A Study of Red./Ox. Thermodynamic and Catalytic Properties of Metal Oxide Materials

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Abstract

Redox thermodynamic properties and catalytic activities of metal oxides were studied to gain insight into the fundamental relationships between those properties. Catalysts based on iron oxides, vanadium oxides, and molybdenum oxides were studied because of their industrial importance to the water-gas-shift and partial-oxidation reactions.

Redox properties of 5wt% and 15wt% V2O5/Al2O3 catalysts calcined at 753 K and 973 K were measured using coulometric titration at 748 K. 5wt% V2O5/Al2O3 was found to be thermally stable and its reduction from V+5 to V+4 occurred at P(O2) values between 10-4 and 10-19 atm and from V+4 to V+3 at a PO2 of 10-28 atm. The redox isotherm for a 15 wt % V2O5/Al2O3 calcined at 753 K showed a sharper reduction from V+5 to V+4 at P(O2) of 10-20 atm. Upon calcination at 973 K, the 15 wt % sample underwent a solid state reaction resulting in AlVOx species that reduce in single step from V+5 to V+4 from at P(O2) of 10-6 atm. All of the V2O5/Al2O3 catalysts had similar activities for the selective oxidation of CH3OH to CH2O, suggesting that oxygen removal from the surface is not the rate limiting step for this reaction. For C3H8 oxidative dehydrogenation, the 15 wt % V2O5/Al2O3 sample that was calcined at 973 K was active only for the complete oxidation of propane to CO2 and H2O, while all other catalysts were similarly active and selective to C3H6. The results show that redox thermodynamic influences on reaction rates and selectivities can vary from null to significant and depend on exact mechanism of reaction of interest.

Redox isotherms at 973 K for supported iron oxide were examined as a function of iron loading on zirconia. Zirconia supported iron had a redox isotherm that showed a well-defined steps corresponding to transitions of Fe2O3 → Fe3O4, Fe3O4→FeO and FeO→Fe, with the transition of Fe2O3→Fe3O4 shifting to significantly higher pressures of oxygen compared to bulk iron, which makes surface iron easier to reduce and harder to oxidize compared to bulk iron oxide. Water gas shift reaction rates over supported iron catalysts and bulk iron showed that specific rates for supported samples were orders of magnitude slower than bulk iron due to thermodynamically higher energy barrier of catalyst reoxidation in supported catalysts.

A study of Mo-based mixed oxides showed that the thermodynamic redox properties of Al2(MoO4)3, Zr(MoO4)2, Cr2(MoO4)3, and MgMoO4 at 873 K are nearly identical to each other but differ significantly from that of SrMoO4. None of the mixed oxides exhibit thermodynamic properties similar to that of bulk MoO3. The similarities and differences between these mixed oxides likely result from the presence of isolated (MoO4)2- tetrahedra in the oxidized forms and two different types of Mo-O-Mo bonding in the reduced forms. However, the catalytic activities for methanol oxidation were much lower than that of bulk MoO3. It appears that the low activity for the bulk mixed oxides is the result of the Mo+6 cations within the (MoO4)2- anions being inaccessible to reactants.

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A STUDY OF RED./OX. THERMODYNAMIC AND CATALYTIC PROPERTIES OF METAL OXIDE MATERIALS

Ivan Sergeyevich Baldychev

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in

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Abstract

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Ivan Baldychev
Raymond J. Gorte and John M. Vohs

Redox thermodynamic properties and catalytic activities of metal oxides were studied to gain insight into the fundamental relationships between those properties. Catalysts based on iron oxides, vanadium oxides, and molybdenum oxides were studied because of their industrial importance to the water-gas-shift and partial-oxidation reactions.

Redox properties of 5wt% and 15wt% V_2O_5/Al_2O_3 catalysts calcined at 753 K and 973 K were measured using coulometric titration at 748 K. 5wt% V_2O_5/Al_2O_3 was found to be thermally stable and its reduction from V^{+5} to V^{+4} occurred at P_{O_2} values between 10^{-4} and 10^{-19} atm and from V^{+4} to V^{+3} at a P_{O_2} of 10^{-28} atm. The redox isotherm for a 15 wt % V_2O_5/Al_2O_3 calcined at 753 K showed a sharper reduction from V^{+5} to V^{+4} at P_{O_2} of 10^{-20} atm. Upon calcination at 973 K, the 15 wt % sample underwent a solid state reaction resulting in AlVO_x species that reduce in single step from V^{+5} to V^{+4} from at P(O_2) of 10^{-6} atm. All of the V_2O_5/Al_2O_3 catalysts had similar activities for the selective oxidation of CH_3OH to CH_2O, suggesting that oxygen removal from the surface is not the rate-limiting step for this reaction. For C_3H_8 oxidative dehydrogenation, the 15 wt % V_2O_5/Al_2O_3 sample that was calcined at 973 K was active only for the complete oxidation of propane to CO_2 and H_2O, while all other catalysts were similarly active and selective to C_3H_6. The results show that redox thermodynamic influences on reaction rates and selectivities can vary from null to significant and depend on exact mechanism of reaction of interest.

Redox isotherms at 973 K for supported iron oxide were examined as a function of iron loading on zirconia. Zirconia supported iron had a redox isotherm that showed a well-defined steps corresponding to transitions of Fe_2O_3 → Fe_3O_4, Fe_3O_4→FeO and FeO→Fe, with the transition of Fe_2O_3→Fe_3O_4 shifting to significantly higher pressures
of oxygen compared to bulk iron, which makes surface iron easier to reduce and harder to oxidize compared to bulk iron oxide. Water gas shift reaction rates over supported iron catalysts and bulk iron showed that specific rates for supported samples were orders of magnitude slower than bulk iron due to thermodynamically higher energy barrier of catalyst reoxidation in supported catