<sup>-1</sup>) and V-O-Al (900  $cm^{-1}$ ) vibrations. A fraction of the VO<sub>x</sub> surface sites remains unreduced at 600 °C, which has been previously reported at this temperature for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> with less easily reducible well-dispersed monovanadates.<sup>24</sup> These observations are consistent with the H<sub>2</sub> TPR profile of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> shown in Figure 2.7, where the H<sub>2</sub> consumption peak occurs around 550 °C. As seen in Figure 2.9C, the V=O band at 1017 cm<sup>-1</sup> in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> decreases in intensity and shifts slightly to a higher frequency at 550 °C and further decreases at 600 °C. These changes accompany a gradual increase of the two bands at 710 and 840 cm<sup>-1</sup> with increasing temperatures. The formation of Ti-O-Ti bonds is an indication of Ti species migration during high temperature reduction. Even though VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> have comparable H<sub>2</sub> TPR profiles, their structural changes in the 450-600 °C temperature range are not the same. If we consider the reverse order of deposition, the V=O band in  $1cTiO_2/VO_x/Al_2O_3$  shown in Figure 2.9D begins to reduce at a lower temperature in comparison to the two other VO<sub>x</sub>-containing materials, in agreement with its H<sub>2</sub> TPR profile showing more easily reducible VO<sub>x</sub> sites. In contrast to VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, formation of Ti-O-Ti bonds is delayed until 600 °C, implying that migration of Ti sites is not favorable. Reduction at 600 °C leads to identical spectra for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, which are characterized by the presence of TiO<sub>2</sub> clusters and a small percentage of unreduced monovanadates.



**Figure 2.9.** UV Raman spectra of  $1cTiO_2/Al_2O_3$  (A),  $VO_x/Al_2O_3$  (B),  $VO_x/1cTiO_2/Al_2O_3$  (C),  $1cTiO_2/VO_x/Al_2O_3$  (D) and  $VO_x/16cTiO_2/Al_2O_3$  (E) following reduction by hydrogen between 450 and 600 °C. The black spectra correspond to the initial dehydrated state prior to reduction. The spectra were recorded at RT in flowing N<sub>2</sub>. The insets represent an expanded view of the V=O stretching bands.

The varying behavior of the two mixed metal oxide materials during reduction can be rationalized with the help of the schematics shown in Figure 2.6. Isolated  $TiO_2$  sites present in  $VO_x/1cTiO_2/Al_2O_3$  begin to aggregate and form Ti-O-Ti bonds at lower temperatures. In contrast, Ti-O-Ti bonds only form near reduced  $VO_x$  sites in  $1cTiO_2/VO_x/Al_2O_3$ . These Ti atoms are in proximity of each other and are initially bound to vanadia structures by V-O-Ti bonds. The bonds are broken during the reduction of  $VO_x$  sites and Ti-O-Ti bonds form in order to preserve the 4-

coordinated Ti sites. The reversibility of the  $H_2$  TPR profiles following redox cycles shown in Figure 2.8 implies that significant migration of Ti atoms in  $1cTiO_2/VO_x/Al_2O_3$  is unlikely.

The V=O band in VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> shown in Figure 2.9E disappears completely upon reduction at 450 °C. This result is contrasted with a much less pronounced decrease in intensity of the V=O feature in 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> at 450 °C. Both of these materials exhibit H<sub>2</sub> consumption peak maxima at approximately 450 °C. However, the VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> peak is significantly sharper and thus all of the V=O bonds are reduced at this temperature. This is not the case for 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, which has a broader reduction peak. The broader peak indicates that a considerable fraction of the VO<sub>x</sub> species in 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> requires higher temperature in order to undergo reduction.

The re-oxidation of alumina-supported VO<sub>x</sub>-TiO<sub>2</sub> materials at 450 °C was also probed with UV Raman. The relevant spectra are shown in Figure 2.10. The O<sub>2</sub> treatment resulted in identical spectra for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The Ti-O-Ti bands disappear upon oxidation at 450 °C consistent with *reversible* formation of these bonds.



**Figure 2.10.** UV Raman spectra of alumina-supported  $VO_x$ -TiO<sub>2</sub> materials following reoxidation at 450 °C (A). Expanded view of the V=O band (B).

Figure 2.11 shows a direct comparison between the initial spectra of calcined materials and those following re-oxidation for  $VO_x/1cTiO_2/Al_2O_3$  and  $1cTiO_2/VO_x/Al_2O_3$ . This comparison was enabled by the use of alumina bands as an internal standard, which compensates for changes in the scattering volume. The higher intensity of the V=O in  $VO_x/1cTiO_2/Al_2O_3$  following re-oxidation

suggests that a fraction of the VO<sub>x</sub> species in the initially calcined material remained reduced. The position of the band indicates that the oxidized species formed as a result of the redox cycle are bound to TiO<sub>2</sub> sites. The intensity of the V=O feature for  $1cTiO_2/VO_x/Al_2O_3$  is lower compared to the calcined material. This implies that 450 °C is insufficient to completely oxidize all of the reduced VO<sub>x</sub> species, which is consistent with a previous report, where VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> samples were fully re-oxidized at temperatures above 500 °C following a 600 °C reduction.<sup>24</sup> The differences between the calcined and re-oxidized UV Raman spectra for the two materials suggests that the metal oxide species rearrange on the alumina surface during a redox cycle. Additionally, it is possible that aggregation of VO<sub>x</sub> species in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> occurs following this treatment.



**Figure 2.11.** UV Raman spectra of calcined  $VO_x/1cTiO_2/Al_2O_3$  (A) and  $1cTiO_2/VO_x/Al_2O_3$  (B) in direct comparison to the spectra following re-oxidation. The insets represent an expanded view of the V=O stretching bands.

We complement the UV Raman results with XPS measurements of the oxidized and reduced  $VO_x$  materials. Figure 2.12 shows  $V2p_{3/2}$  and Ti2p spectra of the various materials following

calcination, reduction at 450 °C and reduction at 550 °C. Table 2.2 shows the distribution of V<sup>5+</sup> (517.6 eV),  $V^{4+}$  (516.6 eV) and  $V^{3+}$  (515.7 eV) species after the various treatments.<sup>29</sup> The corresponding deconvoluted V2p<sub>3/2</sub> spectra can be found in Figure B.8. The calcined, aluminasupported materials contain vanadium primarily in the 5+ oxidation state.<sup>87</sup>  $VO_x/TiO_2$  exhibits a balanced distribution of  $V^{5+}$  and  $V^{4+}$  on the surface of the support. This is in agreement with the incorporation of  $V^{4+}$  into the bulk of TiO<sub>2</sub> during the TPR/TPO sequence discussed earlier. The  $1cTiO_2/VO_x/Al_2O_3$  material consists of V<sup>5+</sup> and V<sup>4+</sup> species upon calcination and reduction at 450 °C. The acceptance of a single electron by each V atom during reduction with H<sub>2</sub> in this material is indicative of VO<sub>x</sub> sites in close proximity to each other and hence the existence of polymeric VO<sub>x</sub> species. In contrast, the complete reduction of  $V^{5+}$  to  $V^{3+}$  in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> implies the existence of isolated VO<sub>x</sub> sites. Additionally, the formation of  $V^{4+}$  upon reduction implies the VO<sub>x</sub> species have aggregated at elevated temperatures. Furthermore, we observe a shift of the  $V2p_{3/2}$ binding energy to lower values with increasing reduction temperature, which corresponds to the further reduction of vanadium species and is consistent with the decrease in V=O band intensity in the UV Raman spectra shown in Figure 2.9. Increasing the reduction temperature leads to the more favorable formation of completely reduced V<sup>3+</sup> species. No changes in the Ti oxidation state from the initial Ti<sup>4+</sup> were observed during reduction of the different materials.<sup>87</sup> This supports the hypothesis that the additional Raman bands observed during reduction of VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> are caused solely by the *migration* of surface titanium species and the substitution of V-O-Ti bonds with Ti-O-Ti (and not changes in the titanium oxidation state). The reduction of VO<sub>x</sub>/TiO<sub>2</sub> at 550 °C was accompanied by a change in color from white to blue, which is indicative of the formation of Ti<sup>3+</sup> species.<sup>127</sup> Ti<sup>3+</sup> species have been previously identified by

electron paramagnetic resonance (EPR) as the most abundant sites in  $VO_x/TiO_2$  following reduction.<sup>128</sup> The fact that no change in the XPS binding energy of Ti2p was observed for this material suggests that the Ti<sup>3+</sup> sites are predominantly present in the bulk of the support, which is not probed by XPS.



**Figure 2.12.** V2p<sub>3/2</sub> spectra of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (A), VO<sub>x</sub>/TiO<sub>2</sub> (B), VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (C) and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (D). Ti2p spectra of VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (E), 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (F) and VO<sub>x</sub>/TiO<sub>2</sub> (G). Spectra were collected following calcination at 450 °C ( $\Box$ ), reduction at 450 °C (+) and reduction at 550 °C ( $\Delta$ ).

Catalyst	Calcined at 450 °C			Reduced at 450 °C			Reduced at 550 °C		
	V <sup>5+</sup>	$V^{4+}$	V <sup>3+</sup>	V <sup>5+</sup>	$V^{4+}$	V <sup>3+</sup>	V <sup>5+</sup>	$V^{4+}$	V <sup>3+</sup>
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	0.75	0.25	0	-	-	-	0.51	0.23	0.26
VO <sub>x</sub> /1cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.85	0.06	0.09	0.18	0.54	0.28	0.01	0.47	0.52
1cTiO <sub>2</sub> /VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	0.85	0.15	0	0.21	0.79	0	0.11	0.08	0.81
VO <sub>x</sub> /TiO <sub>2</sub>	0.42	0.58	0	-	-	-	0.09	0.29	0.62

**Table 2.2.** Distribution of vanadium in different oxidation states.

The V oxidation state distribution was also examined for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> following a re-oxidation at 450 °C of materials reduced in H<sub>2</sub> at 450 °C. For VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> the distributions of V<sup>5+</sup>:V<sup>4+</sup>:V<sup>3+</sup> were 0.69:0.23:0.08 and 0.72:0.28:0, respectively. These distributions indicate aggregation of VO<sub>x</sub> species in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> upon redox treatment at elevated temperatures. In addition, they are consistent with the UV Raman spectra shown in Figure 2.10, which show that VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> become equivalent following reduction at 600 °C and re-oxidation at 450 °C. This suggests that the surface species undergo rearrangement at high temperature, which may affect their catalytic behavior in the examined temperature range.

# **2.4 Conclusions**

We investigated the interactions of  $VO_x$  surface species with amorphous TiO<sub>2</sub> domains deposited on alumina and compared these materials to  $VO_x$  supported on bulk alumina and titania. We were able to influence the dispersion of  $VO_x$  and TiO<sub>2</sub> sites and hence the distribution of mixed metal oxide surface structures by a combination of ALD and calcination procedures. Preferential binding of  $VO_x$  to TiO<sub>2</sub> domains was observed by Raman spectroscopy and confirmed with DFT calculations. Varying distributions of V-O-V, V-O-Ti and V-O-Al bonds were shown to affect the reduction behavior of surface  $VO_x$  sites. Mobility and aggregation of surface  $VO_x$  and  $TiO_2$  species occurred at elevated temperatures under hydrogen. Overall, we showed that ALD can be used to influence the distribution of surface species facilitating the identification of individual metal oxide surface structures via a combination of spectroscopic characterization techniques and DFT calculations. The elucidation of  $VO_x$  and  $TiO_2$  species distributions on the alumina support in the initial oxidized states as well as upon reduction will aid in the understanding of their function in catalytic redox reactions.

# 3 Alumina-Supported VO<sub>x</sub>-TiO<sub>2</sub> Materials in Cyclohexane Oxidative Dehydrogenation

# **3.1 Introduction**

The activity of supported VO<sub>x</sub> catalysts in oxidation reactions has been established to be dependent on the nature of the support material.<sup>8-9, 80</sup> In alkane oxidative dehydrogenation (ODH), catalytic activity increases as follows: VO<sub>x</sub>/SiO<sub>2</sub> < VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> < VO<sub>x</sub>/ZrO<sub>2</sub> < VO<sub>x</sub>/TiO<sub>2</sub>. The inverse of this trend is observed for the apparent activation energy.<sup>9, 21-22</sup> A linear relationship has been previously established between the enthalpy of oxygen defect formation and the apparent activation energy for supported VO<sub>x</sub> materials.<sup>22</sup> This trend is consistent with observations of the dependence of ODH activity on the ease of reducibility of surface VO<sub>x</sub> species, which in turn has been postulated to be dependent on the strength of the V-O-S (S, Support) bond.<sup>9, 21, 23</sup> In contrast to the significant effect of the oxide support on alkane ODH activity, Carrero *et al.* have shown that the selectivityconversion trends remain unchanged with varying support materials.<sup>9</sup>

The identity of the oxide support can influence the distribution of vanadium oxide surface structures. For example, epitaxial growth of VO<sub>x</sub> films on crystalline titania has been reported,<sup>86, 129-130</sup> whereas crystalline V<sub>2</sub>O<sub>5</sub> particles preferentially form on the surface of SiO<sub>2</sub>.<sup>80</sup> Despite these structural differences, Goodrow and Bell concluded that, in methanol oxidation, higher activity of VO<sub>x</sub>/TiO<sub>2</sub> compared to VO<sub>x</sub>/SiO<sub>2</sub> cannot be associated with intrinsic electronic properties of VO<sub>x</sub> species. Instead, they postulated that oxygen vacancies present in proximity to the active site lower the activation energy of the rate limiting step.<sup>70</sup> Similarly, Yun *et al.* have found that surface oxygen vacancies on TiO<sub>2</sub> are involved in the reoxidation of VO<sub>x</sub> sites in the Mars-van Krevelen

mechanism in ethanol oxidation.<sup>131</sup> In addition, the energy of O vacancy formation in the bare oxide support has been correlated to ODH activity of supported VO<sub>x</sub> materials, suggesting that the support surface can be involved in the reaction mechanism.<sup>70</sup>

Ternary oxide systems, where a SiO<sub>2</sub> support is first modified with TiO<sub>2</sub> domains prior to the deposition of VO<sub>x</sub>, have been investigated for oxidation reactions in order to create high surface area materials with improved VO<sub>x</sub> reducibility.<sup>72-74</sup> Vining et al. reported that, in methanol oxidation, the activity of VO<sub>x</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> materials increases with increasing TiO<sub>2</sub> coverage at a constant surface density of VOx. They calculated apparent activation energies via density functional theory (DFT) and found that the calculated values decrease as a function of the number of V-O-Ti bonds. In addition, they showed that V centers with three equivalent V-O-S bonds are more energetically favorable.<sup>74</sup> A general trend demonstrating that transition metal oxides preferentially bind to metal oxide modifiers on the surface of silica has been established.<sup>132</sup> This leads to the improvement of the dispersion of  $VO_x$  species in the presence of sub-monolayer domains of TiO<sub>2</sub> on a SiO<sub>2</sub> support.<sup>72</sup> However, at low TiO<sub>2</sub> loadings propane ODH activity remains unchanged from that of VO<sub>x</sub>/SiO<sub>2</sub> suggesting an equivalent role of V-O-Ti and V-O-V bonds in the reaction mechanism. The ODH activity increases when TiO<sub>2</sub> coverages at and above a monolayer are achieved.<sup>72</sup> A particularly high propene yield was observed for a material with a joint monolayer of  $VO_x$  and  $TiO_2$  sites on the silica surface. However, selectivity remained a function of conversion due to the favorable readsorption of propene.<sup>72-73</sup>

The catalyst synthesis method has a significant impact on the distribution of the  $VO_x$  surface sites. The most common preparation methods for supported  $VO_x$  materials include incipient wetness impregnation and grafting. The former offers limited control over the resulting surface species and leads to the formation of  $V_2O_5$  even at low loadings, while the latter may result in the formation of polyvanadates in solution or during the drying step when the pH is no longer monitored to favor isolated VO<sub>x</sub> sites.<sup>9</sup> Achieving improved control over the speciation of surface VO<sub>x</sub> can aid in the understanding of their role in a reaction mechanism. This has been previously accomplished by synthesizing supported VO<sub>x</sub> catalysts with Ångstrom-level precision via atomic layer deposition (ALD).<sup>29, 48</sup>

In this chapter, we evaluate the activity of supported VO<sub>x</sub> materials synthesized by ALD in cyclohexane ODH. We compare the catalytic behavior of VO<sub>x</sub> on bulk alumina and bulk titania to VO<sub>x</sub> supported on alumina modified with TiO<sub>2</sub> domains grown by ALD. We study the effect of the amount of TiO<sub>2</sub> on the surface as well as the order of deposition of the two metal oxides. In Chapter 2, we investigated the interactions of VO<sub>x</sub> with amorphous TiO<sub>2</sub> domains on the surface of alumina both in their initial oxidized state and under reducing conditions at elevated temperatures. We found that a combination of ALD and calcination procedures has an impact on the distribution of surface VO<sub>x</sub> sites and, as a result, their reducibility.<sup>78</sup> Here, we use the insight gained from that extensive characterization study to explain differences in catalytic behavior. The systematic modification of the unreducible alumina support with domains of reducible TiO<sub>2</sub> allows us to gain an improved understanding of the contribution of the TiO<sub>2</sub> support to the superior activity of  $VO_x/TiO_2$ . We focus on cyclohexane ODH due to its diverse reaction network shown in Scheme 1.2, where C-H bond breaking on individual methylene groups leads to the formation of cyclohexene or benzene and the production of CO and CO<sub>2</sub> requires undesirable C-C bond scission.48

# **3.2 Methods**

### 3.2.1 Material Synthesis

VO<sub>x</sub> films were grown via ALD on Al<sub>2</sub>O<sub>3</sub> (32-40 m<sup>2</sup>/g; 70%  $\delta$  phase, 30%  $\gamma$  phase; 99.5% purity, Alfa Aesar NanoArc) and TiO<sub>2</sub> (45 m<sup>2</sup>/g; anatase phase; 99.9% purity, Alfa Aesar NanoArc) at 100 °C with vanadyl triisopropoxide (VOTP, Sigma-Aldrich) and water in a viscous flow reactor described previously.<sup>89</sup> The VOTP bubbler was heated to 45 °C and the water bubbler was at room temperature (RT). 300 s dose times were followed by 450 s nitrogen purge times for the metal precursor and water alike. The total N<sub>2</sub> flow during deposition was 160 sccm. The amount of VO<sub>x</sub> was kept constant at a single ALD cycle in all samples. VOx domains were also deposited on TiO2modifed alumina supports prepared by the deposition of titanium tetraisopropoxide (TTIP, Sigma-Alrich) and water in an Arradiance Gemstar-6 ALD system at 150 °C. The TTIP bubbler was heated to 80 °C and the water bubbler was at RT. A 5 s dose of TTIP was followed by a 180 s hold and 60 s nitrogen purge. Water was dosed for 5 s, held for 5 s and purged with nitrogen for 60 s. The alumina support was modified with varying amounts of TiO<sub>2</sub> (denoted as xcTiO<sub>2</sub>, where x represents the number of ALD cycles). In some cases, TiO<sub>2</sub> was deposited on previously calcined VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. Samples were calcined in air at 450 °C for 4 hours at a heating rate of 5 °C/min. The order of deposition is denoted as follows: VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> represents a sample where the alumina support was first modified with one cycle of TiO<sub>2</sub> ALD, followed by one cycle of VO<sub>x</sub> ALD.

# 3.2.2 Material Characterization

UV (244 nm) laser excited Raman spectra of the alumina-supported  $VO_x$ -TiO<sub>2</sub> materials were collected using a custom-built Raman instrument. The 244 nm excitation comes from a Lexel 95
SHG (second harmonic generation) laser equipped with an intracavity nonlinear crystal, BBO (BaB<sub>2</sub>O<sub>4</sub>), which frequency doubles visible radiation into the mid-ultraviolet region.<sup>12, 90-91</sup> The Raman spectra were collected under a controlled atmosphere with the use of a fluidized bed reactor developed by Chua and Stair to minimize the adverse effects of UV radiation.<sup>92</sup> The catalysts were heated in flowing O<sub>2</sub> at 450 °C for 30 min to remove any absorbed moisture prior to taking measurements. The spectra were collected at RT in flowing O<sub>2</sub>. The UV laser power at the sample position was approximately 5 mW into a spot size of ca. 200  $\mu$ m.<sup>93</sup> The spectral collection time was 40 min. The Raman shift was calibrated by measuring cyclohexane as a standard prior to every experiment.

XPS measurements were carried out on a Thermo Scientific ESCALAB 250Xi instrument (Thermo Scientific) equipped with a monochromatic Al K $\alpha$  X-ray source (hv = 1486.6 eV). The X-ray spot size was 500 µm in diameter. Scans were collected using a pass energy of 50 eV, a 50 ms dwell time and a 0.1 eV step size. An electron flood gun was applied to the sample surface to neutralize surface charging effects. The binding energies were referenced to the adventitious C1s C-C peak at 284.8 eV.

Nitrogen adsorption-desorption isotherms were collected using a Micrometrics 3-Flex instrument in the Reactor Engineering and Catalyst Testing (REACT) Core user facility at Northwestern University. The surface area of the samples was calculated from the adsorption isotherm using the BET method.

### 3.2.3 Catalyst Reducibility

 $H_2$  temperature programmed reduction (TPR) experiments were performed on an Altamira AMI-200 chemisorption instrument in the REACT Core user facility at Northwestern University. The materials were pretreated in flowing 10% O<sub>2</sub>/He at 450 °C for 1 hr. The experiments were carried out in 10%  $H_2/N_2$  from 100 to 600 °C at a 30 °C/min ramp rate. A thermal conductivity detector (TCD) was used to determine the  $H_2$  content of the outlet gas.

#### 3.2.4 Reaction Studies

Gas-phase cyclohexane ODH reaction studies were performed in the REACT Core user facility at Northwestern University. A quartz tube plug flow reactor was used. Cyclohexane vapor was introduced via bubbling of He through a cyclohexane bubbler which remained at a fixed pressure of 1.75 bar and a temperature of 21 °C. The catalytic tests were performed in the temperature range of 400-550 °C. 0.5 - 10 mg of catalyst was diluted with 300 mg of SiO<sub>2</sub> in each reaction to maintain a constant catalyst bed volume and enhance the heat distribution. Reactions were typically performed with  $P_{C6H12} = 2.2$  kPa,  $P_{O2} = 7.9$  kPa and a total flow rate of 100 ml min<sup>-1</sup> with He balance. The materials were pretreated in flowing 20% O<sub>2</sub>/He at 450 °C for 1 hr. The outlet gas was analyzed online using an Agilent 7890A gas chromatograph (GC). A DB-Wax column (Agilent, 30 m x 0.32 mm x 0.25 µm) was used to separate hydrocarbons, which were analyzed by a flame ionization detector (FID), while light hydrocarbons, O<sub>2</sub>, CO and CO<sub>2</sub> were separated through a combination of a HP-Q plot column (Restek, 30 m x 0.53 mm x 20 µm) and a molecular sieve 5Å capillary column (Restek, 15 m x 0.53 mm x 50 µm) and analyzed by a TCD. Carbon balances were closed within at error of  $\pm 3\%$ . Unless otherwise noted, conversion and selectivity are defined as follows:

$$Conversion = \frac{F_{out}(\sum_{i} y_{i,out} + \sum_{j} \frac{y_{j,out}}{6})}{F_{out}(y_{C_{6}H_{12},out} + \sum_{i} y_{i,out} + \sum_{j} \frac{y_{j,out}}{6})} * 100\%$$
(3.1)

$$Selectivity_{i} = \frac{y_{i,out}F_{out}}{F_{out}(\sum_{i}y_{i,out} + \sum_{j}\frac{y_{j,out}}{6})} * 100\%$$
(3.2)

$$Selectivity_{j} = \frac{\frac{y_{j,out}}{6}F_{out}}{F_{out}(\sum_{i}y_{i,out} + \sum_{j}\frac{y_{j,out}}{6})} * 100\%$$
(3.3)

where  $F_{out}$  is the total flow rate out of the reactor,  $y_{i,out}$  is the mol fraction of C<sub>6</sub> product *i* and  $y_{j,out}$  is the mol fraction of C<sub>1</sub> product *j* at the exit of the reactor. All calculations were performed on a per C<sub>6</sub> basis meaning that concentrations of CO and CO<sub>2</sub> were divided by 6.

# **3.3 Results and Discussion**

#### 3.3.1 Catalyst Characterization

The characterization of most of the materials evaluated for cyclohexane ODH is described in Chapter 2. The following results serve to describe the surface composition of  $VO_x/64cTiO_2/Al_2O_3$  in reference to the previously evaluated alumina-supported  $VO_x$ -TiO<sub>2</sub> materials. Figure 3.1 shows UV Raman spectra of  $VO_x/64cTiO_2/Al_2O_3$  and  $VO_x/TiO_2$  in direct comparison to those of bare  $Al_2O_3$  and TiO<sub>2</sub> supports.



**Figure 3.1.** UV Raman spectra of  $VO_x/64cTiO_2/Al_2O_3$  in direct comparison to  $Al_2O_3$  (A),  $VO_x/64cTiO_2/Al_2O_3$  in comparison to  $TiO_2$  (B) and  $VO_x/TiO_2$  together with bare  $TiO_2$  (C). The measured intensity of the  $Al_2O_3$  bands was divided by 10 to allow for a direct comparison with  $VO_x/64cTiO_2/Al_2O_3$ . The bands observed for bare  $Al_2O_3$  are a combination of  $Al_2O_3$  features and ones associated with the stainless steel porous disk of the fluidized bed setup as shown in Figure C.1.

Features associated with the V=O stretching vibration are observed at 1025 and 1028 cm<sup>-1</sup> for  $VO_x/64cTiO_2/Al_2O_3$  and  $VO_x/TiO_2$ , respectively. They indicate the presence of  $VO_x$  monomers on the surface of both materials.<sup>12</sup> These bands are shifted to a higher frequency in comparison to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, which at the constant V surface density, are influenced by the identity of the oxide support, in this case, the formation of V-O-Ti bonds.<sup>12, 104</sup> A number of bands is also present below  $900 \text{ cm}^{-1}$  for VO<sub>x</sub>/64cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Figure 3.1A and 3.1B present direct comparisons of this material with bare Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supports, respectively. The broad feature observed between 700 and 1000 cm<sup>-1</sup> is expected to be a combination of contribution from Al<sub>2</sub>O<sub>3</sub>, Ti-O-Ti linkages and V-O-S bonds.<sup>12, 107</sup> Anatase features have been observed at 147, 198, 398, 515 and 640 cm<sup>-1</sup>.<sup>108</sup> The 515 and 640 cm<sup>-1</sup> bands are clearly shown in the TiO<sub>2</sub> spectrum in Figures 3.1B and 3.1C. The lower wavenumber bands in VO<sub>x</sub>/64cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> include a mixture of features associated with both the porous disk of the fluidized setup and the TiO<sub>2</sub> support. The sharp increase in intensity between 400 and 515 cm<sup>-1</sup> observed for  $VO_x/64cTiO_2/Al_2O_3$  similar to the anatase spectrum demonstrates the formation of crystalline  $TiO_2$  in this material. The surface free energy of  $TiO_2$  is lower than that of Al<sub>2</sub>O<sub>3</sub>, which implies that the formation of a surface oxide layer is preferred to that of crystalline nanoparticles.<sup>8</sup> It is therefore expected that VO<sub>x</sub> domains on the surface of a crystalline  $TiO_2$  film on alumina are present in  $VO_x/64cTiO_2/Al_2O_3$ . Figure 3.1C indicates that all of the bands at frequencies lower than that of V=O are associated with the  $TiO_2$  support.

The initial oxidation state of the surface vanadium species was evaluated by XPS, and the relevant spectra are shown in Figure 3.2. Table 3.1 lists the binding energies associated with O1s and V2p<sub>3/2</sub> peaks. A shift to lower binding energies for both the O1s and the V2p<sub>3/2</sub> peaks is observed with increasing amounts of TiO<sub>2</sub>. This shift may be assigned to XPS final-state effects associated with the increased polarizability of TiO<sub>2</sub> in comparison to Al<sub>2</sub>O<sub>3</sub>.<sup>133-134</sup> O1s binding energies of bare Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supports are reported in Table 3.1 to further confirm that the observed binding energy shifts are due to the identity of the support material. The magnitude of the difference between the O1s and V2p<sub>3/2</sub> binding energies has been previously applied to unambiguously determine the oxidation state of vanadium species.<sup>135</sup> For single crystal and polycrystalline V<sub>2</sub>O<sub>5</sub> the value of this separation varied between 12.8 and 13.6 eV. This indicates that, in their oxidized state, the supported VO<sub>x</sub> species contain primarily V<sup>5+</sup> based on the data shown in Table 3.1.<sup>136</sup> In addition, a comparison of the ratios of peak areas of V 2p<sub>3/2</sub> and O 1s shown in Table 3.1 further confirms that a similar amount of VO<sub>x</sub> species is present on the surface of all of the materials.



**Figure 3.2.** V 2p spectra of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (A), VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (B), VO<sub>x</sub>/64cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (C) and VO<sub>x</sub>/TiO<sub>2</sub> (D). The V 2p<sub>3/2</sub> binding energy region is shown in E-H in the same order.

	O1s		V2p <sub>3/2</sub>			
Material	BE	FWHM*	BE	FWHM*	Δ** [eV]	A <sub>V2p3/2</sub> /A <sub>O1s</sub>
	[eV]	[eV]	[eV]	[eV]		
Al <sub>2</sub> O <sub>3</sub>	531.66	2.27	-	-	-	-
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	531.75	2.30	517.95	2.34	13.8	0.06
VO <sub>x</sub> /16cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	531.30	2.54	517.78	2.08	13.52	0.05
VO <sub>x</sub> /64cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	530.30	1.82	517.41	1.81	12.89	0.05
VO <sub>x</sub> /TiO <sub>2</sub>	530.31	1.51	517.32	1.94	12.99	0.08
TiO <sub>2</sub>	529.79	1.40	-	-	-	-

Table 3.1. O1s and V2p<sub>3/2</sub> binding energies (BE) in supported VO<sub>x</sub> materials.

\*FWHM stands for full width at half maximum

\*\*BE separation between O1s and V2p<sub>3/2</sub>

The thickness of the  $TiO_2$  films was estimated based on the attenuation of the intensity of the Al 2p signal from the support. The signal attenuation and the film thickness of the overlayer are correlated via the following equation:

$$\frac{I}{I_0} = exp\left[-\frac{d}{\lambda cos\theta}\right] \tag{3.4}$$

where I is the intensity of the support under an overlayer of thickness d,  $I_0$  is the intensity of a bare support (d=0),  $\lambda$  is the mean escape depth of photoelectrons at a given energy, and  $\theta$  is the angle with respect to the surface normal, at which the spectra were collected.<sup>137</sup> In order to account for changes in the spectra due to differential charging and instrumental variations, the ratios of the areas of the Al 2p and O 1s peaks were used in place of the intensities I and  $I_0$  under the assumption that the oxygen contribution is the same in all of the investigated materials.  $I_0$  was equal to 0.14 and the relevant I values are shown in Table 3.2. The mean escape depth of Al Ka X-ray excited Al 2p electrons at a kinetic energy of 1412 eV,13 Å, was used for the calculations.<sup>138</sup> The take-off angle was 45°. The TiO<sub>2</sub> film thickness values calculated using equation 3.4 matched the values obtained from surface density calculations based on the weight loading of Ti and the surface area of the material, as shown in Table 3.2. The resulting growth rate was estimated to be 0.4 Å/cycle. This is within the range of previously reported values, where the adsorption of TTIP is a selfsaturated process between 100 and 250 °C and the growth rate depends on the efficient removal of remaining precursor ligands determined by the deposition temperature and the nature of the oxidizing agent.105, 139

Catalyst	Ι	Ti weight %	Surface Area [m <sup>2</sup> /g]	TiO2 Thick1	2 Film ness [Å]	TiO <sub>2</sub> Rate [	Growth Å/cycle]
			-	XPS	ICP	XPS	ICP
VO <sub>x</sub> /16cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.11	6	37	4.4	6.8	0.3	0.4
VO <sub>x</sub> /64cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.04	18	36	23	24	0.4	0.4

Table 3.2. Properties of TiO<sub>2</sub> Films Grown by ALD.

#### 3.3.2 Cyclohexane ODH Reactivity

Cyclohexane ODH activity of supported VOx materials was evaluated in the 400 - 550 °C temperature range. Apparent activation energies with respect to the consumption of cyclohexane were calculated from the slope of ln(rate) vs. 1/T and are reported in Table 3.3. As shown in Figure 3.3,  $VO_x/Al_2O_3$  (blue) is significantly less active than  $VO_x/TiO_2$  (red) in agreement with previous literature reports.<sup>9, 21</sup> Modification of the alumina support with sub-monolayer TiO<sub>2</sub> domains prior to the deposition of VO<sub>x</sub> (green) does not significantly improve ODH activity, although marginally increased rates of cyclohexane consumption are observed at lower temperatures resulting in a decrease in the apparent activation energy. In contrast,  $1cTiO_2/VO_x/Al_2O_3$  (purple) shows increased catalytic activity with an apparent activation energy comparable to  $VO_x/1cTiO_2/Al_2O_3$ . This suggests that 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> contains an increased amount of a similar active site to that which is present in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Cyclohexane ODH activity can be further improved by the deposition of thicker TiO<sub>2</sub> films on the alumina support. VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (orange) shows higher activity than that of catalysts modified with a single ALD cycle of  $TiO_2$ , and VO<sub>x</sub>/64cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (pink) resembles the catalytic behavior of VO<sub>x</sub>/TiO<sub>2</sub>. The alumina support is expected to be completely covered by a TiO<sub>2</sub> film in both VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and  $VO_x/64cTiO_2/Al_2O_3$ .<sup>78</sup> This dissimilar catalytic behavior of the two materials implies that different distributions of active sites are present on the two surfaces and their improved activity cannot be simply explained by the replacement of V-O-Al bonds with V-O-Ti. The apparent activation energies of VO<sub>x</sub> supported on TiO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> fall within the range established between  $VO_x/TiO_2$  (64 kJ/mol) and  $VO_x/Al_2O_3$  (107 kJ/mol) and decrease with increasing TiO<sub>2</sub> loading. An equivalent trend has been reported for  $VO_x/TiO_2/SiO_2$  in methanol oxidation.<sup>74</sup>

Table 3.3. Apparent activation energies of supported VO<sub>x</sub> materials.

Catalyst	E <sub>A,app</sub> [kJ/mol]
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	$107 \pm 3$
VO <sub>x</sub> /1cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	97 ± 2
1cTiO <sub>2</sub> /VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	98 ± 2
VO <sub>x</sub> /16cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	84 ± 2
VO <sub>x</sub> /64cTiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	$78 \pm 2$
VO <sub>x</sub> /TiO <sub>2</sub>	64 ± 2



Figure 3.3. Temperature dependence of the cyclohexane consumption rate for supported VO<sub>x</sub> materials. Experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>.

An inverse relationship between the activity of  $VO_x$  supported on bulk metal oxides in alkane ODH reactions and the ease of reducibility of the  $VO_x$  surface sites determined by the temperature of the H<sub>2</sub> consumption peak maximum in H<sub>2</sub> TPR experiments has been previously reported in the literature.<sup>21-23</sup> The H<sub>2</sub> TPR profiles from Figure 2.7, modified to include  $VO_x/64cTiO_2/Al_2O_3$ , are shown as Figure 3.4.



Figure 3.4. H<sub>2</sub> TPR profiles of supported VO<sub>x</sub> materials.

The catalytic behavior of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> depicted in Figure 3.3 is accurately captured by similar H<sub>2</sub> TPR profiles of the two materials. The comparable temperatures of the H<sub>2</sub> consumption peak maximum can explain the lack of significant differences in the rate of C<sub>6</sub>H<sub>12</sub> disappearance and the fact that hydrogen consumption is first observed at lower temperatures for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> than for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> can explain the slightly higher activity between 400 and 450 °C for the former catalyst. The extensive characterization study described in Chapter 2 indicated that VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> consists of both monomeric and polymeric surface VO<sub>x</sub> structures whereas VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is characterized by well-dispersed VO<sub>x</sub> sites bound to isolated TiO<sub>2</sub> domains.<sup>78</sup> Therefore, VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> includes a distribution of V-O-Al and V-O-V bonds and VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> contains exclusively V-O-Al and V-O-Ti bonds. The nearly identical catalytic behavior and H<sub>2</sub> reducibility profiles of the two materials imply that the contribution of V-O-V and V-O-Ti bonds to the cyclohexane ODH reaction mechanism is equivalent. This is in agreement with a previously published claim that two dimensional vanadium oxide oligomers and VO<sub>x</sub>

monomers bound to highly dispersed sub-monolayer TiO<sub>2</sub> domains supported on SBA-15 are equivalent in propane ODH.<sup>72</sup>  $1cTiO_2/VO_x/Al_2O_3$  includes both monomeric and polymeric  $VO_x$ surface structures bound to TiO<sub>2</sub>, which result in the presence of V-O-Al, V-O-V and V-O-Ti bonds.<sup>78</sup> The H<sub>2</sub> consumption peak of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> has been previously shown to shift to lower temperatures with increasing V loading up to a monolayer coverage at which point the trend was reversed. This implies that at sub-monolayer coverages polymerized VO<sub>x</sub> species are more easily reducible by H<sub>2</sub>.<sup>140</sup> The improved reducibility of  $1cTiO_2/VO_x/Al_2O_3$  can therefore be explained by a combined effect of the presence of polymerized VOx domains and their binding to well-dispersed TiO<sub>2</sub> sites. These more easily reducible VO<sub>x</sub> species lead to an increase in ODH activity as shown in Figure 3.3. Additionally, we have shown by in-situ UV Raman spectroscopy experiments that Ti-O-Ti bonds form on the surface of VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> at lower temperatures than for 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. This implies the presence of isolated TiO<sub>2</sub> monomers which are not bound to VO<sub>x</sub> species in VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. In contrast, well dispersed TiO<sub>2</sub> sites which form V-O-Ti bonds with VO<sub>x</sub> domains are found in  $1cTiO_2/VO_x/Al_2O_3$ .<sup>78</sup> This further confirms that the higher ODH activity of  $1cTiO_2/VO_x/Al_2O_3$  can be assigned to a higher density of more active VO<sub>x</sub> sites with V-O-Ti bonds given that the Ti content is the same in the two materials.

The differences in ODH activity of the remaining catalysts cannot be adequately described by the ease of reducibility of  $VO_x$  sites.  $1cTiO_2/VO_x/Al_2O_3$ ,  $VO_x/16cTiO_2/Al_2O_3$  and  $VO_x/64cTiO_2/Al_2O_3$  exhibit H<sub>2</sub> consumption peaks positioned in a fixed temperature range despite their varying catalytic behavior. This indicates that the role of the TiO<sub>2</sub> support is more substantial than the formation of V-O-Ti bonds leading to improved reducibility of  $VO_x$  surface sites. The enhanced catalytic behavior of  $VO_x/TiO_2$  in oxidation reactions has been previously attributed to

the presence of defects in the form of O vacancies on the surface of the support.<sup>70, 131, 141</sup> Electron paramagnetic resonance (EPR) has been used to detect oxygen vacancies in VO<sub>x</sub>/TiO<sub>2</sub> prior to and following propane ODH. Electrons trapped at Ti(IV) sites and on surface bound molecular oxygen have been hypothesized to influence the redox cycle of this catalyst.<sup>141</sup> The defects have been shown to preferentially form in proximity to VO<sub>x</sub> sites and lower the activation energy of the rate determining H-abstraction from an adsorbed methoxy group in methanol oxidation.<sup>70</sup> It has also been postulated that O vacancies are involved in the reoxidation of the catalytically active VO<sub>x</sub> species in ethanol oxidation, where O<sub>2</sub> from the gas phase adsorbs on a defect site on TiO<sub>2</sub> and migrates to the reduced vanadium center.<sup>131</sup>

Changes in the geometry and electronic structure of crystalline TiO<sub>2</sub> upon defect formation have been extensively studied in the literature.<sup>142</sup> In addition, O vacancies were previously reported to exist in sub-monolayer amorphous TiO<sub>2</sub> domains on SiO<sub>2</sub>.<sup>127</sup> From DFT calculations, it is known that at least one of the two excess electrons from a single defect localizes on the next-nearest neighbor Ti ion. The other can be localized on either the nearest Ti to the defect or another nextnearest neighbor, depending on the model.<sup>142</sup> This implies that in the case of TiO<sub>2</sub> films deposited on Al<sub>2</sub>O<sub>3</sub>, extended networks of TiO<sub>2</sub> are necessary for the formation of O vacancies given that Al sites are unlikely to undergo reduction. Therefore, even though the formation of Ti-O-Ti bonds has been observed for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> under reducing conditions at elevated temperatures by UV Raman spectroscopy, we do not expect the presence of O vacancies in materials modified with a single ALD cycle of TiO<sub>2</sub>.<sup>78</sup> The extent of reduction of 2D TiO<sub>2</sub> clusters on SiO<sub>2</sub> has been correlated to the Ti loading, implying that an increased number of oxygen vacancies can be formed at higher TiO<sub>2</sub> surface coverages.<sup>127</sup> Additionally, the apparent activation energy for methanol oxidation of VO<sub>x</sub> supported on these TiO<sub>2</sub>/SiO<sub>2</sub> materials decreases when an O vacancy is present adjacent to the active site.<sup>74</sup> In the current work, the improved ODH activity of VO<sub>x</sub>/64cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> compared to VO<sub>x</sub>/16cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> can be explained by the higher density of O vacancies in the thicker crystalline TiO<sub>2</sub> film. These defects are more energetically favorable on the surface, where they can participate in the reaction mechanism.<sup>143-144</sup> However, they constitute at most 1-2% of surface O atoms, which implies that at a coverage of 64 cycles of TiO<sub>2</sub> ALD on Al<sub>2</sub>O<sub>3</sub> the surface of the support is saturated with defects and hence becomes equivalent to a bulk TiO<sub>2</sub> support.<sup>70</sup> In order to confirm that VO<sub>x</sub> sites are the active species in these materials, we evaluated the activity of the bulk TiO<sub>2</sub> support and compared it to that of VO<sub>x</sub>/TiO<sub>2</sub>. Figure 3.5 shows the conversion of the two materials in the 400 – 550 °C temperature range. The significantly decreased catalytic performance of the bare support indicates that its only role in VO<sub>x</sub>/TiO<sub>2</sub> catalysts is the enhancement of the activity of VO<sub>x</sub> species. This is consistent with our previous XPS results, described in Chapter 2, which indicate that only the oxidation state of VO<sub>x</sub> species, and not that of TiO<sub>2</sub>, changes significantly following reduction with H<sub>2</sub> at elevated temperatures.<sup>78</sup>



**Figure 3.5.** Catalytic activity of VO<sub>x</sub>/TiO<sub>2</sub> compared to the bare support in the 400 to 550 °C temperature range. 5.2 mg of each material was used. Experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>.

# 3.3.3 Selectivity-Conversion Trajectories

Figure 3.6 shows the selectivity of the supported VO<sub>x</sub> catalysts towards cyclohexene, benzene, CO<sub>2</sub> and CO evaluated at 450 °C. When compared in a fixed conversion range, all of the examined materials follow the same selectivity-conversion curves where the selectivity towards the desired product, cyclohexene, decays exponentially with increasing conversion. This is in agreement with a previously established trend that the selectivity of supported VO<sub>x</sub> materials in propane ODH is independent of the support material and that it is only a function of conversion.<sup>9</sup> Figure 3.7 shows fits of selectivity-conversion trajectories for VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The cyclohexene and benzene products selectivity-conversion data is fit to exponential decay and growth curves, respectively, and the CO<sub>x</sub> data is shown with linear curves. The extrapolation of



these fits to 0% conversion yields selectivity values for  $C_6H_{10}$ ,  $CO_2$  and CO, which add up to 100%.

**Figure 3.6.** Selectivity-conversion profiles for supported VO<sub>x</sub> catalysts in cyclohexane ODH at T = 450 °C and P = 1 atm. All experiments were performed at a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 and with flow rates varying between 50 and 100 ml min<sup>-1</sup>.



Figure 3.7. Fitted selectivity-conversion trajectories for  $VO_x/1cTiO_2/Al_2O_3$  (A) and  $1cTiO_2/VO_x/Al_2O_3$  (B).

According to the delplot method, a finite y-intercept in a plot of molar yield divided by conversion (selectivity) vs. conversion indicates that a given product is primary.<sup>145</sup> As shown in Figures 3.6 and 3.7, cyclohexene, CO<sub>2</sub> and CO are primary products for all of the examined catalysts. The direct formation of CO<sub>x</sub> products from cyclohexane can be a result of C-C bond breaking or the breaking of both C-H bonds on a single methylene group. The energy of a C-C bond is lower than those of primary and secondary C-H bonds, which implies that C-C bond breaking is the more probable event.<sup>54</sup> The extrapolation of the selectivity-conversion trajectory indicates a near zero intercept for benzene, suggesting that it is a higher order product. Moreover, Figure 3.8 shows yield/conversion<sup>2</sup> vs. conversion data, where the trajectory associated with cyclohexene clearly diverges, confirming this is a primary product.<sup>145</sup> The formation of benzene involves a sequential C-H bond abstraction, which is favorable given the lower allylic C-H bond dissociation in

cyclohexene than that of the secondary C-H in cyclohexane.<sup>54</sup> Furthermore, the C-H bond dissociation energy in benzene is significantly higher, which results in the termination of overoxidation by sequential C-H bond breaking at benzene.<sup>57</sup>



Figure 3.8. Second-rank delplots of cyclohexene and benzene for supported VO<sub>x</sub> catalysts.

# **3.4 Conclusions**

We have evaluated the catalytic activity of alumina-supported VO<sub>x</sub>-TiO<sub>2</sub> materials in cyclohexane ODH and compared these catalysts to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/TiO<sub>2</sub>. We have shown that at a constant V surface density the catalytic activity increases with increasing thickness of TiO<sub>2</sub> films on Al<sub>2</sub>O<sub>3</sub>. An approximately 2.5 nm thick film of TiO<sub>2</sub> deposited on Al<sub>2</sub>O<sub>3</sub> is an equivalent support to bulk anatase. We attribute the differences in the activity and apparent activation energy of VO<sub>x</sub> supported on TiO<sub>2</sub> films of varying thickness to the density of oxygen vacancies on the surface of the support. We have shown that the ease of reducibility of VO<sub>x</sub> surface species under H<sub>2</sub> is primarily dependent on the distribution of V-O-Al, V-O-V and V-O-Ti bonds and that the latter two affect this property in a similar manner. For this reason, the H<sub>2</sub> TPR method cannot accurately capture all of the differences in catalytic activity between materials with increased fractions of V-O-V and V-O-Ti bonds. While the composition of the support has a significant impact on cyclohexane ODH activity, the selectivity profile of supported  $VO_x$  materials is only a function of conversion.

# 4 Structure and Activity of Mixed VO<sub>x</sub>-CeO<sub>2</sub> Domains Supported on Alumina in Cyclohexane Oxidative Dehydrogenation

# 4.1 Introduction

Cerium oxide has found a number of catalytic applications due to its remarkable redox properties. It is used industrially in three-way catalytic converters for the treatment of exhaust gases from automobiles and in fluid catalytic cracking for the removal of  $SO_x$  from flue gases.<sup>146-148</sup> The mobility of lattice ions, the ease of changing oxidation state between C<sup>4+</sup> and Ce<sup>3+</sup> and the oxidizing capability of Ce<sup>4+</sup> contribute to the catalytic activity of bulk CeO<sub>2</sub>. However, the oxide favors total oxidation reactions. The selectivity towards partial oxidation products can be improved by introducing dopants or incorporating different elements into the lattice.<sup>148</sup> The deposition of VO<sub>x</sub> species on a CeO<sub>2</sub> support has been reported to result in high activity and selectivity in oxidation reactions.<sup>21-22, 149-154</sup> However, it is difficult to directly observe how the two metal oxides interact with each other and individually contribute to reaction mechanisms.

The role of the CeO<sub>2</sub> support in methanol oxidation catalyzed by VO<sub>x</sub>/CeO<sub>2</sub> has been previously investigated by DFT calculations. Ganduglia-Pirovano *et al.* have found that a special synergistic effect exists between VO<sub>x</sub> species and the CeO<sub>2</sub> support, where ceria undergoes reduction while monomeric VO<sub>x</sub> species remain fully oxidized during the reaction.<sup>68</sup> This direct participation of the support has been reported to lead to stronger binding of methanol to the surface and the lowering of the energy required for H transfer.<sup>69</sup> The overall catalytic activity of VO<sub>x</sub>/CeO<sub>2</sub> materials has been found to decrease with increasing VO<sub>x</sub> domain size based on oxygen defect formation energies.<sup>66-67</sup> Negligible changes in the oxidation state of V in  $VO_x/CeO_2$  under ODH reaction conditions have also been observed by EPR, XANES and <sup>18</sup>O isotope exchange experiments.<sup>151, 155</sup>

The determination of structure-reactivity relationships for  $VO_x/CeO_2$  catalysts is further complicated by the formation of a mixed metal oxide phase, CeVO<sub>4</sub>, between the surface vanadium oxide and the bulk ceria support. This solid-state reaction is promoted by a reducing environment at elevated temperatures and increasing vanadium loadings.<sup>152</sup> The catalytic activity of  $VO_x/CeO_2$ generally decreases with increasing amounts of  $VO_x$ , which is related to both the decreased fraction of exposed CeO<sub>2</sub> surface sites and the formation of CeVO<sub>4</sub>.<sup>151</sup> The activation energy in ethane ODH has been shown to not be affected by the presence of the CeVO<sub>4</sub> phase. This suggests that V-O-Ce bonds present in dispersed VO<sub>x</sub> on a ceria surface and in CeVO<sub>4</sub> are involved in the rate determining step.<sup>155</sup>

CeO<sub>2</sub> domains have been previously dispersed on high surface area supports such as alumina and silica, and vanadium oxide species have been deposited on the mixed oxides to create ternary oxide catalysts.<sup>77, 156-157</sup> CeO<sub>2</sub> has a tendency to sinter at elevated temperatures, and its deposition on an oxide support often leads to the formation of small crystallites. The cerium precursor and synthesis conditions are known to influence the resulting CeO<sub>2</sub> surface speciation.<sup>157</sup> As a result, a number of studies of supported mixed VO<sub>x</sub>-CeO<sub>2</sub> materials are based on interactions of VO<sub>x</sub> species with ceria nanoparticles as opposed to well-dispersed surface sites. For example, Jehng reported that in the presence of CeO<sub>2</sub> particles, VO<sub>x</sub> species tend to bind to the SiO<sub>2</sub> support, which does not allow a rigorous probing of the VO<sub>x</sub>-CeO<sub>2</sub> interface.<sup>158</sup> Vining *et al.* found that, at low Ce surface densities, the catalytic activity of VO<sub>x</sub>/CeO<sub>2</sub>/SiO<sub>2</sub> in methanol oxidation increases in comparison

to  $VO_x/SiO_2$  but does not vary significantly with differing amounts of CeO<sub>2</sub>.<sup>77</sup> However, increased ethane ODH activity of supported VO<sub>x</sub> materials was reported with increasing amounts of CeO<sub>2</sub> on silica beyond a monolayer coverage.<sup>30</sup>

Conformal and thermally stable CeO<sub>2</sub> films have been previously grown on Al<sub>2</sub>O<sub>3</sub> supports by ALD by Onn *et al.*<sup>159</sup> The characterization of these materials with high angle annular dark field (HAADF) STEM imaging revealed complete coverage of alumina with a film of uniform thickness, but also the presence of small particles following calcination at 800 °C. The authors prepared another material for comparison by infiltration with an aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O which resulted in the formation of CeO<sub>2</sub> clusters, leaving behind a significant amount of exposed Al<sub>2</sub>O<sub>3</sub> surface. 0.4 nm thick films of CeO<sub>2</sub> deposited by ALD on alumina were reported to have the same effect on the activity of supported Pd as a bulk ceria support in the watergas shift reaction.<sup>159</sup> This suggests that ALD is a viable method for a systematic study in which the role of V-O-Ce bonds between VO<sub>x</sub> species and well-dispersed CeO<sub>2</sub> sites on an inert oxide support can be distinguished from the contribution of extended CeO<sub>2</sub> structures as well as crystalline CeO<sub>2</sub>.

In this chapter, the impact of CeO<sub>2</sub> domains on the surface distribution and resulting catalytic activity of VO<sub>x</sub> species is examined by synthesizing mixed metal oxide materials on an alumina support by ALD. Raman spectroscopy and XPS are used to determine the surface metal oxide speciation of catalysts synthesized with single ALD cycles of VO<sub>x</sub> and CeO<sub>2</sub> with varying order of deposition and to compare the resulting structures to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub>. These materials are also evaluated for cyclohexane ODH, where differences in activity and product distributions are interpreted based on the structural information gained from spectroscopic characterization.

## 4.2 Methods

#### 4.2.1 Material Synthesis

VO<sub>x</sub> films were grown via ALD on Al<sub>2</sub>O<sub>3</sub> (32-40 m<sup>2</sup>/g; 70%  $\delta$  phase, 30%  $\gamma$  phase; 99.5% purity, Alfa Aesar NanoArc) and CeO<sub>2</sub> (30-50 m<sup>2</sup>/g; 99.5% purity, Alfa Aesar) at 100 °C with vanadyl triisopropoxide (VOTP, Sigma-Aldrich) and water in a viscous flow reactor described previously.<sup>89</sup> The VOTP bubbler was heated to 45 °C and the water bubbler was at room temperature (RT). VO<sub>x</sub> domains were also deposited on CeO<sub>2</sub>-modifed alumina supports prepared by the deposition of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV) (Ce(TMHD)<sub>4</sub>, Strem) and ozone at 230 °C. The Ce(TMHD)<sub>4</sub> bubbler was heated to 180 °C. In both ALD processes, a 300 s dose of the reactant was followed by a 450 s nitrogen purge time. The total N<sub>2</sub> flow during deposition was 160 sccm. The amounts of VO<sub>x</sub> and CeO<sub>2</sub> were kept constant at single ALD cycles. The Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> supports were dried in the reactor under N<sub>2</sub> flow at 230 °C for 1 hr prior to the ALD process. The order of deposition of the two metal oxides on alumina was varied. This is denoted as follows: VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> represents a sample where the alumina was first modified with a single cycle of CeO<sub>2</sub>, followed by one cycle of VO<sub>x</sub> ALD. Samples were calcined in air at 450 °C for 4 hours at a heating rate of 5 °C/min.

# 4.2.2 Material Characterization

The samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo iCAP 7600 instrument calibrated with V and Ce standards of known concentration in order to determine the metal content.

UV (244 nm) and visible (488 nm) laser excited Raman spectra were collected using a custombuilt Raman instrument. The 244 nm excitation comes from a Lexel 95 SHG (second harmonic generation) laser equipped with an intracavity nonlinear crystal, BBO (BaB<sub>2</sub>O<sub>4</sub>), which frequency doubles visible radiation into the mid-ultraviolet region.<sup>12, 90-91</sup> The Raman spectra were collected under a controlled atmosphere with the use of a fluidized bed reactor developed by Chua and Stair to minimize the adverse effects of UV radiation.<sup>92</sup> The catalysts were heated in flowing O<sub>2</sub> at 450 °C for 30 min to remove any absorbed moisture prior to taking measurements. The spectra were collected at RT in flowing O<sub>2</sub>. The visible laser power at the sample position was approximately 50 mW and that of the UV laser was 5 mW into a spot size of ca. 200  $\mu$ m.<sup>93</sup> The spectral collection time was 40 min. The Raman shift was calibrated by measuring cyclohexane as a standard prior to every experiment. In addition, in-situ reduction measurements of CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> were carried out with UV-excited Raman spectroscopy. The samples were reduced at a desired temperature between 450 and 600 °C in flowing 10%H<sub>2</sub>/N<sub>2</sub> for 1 hour and cooled down to RT in nitrogen. The catalysts were also re-oxidized in flowing O<sub>2</sub> at 450 °C. The spectra were collected at RT in flowing N<sub>2</sub>.

XPS measurements were carried out on a Thermo Scientific ESCALAB 250Xi instrument (Thermo Scientific) equipped with a monochromatic Al K $\alpha$  X-ray source (hv = 1486.6 eV). The X-ray spot size was 500 µm in diameter. Scans were collected using a pass energy of 50 eV, a 50 ms dwell time and a 0.1 eV step size. An electron flood gun was applied to the sample surface to neutralize surface charging effects. The binding energies were referenced to the adventitious C1s C-C peak at 284.8 eV.

## 4.2.3 Reaction Studies

Gas-phase cyclohexane ODH reaction studies were performed in the REACT Core user facility at Northwestern University. A quartz tube plug flow reactor was used. Cyclohexane vapor was introduced via bubbling of He through a cyclohexane bubbler which remained at a fixed pressure of 1.75 bar and a temperature of 21 °C. The catalytic tests were performed in the temperature range of 400-550 °C. Generally 1 - 35 mg of catalyst was diluted with 300 mg of SiO<sub>2</sub> in each reaction to maintain a constant catalyst bed volume and enhance the heat distribution. Lower amounts of bare CeO<sub>2</sub>, on the order of 0.1 mg, were tested to achieve conversions below 10 %. Reactions were typically performed with  $P_{C6H12} = 2.2$  kPa,  $P_{O2} = 7.9$  kPa and a total flow rate of 100 ml min<sup>-1</sup> with He balance. The materials were pretreated in flowing 20% O<sub>2</sub>/He at 450 °C for 1 hr. The outlet gas was analyzed online using an Agilent 7890A gas chromatograph (GC). A DB-Wax column (Agilent, 30 m x 0.32 mm x 0.25 µm) was used to separate hydrocarbons, which were analyzed by a flame ionization detector (FID), while light hydrocarbons, O<sub>2</sub>, CO and CO<sub>2</sub> were separated through a combination of an HP-Q plot column (Restek, 30 m x 0.53 mm x 20 µm) and a molecular sieve 5Å capillary column (Restek, 15 m x 0.53 mm x 50 µm) and analyzed by a TCD. Carbon balances were closed within an error of ±3%. Unless otherwise noted, conversion and selectivity are defined as follows:

$$Conversion = \frac{F_{out}(\sum_{i} y_{i,out} + \sum_{j} \frac{y_{j,out}}{6})}{F_{out}(y_{c_{6}H_{12},out} + \sum_{i} y_{i,out} + \sum_{j} \frac{y_{j,out}}{6})} * 100\%$$
(4.1)

$$Selectivity_{i} = \frac{y_{i,out}F_{out}}{F_{out}(\sum_{i}y_{i,out} + \sum_{j}\frac{y_{j,out}}{6})} * 100\%$$
(4.2)

$$Selectivity_{j} = \frac{\frac{y_{j,out}}{6}F_{out}}{F_{out}(\sum_{i}y_{i,out} + \sum_{j}\frac{y_{j,out}}{6})} * 100\%$$
(4.3)

where  $F_{out}$  is the total flow rate out of the reactor,  $y_{i,out}$  is the mol fraction of C<sub>6</sub> product *i* and  $y_{j,out}$  is the mol fraction of C<sub>1</sub> product *j* at the exit of the reactor. All calculations were performed on a per C<sub>6</sub> basis, meaning that concentrations of CO and CO<sub>2</sub> were divided by 6.

## 4.3 Results and Discussion

## 4.3.1 Surface Characterization of Supported VO<sub>x</sub> Materials

The metal content in all of the materials was quantified by ICP-OES. The V and Ce surface densities calculated based on the range of support surface areas provided by the manufacturer are shown in Table 4.1. The V surface density remained relatively constant between 1 and 2 V/nm<sup>2</sup> with an increased value in the 2-3 V/nm<sup>2</sup> range on the ceria support. The Ce content depended on the order of deposition of the two metal oxides by ALD. The materials remained under a controlled N<sub>2</sub> atmosphere in the ALD reactor chamber in between depositions and hence they were dehydrated to a similar extent. The reason for the dissimilarity in the surface densities of CeO<sub>2</sub> species may be that the presence of VO<sub>x</sub> surface sites on the alumina support creates an increased number of active sites for Ce(TMHD)<sub>4</sub> precursor reaction. The significantly lower density of CeO<sub>2</sub> species in comparison to VO<sub>x</sub> resulting from a single ALD cycle may be associated with steric constraints due to the bulkiness of the Ce(TMHD)<sub>4</sub> precursor. Another reason previously postulated in the literature is that the precursor shows low reactivity with an oxidized surface resulting in limited adsorption during the precursor dose.<sup>160</sup> The growth rates for Ce(TMHD)<sub>4</sub>.<sup>159</sup>.

Material	V/nm <sup>2</sup>	Ce/nm <sup>2</sup>
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	1.9 – 2.3	
VO <sub>x</sub> /CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.2 – 1.4	0.03 - 0.04
CeO <sub>2</sub> /VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	0.8 – 1	0.13 – 0.16
VO <sub>x</sub> /CeO <sub>2</sub>	2.2 - 3.6	

**Table 4.1.** Surface densities of V and Ce for the investigated materials.

The materials were further characterized by Raman spectroscopy in order to gain insight about the surface speciation of vanadium oxide in the presence of CeO<sub>2</sub>. A multiwavelength excitation approach made it possible to distinguish between monomeric and polymeric  $VO_x$  species as well as crystalline V<sub>2</sub>O<sub>5</sub>. Selective resonance enhancement of UV Raman towards isolated and less polymerized VO<sub>x</sub> sites and that of visible Raman towards highly polymerized VO<sub>x</sub> species and crystalline V<sub>2</sub>O<sub>5</sub> enables this differentiation.<sup>12</sup> UV Raman spectra of the examined materials are shown in Figure 4.1. A V=O stretching vibration centered between 1014 and 1025 cm<sup>-1</sup>, which indicates the presence of isolated VO<sub>x</sub> surface sites, was observed for all of the materials. The similarity of the VOx/Al2O3 (blue) and VOx/CeO2/Al2O3 (green) spectra suggests that the deposition of a single ALD cycle of CeO<sub>2</sub> prior to VO<sub>x</sub> growth does not significantly impact the resulting monomer surface speciation. In contrast, the CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> spectrum (purple) shows a shift of the V=O band to a lower wavenumber and increased relative intensities of peaks below 1000 cm<sup>-1</sup>. A comparison of CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and bare Al<sub>2</sub>O<sub>3</sub> is shown in Figure 4.1B. Bands associated with an alumina support have been previously reported to appear stronger in the presence of reduced low loading VO<sub>x</sub> species supported on  $\theta$ -Al<sub>2</sub>O<sub>3</sub>.<sup>24</sup> The lower intensity of the vanadyl band in comparison to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and the enhanced signal from the

underlying support can therefore be indicative of the interaction of the Ce(TMHD)<sub>4</sub> precursor with VO<sub>x</sub> surface sites, which undergo reduction during the ALD process. The decrease in V=O signal intensity could also be associated with the consumption of these functionalities to form a CeVO<sub>4</sub> phase. However, this typically occurs at temperatures above 500 °C under reducing conditions in materials with increased V loading. Additionally, bands associated with CeVO<sub>4</sub> at 260, 368, 770 and 842 cm<sup>-1</sup> cannot be easily distinguished from the Al<sub>2</sub>O<sub>3</sub> features in the spectra in Figure 4.1B.<sup>152, 155, 162</sup> CeO<sub>2</sub> exhibits strong electronic absorption in the UV region due to the higher energy of UV light than that of the band gap of the metal oxide.<sup>162-164</sup> This results in significantly lower intensities of features assigned to VO<sub>x</sub> species on the surface of a ceria support.<sup>162</sup> Figure 4.1C shows VO<sub>x</sub>/CeO<sub>2</sub> in direct comparison with a bare CeO<sub>2</sub> support, where a V=O stretching vibration is observed at 1025 cm<sup>-1</sup> for the former material. Bands observed at 708-714 and 857-880 cm<sup>-1</sup> have been previously assigned to V-O-Ce bridging modes.<sup>140, 162</sup> However, features at these frequencies cannot be easily distinguished from the contribution of the alumina and ceria supports at the 244 nm excitation wavelength, as shown in Figure 4.1. Given the comparable surface density of V on both alumina and ceria supports, the difference between the V=O frequencies is expected to be due to the identity of the support material.<sup>165</sup>



**Figure 4.1.** UV Raman spectra of supported VO<sub>x</sub> materials (A). A direct comparison of CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and the Al<sub>2</sub>O<sub>3</sub> support is shown in (B) and a direct comparison of VO<sub>x</sub>/CeO<sub>2</sub> and CeO<sub>2</sub> can be found in (C). The bands observed for bare Al<sub>2</sub>O<sub>3</sub> are a combination of Al<sub>2</sub>O<sub>3</sub> features and ones associated with the stainless steel porous disk of the fluidized bed setup as shown in Figure C.1.

Visible Raman spectra were collected to characterize polymeric VO<sub>x</sub> surface sites. They are shown in Figure 4.2. A band associated with the V=O stretching frequency is observed in all of the materials except for CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (purple), indicating that the deposition of CeO<sub>2</sub> domains following the growth of vanadium oxide can improve the dispersion of the latter. The shape of the vanadyl band observed for VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (green) is similar to that on VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (blue). However, its width is broader and matches that of VO<sub>x</sub>/CeO<sub>2</sub> (red). The V=O band in VO<sub>x</sub>/CeO<sub>2</sub> at 488 nm excitation is apparent due to the lack of self-absorption from the CeO<sub>2</sub> support. Increasing intensity of the V=O has been previously reported with increasing excitation wavelengths. A band at 1008 cm<sup>-1</sup> was assigned to monomeric VO<sub>x</sub>, 1015 cm<sup>-1</sup> to dimeric, 1022-1030 cm<sup>-1</sup> to trimeric and 1044 cm<sup>-1</sup> to polymeric VO<sub>x</sub> species.<sup>162</sup> This suggests that a mixture of various VO<sub>x</sub> domains exists on the surface of VO<sub>x</sub>/CeO<sub>2</sub>. Similarly, a distribution of VO<sub>x</sub> species with both V-O-Al and V-O-Ce bonds is expected on the surface of VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Crystalline V<sub>2</sub>O<sub>5</sub> was not detected in any of the supported VO<sub>x</sub> materials as indicated by the absence of a sharp V=O band at approximately 995 cm<sup>-1</sup>.<sup>12, 162</sup>



Figure 4.2. Visible Raman spectra of supported VO<sub>x</sub> materials.

The CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> material was further examined by performing an in-situ reduction UV Raman study. The resulting spectra, following reduction between 450 and 600 °C in 50 °C increments are shown in Figure 4.3. A sharper vanadyl band centered at a higher frequency is observed following H<sub>2</sub> treatment at elevated temperatures (Figure 4.3C). This change is accompanied by the disappearance of a feature centered at approximately 990 cm<sup>-1</sup>. This feature was observed for a bare alumina support in Figure 4.1B, and hence a plausible explanation for the observed differences is that under reducing conditions new bonds form with the Al<sub>2</sub>O<sub>3</sub> support. A shift to a higher frequency could also be explained by the clustering of VO<sub>x</sub> species, given that the vanadyl band shifts to higher wavenumbers with increasing vanadium loading.<sup>12, 162</sup> The relatively high intensity of bands not associated with VO<sub>x</sub> species suggests that these sites exist primarily in their reduced state under the investigated conditions. As shown in Figure 4.3B the structural changes observed upon reduction cannot be reversed by O<sub>2</sub> treatment at 450 °C. This suggests that the surface speciation of vanadium oxide may differ under reaction conditions from that obtained following calcination in air as a consequence of redox cycling.



**Figure 4.3.** UV Raman spectra of  $CeO_2/VO_x/Al_2O_3$  following in-situ reduction under H<sub>2</sub> in the 450 – 600 °C temperature range (A) and a direct comparison of the initial oxidized material and that following treatment under O<sub>2</sub> at 450 °C after reduction (B). Expansions of the V=O bands are shown for the reduction process in (C) and following re-oxidation in (D).

The oxidation state of surface metal oxide species was further probed by XPS. Figure 4.4 shows the V2p<sub>3/2</sub> and Ce3d spectra of supported VO<sub>x</sub> materials. Binding energies of the O1s and V2p<sub>3/2</sub> peaks are reported in Table 4.2. A shift and narrowing of the O1s and  $V2p_{3/2}$  peaks is observed on the CeO<sub>2</sub> support in comparison to Al<sub>2</sub>O<sub>3</sub>, which can be associated with differences in polarizability of the two metal oxide supports.<sup>133</sup> Based on the magnitude of the difference between the O1s and the V2p<sub>3/2</sub> binding energies, the VO<sub>x</sub> species supported on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> contain primarily  $V^{5+}$  as shown in Table 4.2. The increase in FWHM in VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> in comparison to Table 3.1 may be associated with differences in VO<sub>x</sub> speciation dependent on the support pretreatment prior to ALD. When  $CeO_2$  is deposited following the growth of  $VO_x$  domains on Al<sub>2</sub>O<sub>3</sub>, the difference between the two peaks increases and becomes comparable to that reported for VO<sub>2</sub> at 14.35 eV.<sup>136</sup> This suggests the presence of an increased fraction of reduced  $V^{4+}$  species in this material, which is in agreement with the low intensity V=O band in comparison to Al<sub>2</sub>O<sub>3</sub> features in UV Raman spectra shown in Figure 4.1. Ratios of peak areas corresponding to  $V2p_{3/2}$ and O1s are also reported in Table 4.2. An increased amount of  $VO_x$  species is present on the CeO<sub>2</sub> support, which can be explained by the higher average surface area of  $CeO_2$  in comparison to Al<sub>2</sub>O<sub>3</sub>. This is in agreement with metal loadings determined by ICP-OES. Figure 4.4 also includes Ce3d spectra. Figure 4.4G shows the Ce3d spectrum for VO<sub>x</sub>/CeO<sub>2</sub> where the multiplet splitting is consistent with Ce<sup>4+</sup>. The remaining spectra in Figures 4.4E and 4.4F are much lower in intensity due to the low Ce loading on the Al<sub>2</sub>O<sub>3</sub> surface. A peak at 917 eV can be discerned in Figure 4.4F for the  $CeO_2/VO_x/Al_2O_3$  material which is not present in  $Ce^{3+}$  spectra and hence is indicative of the presence of Ce<sup>4+</sup>. This peak cannot be distinguished in Figure 4.4E (VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>).

However, this is most likely due to the low signal-to-noise ratio. The binding energies of the detectable features suggest the presence of  $Ce^{4+}$  in this material as well.



Figure 4.4.  $V2p_{3/2}$  spectra of  $VO_x/Al_2O_3$  (A),  $VO_x/CeO_2/Al_2O_3$  (B),  $CeO_2/VO_x/Al_2O_3$  (C) and  $VO_x/CeO_2$  (D). Ce3d spectra of  $VO_x/CeO_2/Al_2O_3$  (E),  $CeO_2/VO_x/Al_2O_3$  (F) and  $VO_x/CeO_2$  (G).

<b>Table 4.2.</b> Ors and $\sqrt{2}p_{3/2}$ officing energies (DL) in supported $\sqrt{0}$ materia.	able 4.2. OTS and $v_{2}p_{3/2}$ binding energies (BE) in support	Shed $v O_x$ materia
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	O1s		V2p <sub>3/2</sub>			
Catalyst	BE [eV]	FWHM*	BE [eV]	FWHM*	$\Delta^{**}$ [eV]	Av2p3/2/A01s
		[eV]		[eV]		
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	531.77	2.30	517.90	2.49	13.87	0.04
VO <sub>x</sub> /CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	531.55	2.33	517.65	2.50	13.86	0.04
CeO <sub>2</sub> /VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	531.62	2.33	517.50	2.38	14.12	0.02
VO <sub>x</sub> /CeO <sub>2</sub>	529.89	1.58	517.52	2.05	12.37	0.07

\*FWHM stands for full width at half maximum

\*\*BE separation between O1s and V2p<sub>3/2</sub>

## 4.3.2 Cyclohexane ODH Reactivity

Cyclohexane ODH activity was evaluated in the 400-550 °C temperature range. A comparison of the activity of the bare CeO<sub>2</sub> support and VO<sub>x</sub>/CeO<sub>2</sub> is shown in Figure 4.5. CeO<sub>2</sub> is an oxidation catalyst and its activity is significantly higher under the investigated reaction conditions than that of VO<sub>x</sub>/CeO<sub>2</sub>. This indicates that the deposition of VO<sub>x</sub> species on the surface of ceria covers a substantial fraction of the CeO<sub>2</sub> active sites. At 2 V/nm<sup>2</sup> 70% of the surface CeO<sub>2</sub> sites are expected to remain exposed. Oxygen adsorption studies coupled with Raman spectroscopy indicate that the active surface oxygen becomes passivated by the formation of bridging bonds to VO<sub>x</sub> sites.<sup>162</sup> This is associated with the preferential binding of VO<sub>x</sub> species to the most easily reducible CeO<sub>2</sub> surface sites, which would otherwise form vacancies leading to high activity of the bare support in oxidation reactions.<sup>151-152, 162, 166</sup> The high activity of ceria is due to the presence of labile surface oxygen, which has been reported to favor CO<sub>2</sub> formation in alkane ODH reactions.<sup>149-150, 152</sup>


**Figure 4.5.** Comparison of the activity of a bare ceria support and VO<sub>x</sub>/CeO<sub>2</sub> in the 400 – 550 °C temperature range. 5.2 mg of each material was used. Experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>.

The contribution of VO<sub>x</sub> and CeO<sub>2</sub> surface sites was further examined by comparing the selectivity-conversion profiles of VO<sub>x</sub>/CeO<sub>2</sub> and the bare support at 450 °C. The results are shown in Figure 4.6. At similar conversions, the most significant difference between the two materials is the much higher propensity of the CeO<sub>2</sub> support for C-C bond scission, as indicated by the relatively higher selectivity towards CO<sub>2</sub> at the expense of benzene. The differences in selectivity may arise from different individual contributions of the VO<sub>x</sub> and CeO<sub>2</sub> surface species, but also from the formation of V-O-Ce linkages. The fact that the CeO<sub>2</sub> support is essentially unselective towards benzene suggests that this product is either primarily formed on VO<sub>x</sub> sites or that VO<sub>x</sub> domains preferentially bind to CeO<sub>2</sub> sites which have the highest activity, but favor total oxidation of the alkane. In contrast, a significant amount of CO<sub>2</sub> is produced even after the deposition of VO<sub>x</sub> domains. At sub-monolayer VO<sub>x</sub> coverages, exposed CeO<sub>2</sub> sites remain on the surface and

may be responsible for the increased total oxidation in comparison to catalysts discussed in Chapter 3, where the support surface is not itself highly active. In propane ODH studies, the  $CeO_2$  support has been previously reported to almost exclusively form  $CO_2$ .<sup>150</sup> However, in this reaction it is impossible to distinguish whether the total oxidation product forms as a result of a direct reaction from propane or a sequential one through propene.



**Figure 4.6.** Selectivity towards cyclohexene, benzene,  $CO_2$  and CO as a function of conversion at 450 °C for CeO<sub>2</sub> and VO<sub>x</sub>/CeO<sub>2</sub>. All experiments were performed at a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 and with flow rates varying between 50 and 100 ml min<sup>-1</sup>.

The cyclohexane ODH reaction mechanism on  $CeO_2$  and  $VO_x/CeO_2$  was further examined by studying the rates of reactant consumption and product formation with two distinct reactant feed mixtures. Figure 4.7 shows the rate of consumption of cyclohexane and that of cyclohexene in the presence of  $CeO_2$  and  $VO_x/CeO_2$  catalysts. The rates of formation of cyclohexene, benzene and

 $CO_2$  from cyclohexane and the rates of formation of benzene and  $CO_2$  from cyclohexene are shown in Figure 4.8. The corresponding activation energies are reported in Table 4.3. As shown in Figure 4.7, the rate of consumption of cyclohexene is higher for both materials, which is consistent with the lower energy of the allylic C-H bonds present in cyclohexene. This is also evident in the lower apparent activation energy of cyclohexene consumption in comparison to cyclohexane for  $VO_x/CeO_2$ . In contrast, the apparent activation energy of cyclohexene consumption increases for  $CeO_2$ . This might be indicative of the participation of different surface sites in the transformations of the alkane and the alkene on the bare support.



**Figure 4.7.** Temperature dependence of cyclohexane (squares) and cyclohexene (diamonds) consumption for CeO<sub>2</sub> (open symbols) and VO<sub>x</sub>/CeO<sub>2</sub> (closed symbols) normalized to the amount of catalyst. All experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>x</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>.

In cyclohexane ODH, total oxidation is significantly more favorable on the bare  $CeO_2$  support as indicated by the lesser slope of the ln(rate<sub>CO2</sub>) vs. 1/T plot and the resulting lower activation energy.

Additionally, there is a significant difference between the rates of formation of benzene on  $VO_x/CeO_2$  and the CeO<sub>2</sub> support with the latter showing a much higher apparent activation energy. The high  $E_{A,app}$  associated with the formation of benzene on CeO<sub>2</sub> is consistent with the low selectivity towards this product shown in Figure 4.6. The rates of formation of benzene and CO<sub>2</sub> from cyclohexene are presented in Figures 4.8C for CeO<sub>2</sub> and 4.8D for VO<sub>x</sub>/CeO<sub>2</sub>. The apparent activation energies of benzene formation from cyclohexene are within experimental error of one another for CeO<sub>2</sub> and VO<sub>x</sub>/CeO<sub>2</sub>. However, the increased rate observed for CeO<sub>2</sub> is indicative of a higher number of surface active sites which can transform cyclohexene to benzene. The apparent activation energy of CO<sub>2</sub> formation is higher than that of benzene for both materials. Interestingly, the total oxidation of cyclohexene is less favorable than that of cyclohexane on CeO<sub>2</sub>, as evidenced by the higher  $E_{A,app}$  for CO<sub>2</sub> formation shown in Table 4.3.

The data shown in Figures 4.7 and 4.8 and Table 4.3 suggests that at least two types of active sites are present on the ceria support surface. One type is responsible for the transformation of cyclohexane to cyclohexene and the other leads to total oxidation of cyclohexane. The fact that, in the absence of cyclohexane, cyclohexene is primarily converted to benzene suggests that the alkene does not adsorb to the surface in a similar fashion to cyclohexane. One possibility is that cyclohexane adsorbs to multiple surface sites prior to its total oxidation, which is not be achieved for cyclohexene. The addition of VO<sub>x</sub> seems to cover the reactive CeO<sub>2</sub> surface sites, which lowers the amount of CO<sub>2</sub> formed in cyclohexane ODH for VO<sub>x</sub>/CeO<sub>2</sub>. VO<sub>x</sub> domains are also responsible for the formation of benzene, but it cannot be excluded that benzene is also formed on the exposed CeO<sub>2</sub> surface.



**Figure 4.8.** Temperature dependence of the rates of product formation for cyclohexene (**x**), benzene (**A**) and CO<sub>2</sub> (**•**) from cyclohexane for CeO<sub>2</sub> (A) and VO<sub>x</sub>/CeO<sub>2</sub> (B) and from cyclohexene for CeO<sub>2</sub> (C) and VO<sub>x</sub>/CeO<sub>2</sub> (D) normalized to the amount of catalyst. All experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>x</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>. The rates were calculated on a per C<sub>6</sub> basis, meaning that the rate of CO<sub>2</sub> formation was divided by 6.

Catalyst	E <sub>A,C6H12</sub> *	E <sub>A,C6H10</sub> *	E <sub>A,C6H6</sub> *	E <sub>A,CO2</sub> *	E <sub>A,C6H10</sub> **	Е <sub>А,С6Н6</sub> **	E <sub>A,CO2</sub> **
CeO <sub>2</sub>	27 ± 11	$23 \pm 9$	163 ± 28	15 ± 8	48 ± 3	43 ± 3	81 ± 1
VO <sub>x</sub> /CeO <sub>2</sub>	81 ± 3	$56 \pm 2$	$118\pm4$	$119\pm3$	$53\pm 6$	$36 \pm 4$	$54 \pm 2$

**Table 4.3.** Apparent activation energies for  $CeO_2$  and  $VO_x/CeO_2$  based on reactant consumption and product formation in cyclohexane and cyclohexene ODH reactions.

*All apparent activation energies are reported in kJ/mol.* \*C<sub>6</sub>H<sub>12</sub> feed \*\*C<sub>6</sub>H<sub>10</sub> feed

The selectivity profile of  $VO_x/CeO_2$  was further compared to  $VO_x$  supported on inert  $Al_2O_3$  and mixed VO<sub>x</sub>-CeO<sub>2</sub> on alumina. The relevant selectivity-conversion trends at 450 °C are shown in Figure 4.9. First, the increased formation of CO<sub>2</sub> at the expense of benzene on VO<sub>x</sub>/CeO<sub>2</sub> is evident from a direct comparison of VO<sub>x</sub>/CeO<sub>2</sub> and VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The selectivity-conversion trajectories for all of the products are similar for  $VO_x/CeO_2/Al_2O_3$  (green) and  $VO_x/Al_2O_3$  (blue), which further implies that the replacement of V-O-Al bonds with V-O-Ce does not affect the product distribution at a given conversion. In addition, at this low surface density, CeO<sub>2</sub> sites do not seem to directly participate in the reaction mechanism, as evidenced by the low contribution of total oxidation products. In contrast, at a three times higher surface density,  $CeO_2$ , in  $CeO_2/VO_x/Al_2O_3$  materials, leads to appreciable formation of  $CO_2$  at a level equivalent to that in  $VO_x/CeO_2$ . In-situ UV Raman experiments shown in Figure 4.3 indicated a shift of the V=O frequency to higher wavenumbers, indicative of structural changes in the VO<sub>x</sub> sites under reducing conditions at elevated temperatures. One of the reasons for this shift could be migration of VO<sub>x</sub> sites and the formation of a higher fraction of V-O-Al bonds leaving behind exposed CeO<sub>2</sub>, which might agglomerate and become more active than isolated CeO<sub>2</sub> sites in VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> has been previously

reported to promote  $CO_2$  formation in the oxidative dehydrogenation of ethylbenzene.<sup>156</sup> Similarly,  $CeO_2/SiO_2$  favors total oxidation in ethane ODH.<sup>30</sup>



**Figure 4.9.** Selectivity-conversion trends for supported VO<sub>x</sub> catalysts at 450 °C. All experiments were performed at a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 and with flow rates varying between 50 and 100 ml min<sup>-1</sup>.

The rates of consumption of cyclohexane as a function of temperature for supported  $VO_x$  materials are shown in Figure 4.10. The mixed metal oxide materials are similar in their ODH activity to

VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> when normalized to the V loading. At low temperatures, the activity of  $VO_x/CeO_2/Al_2O_3$  is increased, which may be related to either the influence of CeO<sub>2</sub> domains on VO<sub>x</sub> activity via the formation of V-O-Ce bonds or the presence of more polymeric VO<sub>x</sub> species as indicated by the width of the V=O band in visible Raman shown in Figure 4.2. In a study of ethane ODH, Iglesias-Juez et al. have shown that the catalytic activity of VO<sub>x</sub>/CeO<sub>2</sub>/SiO<sub>2</sub> increases both with increasing V loading at a constant amount of Ce and at a constant V loading with increasing Ce content.<sup>30</sup> At low Ce surface densities, Vining *et al.* have found that methanol oxidation activity of VO<sub>x</sub>/CeO<sub>2</sub>/SiO<sub>2</sub> increases in comparison to VO<sub>x</sub>/SiO<sub>2</sub>, but remains constant between 0.2 and 0.9 Ce/nm<sup>2,77</sup> The initial increase in oxidation activity is likely due to the formation of V-O-Ce bonds, while extended networks of CeO<sub>2</sub> are required for surface CeO<sub>2</sub> species to participate in the reaction mechanism and further improve catalytic activity. VO<sub>x</sub>/CeO<sub>2</sub> exhibits increased activity in comparison to alumina-supported materials. Reporting the rate of cyclohexane consumption per amount of vanadium for this material leads to overestimation of the intrinsic activity of the  $VO_x$  sites due to the presence of active surface  $CeO_2$  species. However, as shown in Figure 4.10B, when the rates are normalized to the overall amount of catalyst, VO<sub>x</sub>/CeO<sub>2</sub> remains the most active. The lower activity of CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> per gram of catalyst may be explained by the lower amount of equally active V species, as evidenced by XPS and ICP-OES.



**Figure 4.10.** Temperature dependence of the rate of cyclohexane consumption for supported VO<sub>x</sub> materials normalized to the amount of V (A) and to the amount of catalyst (B). Experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>.

Rates of formation of cyclohexene, benzene and CO<sub>2</sub> as a function of temperature for supported VO<sub>x</sub> materials normalized to the amount of catalyst are shown in Figure 4.11. Figures 4.11A and 4.11B show VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, respectively. These two materials show similar catalytic behavior, where the rates of formation of cyclohexene and benzene exceed that of CO<sub>2</sub>. The rate of CO<sub>2</sub> formation for CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, shown in Figure 4.11C, is equivalent to those of C<sub>6</sub> products. However, it does not differ considerably from the CO<sub>2</sub> formation rate for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The main difference between the three materials is apparent in the rates of formation of C<sub>6</sub> products, which are formed to a lesser extent on CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. The rates of formation of each one of the products increase for VO<sub>x</sub>/CeO<sub>2</sub> (Figure 4.11D) and the rate of CO<sub>2</sub>

formation is not significantly different from the rates of formation of  $C_6$  products, similarly to  $CeO_2/VO_x/Al_2O_3$ .



**Figure 4.11.** Temperature dependence of the rates of formation of cyclohexene (**x**), benzene ( $\blacktriangle$ ) and CO<sub>2</sub> (•) for VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (A) VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (B), CeO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (C) and VO<sub>x</sub>/CeO<sub>2</sub> (D) normalized o the amount of catalyst. Experiments were conducted at P = 1 atm and a fixed C<sub>6</sub>H<sub>12</sub>:O<sub>2</sub>:He ratio of 2.2:7.9:89.9 at a constant flow rate of 100 ml min<sup>-1</sup>. The rates were calculated on a per C<sub>6</sub> basis, meaning that the rate of CO<sub>2</sub> formation was divided by 6.

Apparent activation energies were calculated from the slope of ln(rate) vs. 1/T for the consumption of  $C_6H_{12}$  and the formation of  $C_6H_{10}$ ,  $C_6H_6$  and  $CO_2$  and are shown in Table 4.4. The most pronounced differences are observed for the energy of cyclohexene and  $CO_2$  formation. Depositing  $CeO_2$  after VO<sub>x</sub> domains on Al<sub>2</sub>O<sub>3</sub> results in the formation of distinct surface sites, which have a significantly lower barrier to the total oxidation product and an increased one for the formation of  $C_6H_{10}$ . A lower barrier towards  $CO_2$  formation was earlier reported for the bare  $CeO_2$  support. The surface of the bulk support is likely composed of a variety of  $CeO_2$  sites and the much lower  $E_{A,app}$ in Table 4.3 is an average value with contributions from all of the active species. In addition, the deposition of  $VO_x$  on  $CeO_2$  leads to an increase in  $CO_2$  formation  $E_{A,app}$  due to the covering of the most active  $CeO_2$  sites with  $VO_x$  domains. This lower activation energy observed for  $CeO_2/VO_x/Al_2O_3$  can therefore be associated with the aggregation of  $CeO_2$  species on the alumina surface, which lead to total oxidation. The increased  $C_6H_{10}$  formation activation energy, on the other hand, may be associated with the presence of reduced  $VO_x$  sites in  $CeO_2/VO_x/Al_2O_3$ , which are not equally reactive to  $VO_x$  comprised of  $V^{5+}$ .

Catalyst	E <sub>A,appC6H12</sub>	E <sub>A,appC6H10</sub>	E <sub>A,appC6H6</sub>	E <sub>A,appCO2</sub>
VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	$106 \pm 2$	$64\pm7$	$130 \pm 9$	111 ± 2
VO <sub>x</sub> /CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	90 ± 7	$80\pm9$	$139 \pm 10$	101 ± 2
CeO <sub>2</sub> /VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	107 ± 12	$110 \pm 4$	$136 \pm 3$	81 ± 1

**Table 4.4.** Apparent activation energies of supported VO<sub>x</sub> materials.

## **4.4 Conclusions**

ALD-synthesized mixed VO<sub>x</sub>-CeO<sub>2</sub> materials supported on alumina were investigated in cyclohexane oxidative dehydrogenation and compared to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub> to elucidate the effect of  $CeO_2$  domains on the surface structure distribution of  $VO_x$  species and the resulting catalytic activity. Spectroscopic characterization revealed that the deposition of VO<sub>x</sub> domains following CeO<sub>2</sub> on alumina yields a mixture of monomeric and polymeric VO<sub>x</sub> species with V-O-Ce linkages, whereas reversing the order of deposition of the two metal oxides leads to the formation of reduced VO<sub>x</sub> monomers. Cyclohexane ODH studies showed that a variety of surface active sites with different reactivity towards cyclohexane and cyclohexene is present on the CeO<sub>2</sub> surface. The ceria sites, which favored total oxidation of cyclohexane were selectively covered by VO<sub>x</sub> domains in VO<sub>x</sub>/CeO<sub>2</sub>. The apparent activation energies were shown to depend on the nature of V-O-Support bonds and decrease with the addition of V-O-Ce. The activity of catalysts with low CeO<sub>2</sub> loadings was significantly lower than that of VO<sub>x</sub>/CeO<sub>2</sub>, which is indicative of the contribution of the bulk support to the reaction mechanism. However, selectivity-conversion trends could be altered by the deposition of small CeO<sub>2</sub> domains, indicating that small CeO<sub>2</sub> clusters on an alumina support favor total oxidation similarly to exposed CeO<sub>2</sub> surface sites in VO<sub>x</sub>/CeO<sub>2</sub>.

# **5** Conclusions and Future Directions

#### 5.1 Objectives Met and Outstanding Challenges

The overall aim of this dissertation was to improve the understanding of the contribution of reducible support materials to the activity of  $VO_x$  species in alkane oxidative dehydrogenation reactions through a combination of atomically precise synthesis, extensive spectroscopic characterization and gas-phase reaction studies. Three main objectives were proposed to accomplish this goal:

- (1) Demonstrate the effect of the presence of TiO<sub>2</sub> domains of varying size on the distribution of VO<sub>x</sub> surface sites in their oxidized state and the interactions of the two metal oxides under a reducing environment.
- (2) Determine the role of the reducible TiO<sub>2</sub> support in the improvement of cyclohexane ODH activity of VO<sub>x</sub>/TiO<sub>2</sub> in comparison to VO<sub>x</sub> supported on inert Al<sub>2</sub>O<sub>3</sub>.
- (3) Gain insight into the individual contributions of  $VO_x$  and  $CeO_2$  surface active sites to the overall catalytic behavior of  $VO_x/CeO_2$  in cyclohexane ODH.

The first objective was addressed in Chapter 2, where the interactions of VO<sub>x</sub> species at a constant surface density between 1 and 2 V/nm<sup>2</sup> with varying amounts of amorphous TiO<sub>2</sub> domains on alumina were investigated and compared to VO<sub>x</sub> supported on bulk Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. We have determined that a combination of ALD and calcination procedures can be used to influence the distribution of metal oxide surface species. VO<sub>x</sub> and TiO<sub>2</sub> domains were shown to preferentially bind to each other on an Al<sub>2</sub>O<sub>3</sub> support surface by Raman spectroscopy coupled with DFT calculations. Varying distributions of V-O-V, V-O-Ti and V-O-Al bonds had a significant effect on the ease of reducibility of  $VO_x$  species as determined by H<sub>2</sub> TPR. The structural changes that were the cause for this varying reducibility were identified by in-situ UV Raman experiments, where it was determined that metal oxide surface sites are mobile during reduction at elevated temperatures. An XPS analysis revealed that reduction under H<sub>2</sub> has a significant impact on the oxidation state of vanadium, but not titanium, implying that VO<sub>x</sub> domains are the active sites in mixed VO<sub>x</sub>-TiO<sub>2</sub> materials on Al<sub>2</sub>O<sub>3</sub> for reactions that follow a redox mechanism.

An extensive array of spectroscopic characterization techniques was used to determine the structures of VO<sub>x</sub> and TiO<sub>2</sub> species discussed in Chapter 2. However, there exist limitations on the level of detail that can be determined experimentally when describing the metal oxide surface speciation. DFT calculations were applied in this work to confirm the hypotheses established based on experimental results. These calculations focused on individual monomeric VO<sub>x</sub> sites. As discussed in the Introduction, even monomeric VO<sub>x</sub> species depicted in Figure 1.1 may exhibit varying reduction behavior and hence contribute to reaction mechanisms to a different extent.<sup>25</sup> For this reason, it would be beneficial to extend the set of structures examined by DFT to a range of monomeric VO<sub>x</sub> sites as well as different polymeric chains of VO<sub>x</sub>. Additionally, VO<sub>x</sub> surface structures on alumina covered with a monolayer of  $TiO_2$  could be compared to  $VO_x/TiO_2$  to identify any differences in the interactions of VO<sub>x</sub> sites with amorphous TiO<sub>2</sub> in comparison to the crystalline bulk structure. The V=O stretching vibration bands observed with Raman spectroscopy are typically broad due to the contribution of a distribution of different surface  $VO_x$  sites. The development of a library of V=O frequencies associated with individual surface sites in varying environments would be beneficial in the determination of whether a given structure is likely to be

present on the surface of a catalyst of interest based on the range of frequencies comprising the experimentally observed V=O feature.

The second objective was discussed in Chapter 3, where supported VO<sub>x</sub> materials were evaluated for cyclohexane oxidative dehydrogenation and their catalytic activity was compared to the ease of reducibility of VO<sub>x</sub> species. The relative distribution of V-O-V, V-O-Ti and V-O-Al bonds had an effect on the temperature of the H<sub>2</sub> consumption peak maximum in H<sub>2</sub> TPR experiments. However, the differences in VO<sub>x</sub> reducibility alone could not exhaustively explain the observed variability in ODH activity. The increased activity of VO<sub>x</sub> supported on TiO<sub>2</sub> films above a monolayer coverage was attributed to the formation of oxygen vacancies within the TiO<sub>2</sub> structure. The density of these vacancies is expected to increase with increasing TiO<sub>2</sub> film thickness and it is favorable for them to migrate from the bulk to the surface.<sup>143-144</sup> In addition, O vacancies constitute at most 1-2% of surface O atoms, which implies that a sufficiently thick film of ALDdeposited TiO<sub>2</sub> on the surface of Al<sub>2</sub>O<sub>3</sub> will result in an equivalent surface density of O vacancies as bulk TiO<sub>2</sub>.<sup>70</sup> This was confirmed by the comparable rates of cyclohexane consumption observed for VO<sub>x</sub>/TiO<sub>2</sub> and VO<sub>x</sub> supported on a 2.4 nm TiO<sub>2</sub> film deposited on Al<sub>2</sub>O<sub>3</sub>. While the catalytic activity was distinctly dependent on the composition of the support, the selectivity-conversion trends remained unchanged for the examined supported VO<sub>x</sub> materials.

Oxygen defect formation energies and the charge distribution following the formation of an O vacancy have been previously evaluated for rutile and anatase TiO<sub>2</sub> by performing DFT calculations. These studies indicate that the remaining charge is distributed on Ti atoms, which are not in direct proximity to the vacancy site.<sup>142</sup> This suggests that oxygen vacancies are unlikely to form within small TiO<sub>2</sub> clusters on an irreducible Al<sub>2</sub>O<sub>3</sub> support. An investigation of the oxygen

defect formation energy as a function of  $TiO_2$  domain size on an alumina support as well as the associated charge distribution is the subject on an ongoing collaboration. This study will aid in determining of the significance of the contribution of these vacancies to the catalytic activity of alumina supported VO<sub>x</sub>-TiO<sub>2</sub> materials at different surface TiO<sub>2</sub> densities as well as the smallest TiO<sub>2</sub> cluster size allowing for the formation of a vacancy.

The final objective to gain an improved understanding of the contribution of the redox active CeO<sub>2</sub> support surface and VO<sub>x</sub> sites to the catalytic activity of VO<sub>x</sub>/CeO<sub>2</sub> through the deposition of VO<sub>x</sub> and CeO<sub>2</sub> domains on an inert Al<sub>2</sub>O<sub>3</sub> support via ALD was explored in Chapter 4. This study was motivated by the higher ODH activity of the bare CeO<sub>2</sub> in comparison to VO<sub>x</sub>/CeO<sub>2</sub>. In addition, the two materials were shown to follow distinct selectivity-conversion profiles, where the CeO<sub>2</sub> support favored total oxidation to CO<sub>2</sub>. Materials prepared with single ALD cycles of VO<sub>x</sub> and CeO<sub>2</sub> in varying order of deposition were characterized by Raman spectroscopy and XPS and evaluated for their activity and selectivity in cyclohexane ODH. The low reactivity of the Ce(TMHD)<sub>4</sub> precursor with the Al<sub>2</sub>O<sub>3</sub> surface resulted in a VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> material structurally and catalytically similar to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>. In contrast, the deposition of CeO<sub>2</sub> following VO<sub>x</sub> on alumina led to the development of a material with distinct surface structures. The ODH activity was dependent on the nature of the V-O-S bonds, and small clusters of CeO<sub>2</sub> at low surface densities were shown to favor total oxidation similarly to exposed CeO<sub>2</sub> surface sites in VO<sub>x</sub>/CeO<sub>2</sub>.

The interactions of  $VO_x$  species with CeO<sub>2</sub> domains on the surface of Al<sub>2</sub>O<sub>3</sub> and the role of CeO<sub>2</sub> domains in the reaction mechanism should be further explored by varying the amount of CeO<sub>2</sub> species on the support surface. However, in order for this to be accomplished, the CeO<sub>2</sub> ALD process requires further optimization. The deposition previously described in the literature relies

on a home-built ALD system, where fresh Ce(TMHD)<sub>4</sub> precursor is introduced prior to every ALD cycle and the ligands are removed by *ex-situ* treatment at 400 °C in static air.<sup>159, 167</sup> CeO<sub>2</sub> films have also been previously deposited with Ce(TMHD)<sub>4</sub> and ozone.<sup>168</sup> O<sub>3</sub> was picked as the oxidizing agent in this work in order to refrain from performing the oxidation half-reaction ex-situ. However, it would be beneficial to investigate whether the ligands are completely removed by the ozone treatment. This could be accomplished by performing IR spectroscopy and examining the carbonyl stretch absorption region. Any carbonyl features would be expected to disappear upon complete ligand removal. In addition, CeO<sub>2</sub> growth beyond a single ALD cycle was not accomplished in this work. The deposition of multiple CeO<sub>2</sub> ALD cycles was attempted without introducing fresh Ce(TMHD)<sub>4</sub> - however, it did not result in increased amounts of Ce as detected by XPS. There are two possible reasons for this behavior. One is that the ligands were not effectively removed and the Ce(TMHD)<sub>4</sub> precursor dosed in subsequent cycles could not react with remaining surface OH groups. However, this is unlikely due to the fact that VO<sub>x</sub> domains were successfully deposited following the growth of CeO<sub>2</sub> species without removing the substrate from the ALD reactor. Any remaining TMHD ligands would be expected to create the same steric constraints for the VOTP precursor as they would for Ce(TMHD)<sub>4</sub> doses following the first CeO<sub>2</sub> ALD cycle. The other possibility is that the Ce(TMHD)<sub>4</sub> precursor is not stable when it remains heated at 180 °C. It has been previously reported that the synthesis of alkaline earth precursors based on β-diketonates may result in the presence of solvent residues and additional ligands, which lead to a more rapid degradation of the precursor. It was shown that improved growth rates during ALD can be achieved by in-situ gas-phase synthesis of the metal precursor.<sup>169</sup> An alternative solution would be to use a different  $CeO_2$  precursor for the growth of thicker ALD films.

Tris(isopropyl-cyclopentadienyl)cerium (Ce(iPrCp)<sub>3</sub>) has previously been used in plasmaenhanced ALD and may be an attractive candidate for CeO<sub>2</sub> thin film deposition by thermal ALD without the need for modification of the ALD rector.<sup>170</sup>

VO<sub>x</sub>/CeO<sub>2</sub> catalysts are comprised of an increased number of distinct active sites in comparison to other supported VO<sub>x</sub> materials. On the CeO<sub>2</sub> support alone, the selectivity-conversion trends reveal that different reaction pathways are favorable than those observed for supported VO<sub>x</sub> materials. A large fraction of CeO<sub>2</sub> surface sites remains exposed in VO<sub>x</sub>/CeO<sub>2</sub> materials with sub-monolayer VO<sub>x</sub> coverage discussed in this work, which impacts the resulting product distribution in cyclohexane ODH. The role of these catalytically active sites could be better understood by performing a detailed kinetic study, where the C<sub>6</sub> products of cyclohexane ODH are individually introduced as reactants at the same reaction conditions. This was previously analyzed by Feng *et al.* to determine the contribution of direct and sequential reaction pathways in cyclohexane ODH over VO<sub>x</sub> supported on anodic aluminum oxide.<sup>48</sup> Such an investigation would facilitate an improved understanding of the reason for the low selectivity towards benzene observed for bare CeO<sub>2</sub> and its impact on CeO<sub>2</sub>-supported VO<sub>x</sub> catalysts.

Overall, this dissertation demonstrates how ALD can be used to synthesize catalysts with angstrom level control, which, in combination with spectroscopic characterization and gas-phase alkane ODH reaction studies, allows for an improved understanding of the individual roles of surface metal oxide species in supported mixed metal oxide catalysts. This further enables the distinction between changes in catalytic behavior due to the formation of V-O-S bonds and those associated with the structure of the support itself. Gaining a fundamental understanding of how VO<sub>x</sub> active sites are impacted by oxides present in their vicinity may lead to the rational design of catalysts with improved alkene yields in alkane ODH reactions.

# **5.2 Future Directions**

#### 5.2.1 Active Site Quantification

Turnover frequencies for redox reactions over supported VO<sub>x</sub> catalysts are commonly reported on a per V atom basis. This implies that every V atom on the surface of a catalyst is equally contributing to the reaction mechanism. However, the rate per V atom is dependent on V surface density, the local environment and reaction conditions. In order to address this issue, Nair and Baertsch proposed that surface VO<sub>x</sub> active sites can be quantified with the use of anaerobic reactions. In their study, the number of redox active sites in alumina-supported MoO<sub>x</sub>, WO<sub>x</sub> and VO<sub>x</sub> was determined by performing ethanol oxidative dehydrogenation during which oxygen was removed from the reactant stream and the transient decay in activity was monitored by a mass spectrometer and a gas chromatograph. In this reaction, the only product which forms on redox active sites is acetaldehyde and hence each molecule of acetaldehyde formed following oxygen removal directly corresponded to a surface redox active site. This allowed for the determination that the number of redox active sites is dependent on the identity of the metal oxide and its surface density, but the intrinsic redox reaction rate per active site is independent of these factors.<sup>171</sup>

A similar quantification study of catalytically active surface  $VO_x$  species in cyclohexane ODH could be envisioned. Our initial attempt of such an investigation did not provide meaningful results due to the fact that the detected concentrations of C<sub>6</sub> products were not significant during the steady-state reaction and did not allow for the monitoring of their decay following oxygen removal from the reactant stream. In contrast, a substantial amount of  $CO_2$  was detected during the

cyclohexane ODH reaction. The discrepancy in product distributions in this study and that discussed in Chapter 3 is most likely associated with the relative concentrations of reactants in the feed. The anaerobic titrations were attempted in excess alkane concentration while the  $C_6H_{12}$ :O<sub>2</sub> ratio in previous studies was maintained at 1:2. Therefore, further optimization of the reaction conditions is necessary to successfully carry out this investigation. In addition, contrary to ethanol oxidative dehydrogenation, a number of different products can be formed on redox active sites in cyclohexane ODH via sequential reactions. This may result in competitive adsorption of the alkane and alkene on surface  $VO_x$  sites and hence complicate the quantification of active species. However, the consistent monitoring of all reaction products could provide information on the relative number of active sites in a series of supported VO<sub>x</sub> materials. Additionally, anaerobic experiments with a cyclohexene feed would allow to separately calculate the number of sites that can perform the transformation to benzene, which is expected to be the final product of sequential partial oxidation. Active site quantification performed for alumina-supported VOx-TiO2 materials would provide additional insight into whether the varying surface site distributions of ALDsynthesized materials have an impact on the amount of active sites and their intrinsic reaction rates in cyclohexane ODH.

#### 5.2.2 Redox Inactive Metal Oxide Modifiers

The work discussed in this dissertation focused on the impact of reducible oxide supports on the alkane ODH activity of  $VO_x$  surface sites. The main influence of these metal oxides is the increased activity of the supported  $VO_x$  catalysts. The selectivity to the desired alkene has been previously postulated to be dependent on acid-base properties of the oxide support.<sup>23</sup> For this reason, an

VO<sub>x</sub> supported on MgO has been previously reported to be active for alkane ODH reactions.<sup>172</sup> The strong acid-base reaction between VO<sub>x</sub> and MgO distinguishes these catalysts from other supported VO<sub>x</sub> materials. It results in the formation of a mixed metal oxide phase with a mixture of surface VO<sub>x</sub> species and VO<sub>x</sub> incorporated into the bulk structure.<sup>80</sup> VO<sub>x</sub>/MgO exhibits an increased temperature of the maximum of the H<sub>2</sub> consumption peak in H<sub>2</sub> TPR and decreased activity towards propane ODH.<sup>23</sup> Gao *et al.* have previously shown that varying the ratio of Mg and V leads to the formation of a range of Mg vanadates with unique activities in propane ODH.<sup>173</sup> A systematic study of MgO and VO<sub>x</sub> domains deposited by ALD would further improve the understanding of the structural differences obtained by varying the relative amounts of MgO and VO<sub>x</sub> and their impact on catalytic activity. In addition, a direct comparison between VO<sub>x</sub>/MgO/Al<sub>2</sub>O<sub>3</sub> and VO<sub>x</sub>/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials would enable a better understanding of how basic oxides can influence the catalytic properties of VO<sub>x</sub>. MgO ALD has been previously achieved with a bis(ethylcyclopentadienyl)magnesium (Mg(CpEt)<sub>2</sub>) precursor and H<sub>2</sub>O in a viscous flow reactor.<sup>174</sup>

Alumina-supported VO<sub>x</sub> catalysts modified with WO<sub>x</sub> domains have been previously evaluated for propane ODH. WO<sub>x</sub> species were reported to be inert and to promote the adsorption of propane resulting in an increased selectivity towards propene. They did not have a significant effect on the structure and reducibility of VO<sub>x</sub> sites as determined by H<sub>2</sub> TPR.<sup>175</sup> The reducibility of WO<sub>x</sub> sites has been shown to be dependent on the relative amounts of VO<sub>x</sub> and WO<sub>x</sub> species.<sup>176</sup> Moreover, an increase in the W:V ratio up to 1 has been reported to improve catalytic performance in chlorobenzene oxidation, while further addition of WO<sub>x</sub> has no significant effect on activity and eventually leads to catalyst deactivation. This indicates that there exists a difference in the influence of amorphous and crystalline WO<sub>x</sub> on the catalytic activity of supported VO<sub>x</sub> sites.<sup>177</sup> An investigation of the alkane ODH activity of ALD synthesized alumina-supported VO<sub>x</sub>-WO<sub>x</sub> materials would reveal whether this difference is also apparent in oxidative dehydrogenation reactions. In a manner similar to the materials discussed in Chapter 3, the effect of the thickness of the WO<sub>x</sub> film could be separated from the distinction between amorphous and crystalline WO<sub>x</sub> species. A precursor for WO<sub>x</sub> ALD (WO<sub>2</sub>(N-N'-Di-tert-butylamidinate)<sub>2</sub>) has been previously synthesized by Mouat *et al.*, and WO<sub>3</sub> thin films were successfully grown with H<sub>2</sub>O as an oxidant on Si(100) wafers covered with a SiO<sub>2</sub> thin film.<sup>178</sup>

The exhaustive evaluation of TiO<sub>2</sub>, CeO<sub>2</sub>, MgO and WO<sub>x</sub> modifiers would elucidate the distinction between the influence of redox activity and acid-base properties of different oxides on the catalytic performance of VO<sub>x</sub> surface sites in alkane ODH reactions. The information gained from this investigation could serve as a guide in the synthesis of novel mixed-metal-oxide materials with improved control over the resulting catalytic behavior in alkane ODH reactions.

## 5.2.3 Desorption and Re-adsorption of the Alkene

The higher reactivity of the alkene in comparison to the alkane reactant in oxidative dehydrogenation poses a difficulty in designing a catalyst surface that can selectively form the desired product. Carrero *et al.* postulated that in order to prevent total oxidation, the energy profile of propane ODH needs to be changed. Specifically, catalysts with the capability to suppress the re-adsorption of the alkene could lead to improved product yields.<sup>9</sup> Favorable re-adsorption of alkenes has been correlated to the presence of Lewis acid sites, and a number of strategies have

been proposed to limit their presence. Gärtner *et al.* speculated that using supports with low surface areas would limit the number of accessible Lewis acid sites, that surfaces which can dynamically rearrange could prevent the formation of surface defect sites and that site isolation of redox active species would limit the number of reactive oxygen atoms per site and, as a result, inhibit total oxidation.<sup>179</sup> However, the use of supports without strong Lewis acid sites such as silica typically leads to low catalytic activity.<sup>9</sup>

It is difficult to prevent aggregation of  $VO_x$  surface sites at elevated reaction temperatures without the use of metal oxide modifiers. However, these structures can provide additional labile oxygen leading to the favorable formation of  $CO_x$  products. A systematic DFT study of the adsorption and desorption energies for an alkane and the corresponding alkene could provide additional insight into the design of novel catalytic structures. These energies could be evaluated as a function of the varying identity of metal oxide modifiers to identify promising candidates, which allow for sufficient adsorption of the alkane, but favor desorption of the alkene in order to maintain sufficient catalytic activity and simultaneously improve product yield. The impact of these oxides could be assessed in parallel to the changes in adsorption and desorption energies with increasing  $VO_x$ cluster size to determine whether the deposition of the ternary phase has the potential to reduce the extent of sequential reactions associated with polymeric  $VO_x$  species.

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# Appendix A: SiO<sub>2</sub>-Supported MoO<sub>3</sub> in Olefin Metathesis

#### A collaboration between

HAADF images were collected by Lawrence Crosby. The grafting of MoO<sub>3</sub> domains was performed by Titel Jurca. The SiO<sub>2</sub> support was synthesized by Kunlun Ding. The remaining characterization and reaction studies were performed by Izabela Samek.

Izabela A. Samek, Lawrence Crosby, Titel Jurca, Kunlun Ding, Randall Q. Snurr, Peter C. Stair

## A.1 Introduction

Olefin metathesis, discovered in 1955, has been gaining renewed interest in light of the global propene shortage.<sup>180-181</sup> The process involves the interconversion of carbon-carbon double bonds to form hydrocarbons of a desired length. In summary, the reaction proceeds as follows:

$$2RCH=CHR' \implies RCH=CHR + R'CH=CHR'$$

where R and R' are functionalized alkyls or hydrogen groups.<sup>50</sup> This versatile reaction has found industrial applications in the formation of petrochemicals, oleochemicals, polymers and specialty chemicals.<sup>180</sup> Fundamental insights into the olefin metathesis reaction were obtained based on studies of well-defined homogeneous organometallic catalysts. These investigations allowed to determine that metal carbide complexes are involved in the metathesis reaction mechanism.<sup>182</sup> Heterogeneous metathesis catalysts and their corresponding active sites and surface intermediates are not understood equally well.<sup>181</sup>

Supported  $MoO_x$ ,  $WO_x$  and  $ReO_x$  are currently used in industrial metathesis processes. However, their activities remain lower than those of homogeneous catalysts.<sup>181, 183</sup> Various promoters and

pretreatment conditions have been investigated to improve the catalytic activity of these materials.<sup>184</sup> To be industrially applicable, pretreatment protocols cannot be excessively complicated. High temperature calcination and inert gas purging have been previously studied, but these methods did not yield a significant improvement in metathesis activity.<sup>50, 181</sup> A pretreatment of SiO<sub>2</sub>-supported MoO<sub>x</sub> and WO<sub>x</sub> in an olefin-containing atmosphere at elevated temperature has been reported by Ding *et al.* This procedure resulted in a 100-1000 fold increase in propylene metathesis activity, which led to a catalytic performance comparable to that of supported organometallic catalysts.<sup>184</sup>

High metathesis activity has been reported for well-dispersed supported  $MoO_x$  surface sites, which suggests that the nature of the active species is monomeric.<sup>184-187</sup> More specifically, Ding *et al.* proposed that isolated  $Mo(=O)_2$  dioxo species are the metathesis active sites in  $MoO_3/SiO_2$ catalysts based on a combination of isotope tracing experiments, UV Raman spectroscopy and electron microscopy.<sup>184</sup> However, the surface  $MoO_x$  sites are typically a mixture of a variety of species with only 1-2% of the total atoms exhibiting metathesis activity.<sup>181, 184, 188-189</sup> For this reason, there exists a need for the synthesis of well-defined surface  $MoO_x$  structures in order to better understand and improve olefin metathesis catalyst performance.

Grafting of MoO<sub>2</sub>Cl<sub>2</sub>(dme) (dme = 1,2-dimethoxyethane) on activated carbon has been previously reported to favor the formation of isolated Mo(=O)<sub>2</sub> dioxo sites, which was the motivation for this work.<sup>190</sup> Here, supported MoO<sub>x</sub> catalysts, prepared by grafting of MoO<sub>2</sub>Cl<sub>2</sub>(dme) on high surface area silica, were studied in propene metathesis reactions in an attempt to create materials with an increased number of metathesis active sites. The structure of these catalysts in their oxidized state was evaluated with Raman spectroscopy, high-angle annular dark field (HAADF) imaging and XPS. The catalytic activity of these materials was investigated at RT following a pretreatment in an olefin-containing atmosphere at 550 °C. The regeneration of these materials under an inert gas flow at 550 °C was investigated by temperature programmed desorption studies. Active site counting with isotope tracing experiments was performed to compare the grafted materials with ones prepared by incipient wetness impregnation (IWI). Catalyst deactivation was studied as a function of the reactant mixture.

#### A.2 Methods

# A.2.1. Material Preparation

The SiO<sub>2</sub> support was synthesized via a sol-gel process described elsewhere.<sup>184</sup> MoO<sub>x</sub> species were grafted onto the support surface based on the procedure outlined for the grafting of MoO<sub>2</sub>Cl<sub>2</sub>(dme) on activated carbon.<sup>190</sup> Supported MoO<sub>x</sub> materials were calcined at 600 °C in air for 10 hours at a heating rate of 1.5 °C/min. The Mo weight loading was quantified by ICP-OES performed by Galbraith Laboratories, Inc. This work discusses a material with 2.8 weight % of MoO<sub>3</sub> denoted as 2.8MoO<sub>3</sub>/SiO<sub>2</sub>. 6.7 weight % of MoO<sub>3</sub> was also deposited by IWI of H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> for a direct comparison with previously investigated materials.<sup>184</sup> Unless otherwise noted, the catalysts discussed in this work refer to those prepared by grafting.

# A.2.2. Material Characterization

High spatial resolution HAADF imaging with an inner diameter of 68 mrad and an outer diameter of 230 mrad was performed on a JEOL JEM-ARM200CF electron microscope operating at 200 kV. The probe side Cs-corrector resulted in a probe size of approximately 0.078 nm. Dry powder specimens on a Cu grid with a carbon film support were used for these measurements.

UV (244 nm) and visible (488 nm) laser excited Raman spectra of the silica-supported MoO<sub>x</sub> materials were collected using a custom-built Raman instrument. The 244 nm excitation comes from a Lexel 95 SHG (second harmonic generation) laser equipped with an intracavity nonlinear crystal, BBO (BaB<sub>2</sub>O<sub>4</sub>), which frequency doubles visible radiation into the mid-ultraviolet region.<sup>12, 90-91</sup> The Raman spectra were collected under a controlled atmosphere with the use of a fluidized bed reactor developed by Chua and Stair to minimize the adverse effects of UV radiation.<sup>92</sup> The catalysts were heated in flowing 20%O<sub>2</sub>/He at 550 °C for 30 min to remove any absorbed moisture prior to taking measurements and purged with He for 30 min prior to cooling. The spectra were collected at RT in flowing He. The visible laser power at the sample position was approximately 50 mW and that of the UV laser was approximately 5 mW into a spot size of ca. 200  $\mu$ m.<sup>93</sup> The spectral collection time was 40 min. The Raman shift was calibrated by measuring cyclohexane as a standard prior to every experiment.

XPS measurements were carried out on a Thermo Scientific ESCALAB 250Xi instrument (Thermo Scientific) equipped with a monochromatic Al K $\alpha$  X-ray source (hv = 1486.6 eV). The X-ray spot size was 500 µm in diameter. Scans were collected using a pass energy of 50 eV, a 50 ms dwell time and a 0.1 eV step size. An electron flood gun was applied to the sample surface to neutralize surface charging effects. The binding energies were referenced to the adventitious C1s C-C peak at 284.8 eV.

#### A.2.3. Propene Metathesis Reaction Studies

Propene metathesis reaction studies were performed in a previously described atmospheric pressure fixed bed flow reactor system.<sup>184</sup> Electronic grade propene and research purity  $N_2$  were provided by Airgas. Oxygen/moisture traps (VICI) were used to further purify the C<sub>3</sub>H<sub>6</sub> and N<sub>2</sub>

feeds. An on-line Agilent 3000A microGC equipped with MS-5A ( $O_2$ ,  $N_2$ ,  $CH_4$ , CO), Plot U ( $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ ) and Alumina ( $C_2$ - $C_5$  alkanes and alkenes) columns.  $N_2$  was used as an internal standard for GC quantification.

# A.2.4. Active Site Quantification

Studies of activation, regeneration and active site quantification were performed with the use of a quadrupole mass spectrometer (SRS RGA200). A detailed procedure of the isotope tracing experiments has been previously described in the literature.<sup>184</sup>

# A.3 Results and Discussion

#### A.3.1 Characterization of MoO<sub>3</sub>/SiO<sub>2</sub>

HAADF images of  $2.8MoO_3/SiO_2$  are shown in Figure A.1. These images indicate that a mixture of monomeric, oligomeric and clustered MoO<sub>3</sub> sites are present on the surface of the support. This is similar to the distribution of MoO<sub>x</sub> sites observed over a range of MoO<sub>3</sub> loadings in MoO<sub>3</sub>/SiO<sub>2</sub> prepared by IWI. In agreement with the previous report, clusters of MoO<sub>3</sub> are the dominant surface structures in MoO<sub>3</sub>/SiO<sub>2</sub>.<sup>184</sup> Monomeric sites constitute a relatively small fraction of the surface MoO<sub>x</sub> species in this material.



**Figure A.1.** HAADF images of 2.8MoO<sub>3</sub>/SiO<sub>2</sub>. Possible Mo monomeric sites are indicated with red arrows and purple circles highlight MoO<sub>3</sub> clusters.

Figure A.2 shows Raman spectra of  $2.8MoO_3/SiO_2$ . Bands observed in the 950-1100 cm<sup>-1</sup> region can be associated with Mo=O stretching vibrations. Bands above 990 cm<sup>-1</sup> have been previously assigned to Mo=O monooxo species, while bands below 990 cm<sup>-1</sup> are associated with symmetric and asymmetric Mo(=O)<sub>2</sub> dioxo vibrations in isolated and polymerized MoO<sub>x</sub> sites.<sup>191-194</sup> Features centered at approximately 983 and 969 cm<sup>-1</sup> observed with UV and visible Raman were assigned to symmetric stretching modes of Mo(=O)<sub>2</sub> dioxo species in monomeric and polymeric sites, respectively. The presence of overtones in the spectrum collected under UV excitation shown in Figure A.2A indicates that the bands below 990 cm<sup>-1</sup> are resonance enhanced.<sup>184</sup> Figure A.2B shows distinct peaks below and above 990 cm<sup>-1</sup>, which suggests the presence of both monooxo and dioxo MoO<sub>x</sub> species on the surface of silica following grafting. Distinct M=O vibrations are not observed in Figure A.2C due to the lack of resonance enhancement at 488 nm excitation.



**Figure A.2.** UV (A,B) and visible (C) excitation wavelength Raman spectra of 2.8MoO<sub>3</sub>/SiO<sub>2</sub>. An expanded view of the UV-excited Mo=O vibrations is shown in B.

C 1s, Mo 3d and Cl 2p spectra of 2.8MoO<sub>3</sub>/SiO<sub>2</sub> are shown in Figure A.3. A feature indicative of the presence of O-C=O bonds is observed following grafting of the MoO<sub>2</sub>Cl<sub>2</sub>(dme) precursor on SiO<sub>2</sub> (Figure A.3A). This feature disappears after calcination, which indicates that it is associated with the precursor ligands, which decompose at elevated temperatures. The oxidation state of Mo can be evaluated based on Figure A.3B, where the presence of a band centered at approximately 233.3 eV implies that the catalyst surface is predominantly composed of Mo<sup>6+</sup> species following grafting, calcination and reaction studies. The sample was exposed to air between the metathesis reaction and the XPS measurement and therefore this result is not representative of the MoO<sub>x</sub> structure under reaction conditions. Figure A.3C shows that chlorine is efficiently removed and not present on the surface of 2.8MoO<sub>3</sub>/SiO<sub>2</sub> following grafting and hence it is not expected to impact the metathesis reaction results.



**Figure A.3.** C 1s (A), Mo 3d (B) and Cl 2p (C) spectra of 2.8MoO<sub>3</sub>/SiO<sub>2</sub> material following grafting (red), calcination at 600 °C (blue) and propene metathesis reaction (yellow).

#### A.3.2 Propene Metathesis Activity of MoO<sub>3</sub>/SiO<sub>2</sub>

The previously reported high-temperature activation of MoO<sub>3</sub>/SiO<sub>2</sub> catalyst under an olefin environment results in initial turnover frequencies comparable to those of high-performance supported organometallic catalysts.<sup>184</sup> However, these materials suffer from rapid deactivation. Figure A.4 shows the deactivation profile of a grafted 2.8MoO<sub>3</sub>/SiO<sub>2</sub> in direct comparison to 6.7MoO<sub>3</sub>/SiO<sub>2</sub> synthesized by IWI. The initial deactivation of 2.8MoO<sub>3</sub>/SiO<sub>2</sub> appears to be more rapid than that of 6.7MoO<sub>3</sub>/SiO<sub>2</sub> suggesting that active sites with varying deactivation rates may be present on the support surface.



**Figure A.4.** Comparison of catalyst deactivation for 2.8MoO<sub>3</sub>/SiO<sub>2</sub> synthesized via grafting and 6.7MoO<sub>3</sub>/SiO<sub>2</sub> prepared by incipient wetness impregnation.

A temperature programmed desorption experiment was performed to monitor the process of regeneration of  $2.8MoO_3/SiO_2$  by inert gas purging. This measurement could potentially identify differences in the nature of the active sites in the two materials. The observed ethene, propene, butene and pentene signals are shown in Figure A.5. The identity of the detected species and their

complete desorption at 300 °C is consistent with an equivalent study previously published for  $MoO_3/SiO_2$  synthesized by IWI indicating that the two types of materials undergo a similar deactivation process. The desorption of these species can be assigned to the decomposition of various inactive surface metallacyclobutanes, which leads to the regeneration of metathesis active sites.<sup>184</sup>



Figure A.5. Temperature programmed desorption during catalyst reactivation under  $N_2$  for 2.8MoO<sub>3</sub>/SiO<sub>2</sub>.

Active site counting by isotope exchange illustrated in Scheme A.1 was performed to determine whether the grafted catalyst has an increased number of metathesis active sites. The formation of <sup>13</sup>CH<sub>2</sub>=CH<sub>2</sub> and <sup>13</sup>CH<sub>2</sub>=CHCH<sub>3</sub> originating from an exchange between Mo=CH<sub>2</sub> and Mo=CHCH<sub>3</sub> with <sup>13</sup>CH<sub>2</sub>=<sup>13</sup>CH<sub>2</sub> was monitored by a mass spectrometer at m/z=29 and m/z=43, respectively. To allow for a direct comparison with previously published results, active site counting was performed following 10 min of propene metathesis reaction. Figure A.6 shows the isotope traces recorded at different times within the reaction for 2.8MoO<sub>3</sub>/SiO<sub>2</sub>. Figures A.6A and A.6D show spectra

environment. The fraction of active sites was determined to be 5.8%. Another isotope tracing experiment was performed 6 hours after the first one. The observed catalyst deactivation was faster following the first active site counting procedure. The fraction of active sites was calculated as 0.5% based on the spectra shown in Figures A.6B and A.6E. Next, high temperature regeneration under an inert atmosphere was performed and the active sites were counted following this procedure. Figures A.6C and A.6F illustrate the products formed during this isotope exchange. The resulting active site fraction was 7.6%, which may be within error of the initial 5.8% value. It is not expected that new metathesis active sites are formed during the regeneration under an inert atmosphere. The active site fraction reported for 2.8MoO<sub>3</sub>/SiO<sub>2</sub> prepared by IWI was 8.6%.<sup>184</sup> This implies that the grafting of MoO<sub>2</sub>Cl<sub>2</sub>(dme) on SiO<sub>2</sub> does not increase the number of metathesis active sites in MoO<sub>3</sub>/SiO<sub>2</sub>. As shown in Figure A.1 a variety of surface MoO<sub>x</sub> species is present on the silica surface following grafting and calcination procedures. The aggregation of MoO<sub>x</sub> sites may be support dependent or a result of the high temperature treatment.



Scheme A.1. Illustration of the isotope exchange during active site counting experiments.



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**Figure A.6.** <sup>13</sup>CH<sub>2</sub>=CH<sub>2</sub> (m/z=29) (A,B,C) and <sup>13</sup>CH<sub>2</sub>=CHCH<sub>3</sub> (m/z=43) (D,E,F) spectra following isotope exchange experiments after high temperature pretreatment in propene (A,D), 6 hours of propene metathesis reaction following the first active site counting experiment (B,E) and after regeneration at high temperature under inert (C,F) for  $2.8MoO_3/SiO_2$ .

# A.3.3. Catalyst Deactivation

The formation of energetically stable yet inactive metallacyclobutanes with time-on-stream has been previously reported for metathesis reactions.<sup>191, 195-197</sup> In order to gain insight into this deactivation process and find out whether it is simply time-dependent, we performed propene metathesis reaction experiments, where the feed of the reaction mixture was interrupted by a N<sub>2</sub> purge at RT. Two different N<sub>2</sub> flow rates were tested in this experiment and their impact on catalyst deactivation in shown in Figure A.7. We found that the purging step does not affect the deactivation profile of MoO<sub>3</sub>/SiO<sub>2</sub>. When C<sub>3</sub>H<sub>6</sub> is reintroduced to the reaction mixture, the conversion does not drop significantly in comparison to that immediately prior to the purge step, but continues to steadily decrease under  $C_3H_6$  flow with time. This implies that  $C_3H_6$  is involved in the deactivation of MoO<sub>3</sub>/SiO<sub>2</sub> catalysts. This is in agreement with a previous study of CH<sub>3</sub>-ReO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, where catalyst deactivation was associated with the products formed during propene metathesis based on solid-state NMR spectroscopy.<sup>195</sup>



Figure A.7. Evaluation of catalyst deactivation with time at reaction conditions (A) and in the absence of propene following a 5 sccm  $N_2$  purge (B) and a 50 sccm  $N_2$  purge (C) for  $5.8MoO_3/SiO_2$  prepared by IWI.

The propene feed was mixed with ethylene to determine whether the latter can accelerate the deactivation of  $MoO_3/SiO_2$  catalysts. It has been previously hypothesized that the deactivation of metathesis active sites in CH<sub>3</sub>-ReO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is due the products formed during the reaction and specifically the presence of ethene.<sup>195</sup> The deactivation profiles with varying amounts of C<sub>2</sub>H<sub>4</sub> in the reaction mixture are shown in Figure A.8. At 12.5% ethylene, the reaction profile is similar to that of pure propylene. The conversion values are within experimental error. A larger drop in propene conversion is observed for a 1:1 C<sub>2</sub>H<sub>4</sub>:C<sub>3</sub>H<sub>6</sub> reactant mixture. This is in agreement with a previous report of decreased propene metathesis activity in the presence of ethylene. In a manner

similar to this work, it has been reported that the negative effect of ethylene on propene metathesis activity cannot be observed at low ethylene concentrations.<sup>195</sup>



**Figure A.8.** 2.8MoO<sub>3</sub>/SiO<sub>2</sub> catalyst deactivation as a function of time in the presence of ethylene in the reaction mixture. The remaining fraction of the feed corresponds to the concentration of C<sub>3</sub>H<sub>6</sub>.

# **A.4 Conclusions and Future Directions**

 $MoO_3/SiO_2$  catalyst prepared by grafting of  $MoO_2Cl_2(dme)$  on a silica surface were characterized in their oxidized state and evaluated for propene metathesis. These materials were expected to possess an increased fraction of metathesis active sites. However, HAADF images showed a distribution of surface  $MoO_x$  species with a limited amount of monomeric sites. The observed catalytic activity of materials prepared by grafting did not significantly differ from that of catalysts prepared by IWI. Rapid deactivation of the metathesis active sites was observed with time-onstream. In addition, active site counting experiments revealed a similar amount of metathesis active sites was present in the grafted materials and those synthesized by IWI. This implies that the grafting of MoO<sub>2</sub>Cl<sub>2</sub>(dme) on a silica surface and the following high temperature treatment result in the aggregation of MoO<sub>3</sub> surface sites, in contrast to previously reported  $(O_c)_2Mo(=O)_2@C$ materials, which were postulated to consist of exclusively isolated Mo(=O)<sub>2</sub> sites on the surface. The results presented in this work are consistent with the report of Ding *et al.*, where different IWI precursors and SiO<sub>2</sub> supports were compared in control experiments, which showed similar initial conversion values independently of the synthesis method.<sup>184</sup> Catalyst deactivation was shown to be dependent on the presence of propene and ethene in the reaction mixture.

The presence of a variety of surface  $MoO_x$  structures in  $MoO_3/SiO_2$  can be attributed to the inhomogeneity of the silica support with different structures being favored on distinct silanol groups. The local silica structure has been previously shown to significantly impact metathesis activity of supported  $MoO_3$  domains.<sup>198</sup> A more effective control over the distribution of available catalytic sites could be accomplished by atomically precise synthesis with ALD. SiO<sub>2</sub> domains could be deposited on an inert support, such as boron nitride, prior to the deposition of  $MoO_x$ . This approach would allow for the formation of isolated active sites, which have been previously shown to improve catalytic activity in metathesis reactions.<sup>199-200</sup> It could also facilitate an improved understanding of any preferential binding of  $MoO_x$  species to different silanol groups and further correlation of these species to the formation of active alkylidene complexes and their transformation to either trigonal-bypiramidal or square planar metallacyclobutanes. The abundance of the trigonal-bypiramidal isomers has been previously correlated with higher metathesis activity.<sup>199</sup>

# **Appendix B: Supplemental Information for Chapter 2**

#### **B.1** Computational Details

#### B.1.1 Relaxation of the Alumina Surface

We performed relaxations on 160 alumina surfaces with randomly distributed Al vacancies to find reasonable structures. In many cases, tetrahedral Al atoms near the surface moved into the plane of the octahedral Al atoms and assumed octahedral bonding positions, as shown in Figure B.1. We found the binding sites between a transformed tetrahedral Al atom and two neighboring octahedral Al atoms to be the most favorable for VO<sub>4</sub> and TiO<sub>4</sub>H binding. Without the formerly tetrahedral Al assuming the position of a neighboring octahedral Al, the next nearest octahedral Al is too far away to form a favorable binding site.

#### **B.1.2** Finding Favorable Surfaces

 $\gamma$ -Alumina has a defective spinel crystal structure, with randomly distributed vacancies on the Al sites. For this work we used a 160-atom unit cell with 96 O atoms, 64 Al atoms, and 8 vacant Al sites. In order to find some reasonable structures with different configurations of vacancies, we tested four different surfaces: two [001] surfaces terminated in different planes and two [111] surfaces terminated in different planes. [001]A is terminated in the plane of octahedral Al atoms, while [001]B is terminated in the tetrahedral plane. Likewise, [111]A and [111]B are terminated in the octahedral and tetrahedral planes, respectively. For each of these four surfaces, we tested 40 random configurations of vacancies with up to 3 (out of 8) Al vacancies on tetrahedral sites. The geometry of each surface was minimized in VASP. We then used the two lowest energy structures, which were both [001] surfaces. Figure B.2 shows histograms of the minimized energy of the 160 surfaces.

#### **B.1.3** Vibration Calculations

DFT vibrational calculations were performed in VASP to help assign Raman peaks to surface structures such as Ti-O-V, Ti-O-Ti, and V-O-Al bonds. The structures were fully optimized prior to performing the frequency calculation so that the largest force on any atom was below 0.02 eV/Å. Frequency calculations were performed using central differencing for the dynamical matrix with a step size of 0.01 Å, with an SCF tolerance of  $10^{-8}$ .

Vibrations for the V=O structure were performed by moving the V atom and four connecting O atoms and leaving all other atoms frozen. Calculations involving the surface Al atoms were also carried out, but we found a change of only 2 wavenumbers or 0.2% in the V=O stretching bond, and a substantially higher computational cost. For structures containing Ti, we included the Ti atoms and connecting O (and –OH) atoms.

Based on our calculated V=O frequency of 959 cm<sup>-1</sup> compared to the experimental value of 1010 cm<sup>-1</sup>, we scaled the frequencies we calculated for other surface bonds (including Ti-O-Ti, Ti-O-V, and V-O-Al) by a factor of 1.05 to correct the systemic underprediction of DFT. V=O frequencies were reported with no scaling factor.

# **B.1.4** Surface Structure Vibrations

Figure B.3 shows the vibrational density of states for various surface structures on alumina. Figure B.4 depicts the examined surfaces. The spectra have been weighted by the relative contributions to the eigenvector of the atoms of interest (e.g., for the Ti-O-Ti modes, contributions from other atoms are projected out of the spectrum). A Gaussian broadening of 20 cm<sup>-1</sup> was applied. The frequencies have been scaled by 1.05.

In Figure B.3A and B.3C, the V=O stretching peak is clear at 1000 cm<sup>-1</sup>. Figure B.3B shows the Ti-O-Ti stretching modes clearly around 800 cm<sup>-1.</sup> The dashed line in Figure B.3B is from a Ti<sub>3</sub> structure on the alumina surface. This structure also has a peak at 921 cm<sup>-1</sup> which suggests that larger Ti surface structures where Ti is connected to multiple other Ti atoms may have higher frequency bands.

#### B.1.5 VO<sub>4</sub> on Extended TiO<sub>4</sub> Domains

We created an extended surface by duplicating Surface 2 and added three Ti atoms with a V=O on top of them. The V is connected only to Ti and not to any Al atoms. The computed V=O stretching frequency is 1067 cm<sup>-1</sup>. Due to the size of this system, the frequency was computed by vibrating only the V and double-bonded O atom. This structure is depicted in Figure B.5. Based on the low surface densities of V and Ti and the high predicted vibration of the V=O band for this structure, it is unlikely that such structures are present in the synthesized materials. The computed V=O frequency is in contrast to that calculated for VO<sub>4</sub> on a bulk anatase support depicted in Figure B.6, which has a theoretical V=O band at 1020 cm<sup>-1</sup>. The discrepancy between these two frequencies may be associated with the fact that some of the bridging O atoms in the structure containing 3 Ti atoms on Al<sub>2</sub>O<sub>3</sub> are not fully coordinated in comparison to bulk TiO<sub>2</sub>.

#### B.1.6 Finding a Favorable Binding Site

We assessed the favorability of V and Ti binding near each other on the alumina surface using DFT calculations (Figure 2.4). In order the preserve the stoichiometry of the system and compare the total energies directly, we added a H atom to a randomly chosen –OH group (making a  $H_2O$ ) for the structures in which V and Ti are not adjacent. Thus the total number of H atoms is the same in all of these structures. We find that the total energy is sensitive to the placement of this extra H

atom. As shown in Figure B.7, both H atoms on the H<sub>2</sub>O form hydrogen bonds with neighboring hydroxyl groups (Figure B.7C). The H-O distances for these bonds are 1.86 and 1.79 Å. In Figure B.7B, the water molecule is isolated at a distance and forms only one hydrogen bond with the neighboring –OH group (H-O distance 1.77 Å). We chose to report this structure in Figure 2.4 because it does not contain the additional stabilizing hydrogen bond observed in Figure B.7C. We note that the structures in Figure B.7B and B.7C are both less favorable than the structure reported in Figure B.7A with Ti and V adjacent to each other, which confirms our hypothesis that the Ti and V atoms prefer to bind in proximity of each other on the alumina support.



#### **B.2 Additional Results**

**Figure B.1.** Top down view of the [001] surface of ideal  $\gamma$ -alumina (Surface 1) (A). The relaxed version of the ideal structure shown in A is shown in (B). Side view of the unrelaxed surface shown in A (C). Side view of the relaxed surface shown in B (D). In all structures, O atoms are marked in red, octahedral Al atoms are pink, and tetrahedral Al atoms are yellow. The

highlighted blue sphere represents a tetrahedral Al atom in A and C that moves to an octahedral position in B and D.



**Figure B.2.** Histograms for the minimized energy of 40 configurations of vacancies (each) in [001]A, [001]B, [111]A, and [111]B surfaces.



**Figure B.3.** Projected VDOS for surface structures on alumina. V-O-Al bonds on Surface 1 and Surface 2 (A), Ti-O-Ti bond frequencies for Ti<sub>2</sub> and Ti<sub>3</sub> structures on Surface 2 (B), Ti-O-V frequencies on Surface 2 (C).



VO<sub>4</sub> on Surface 1



VO<sub>4</sub> on Surface 2



Two TiO<sub>4</sub>H sites on Surface 2



Three TiO<sub>4</sub>H sites on Surface 2



VO<sub>4</sub>-TiO<sub>4</sub>H on Surface 2

**Figure B.4.** Depictions of the structures used for VDOS calculations shown in Figure B.3. V atoms are shown in blue and Ti atoms are shown in green.



**Figure B.5.** VO<sub>4</sub> bound to three neighboring TiO<sub>4</sub> sites on Al<sub>2</sub>O<sub>3</sub>. V atom is shown in blue and Ti atoms are shown in green.



**Figure B.6.** Structure of  $VO_4$  on anatase used to calculate the V=O stretching frequency on a bulk TiO<sub>2</sub> support. V atom is shown in blue.



Α

В





67.9 kJ/mol



**Figure B.7.** Top-down view of [001] surface of  $\gamma$ -alumina (2x1 supercell, Surface 2) with V (blue) and Ti (green) atoms on the surface in various configurations: V occupies the most

favorable site with Ti adjacent to it (A), Ti and V occupy equivalent sites in separate unit cells (B). An additional H atom (purple) is added to an -OH group far from the V and Ti atoms (lower right) to preserve the stoichiometry. These structures are equivalent to Figure 2.4A and 2.4C, respectively. A structure similar to B with the extra hydrogen atom (purple) in a different location (middle right) is shown in (C).



**Figure B.8.** Deconvoluted spectra of  $V2p_{3/2}$  for ALD-synthesized samples. The dashed lines represent  $V^{5+}$  in red,  $V^{4+}$  in blue and  $V^{3+}$  in green. The black solid line is the cumulative fit.



**Figure B.9.** Deconvoluted V2p<sub>3/2</sub> spectra of VO<sub>x</sub>/1cTiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (A) and 1cTiO<sub>2</sub>/VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (B) following re-oxidation at 450 °C. The dashed lines represent V<sup>5+</sup> in red, V<sup>4+</sup> in blue and V<sup>3+</sup> in green. The black solid line is the cumulative fit.

# **Appendix C: Supplemental Information for Chapters 3 and 4**



**Figure C.1.** UV Raman spectra of the  $Al_2O_3$  support and the porous disk of the fluidized bed setup. The spectral collection time was 10 min. A broad band above 800 cm<sup>-1</sup> has been previously reported for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the enhanced signal between 800 and 1000 cm<sup>-1</sup> shown in the blue spectrum can be associated with the Al<sub>2</sub>O<sub>3</sub> support.<sup>12</sup> The remaining sharp bands are due to the experimental setup.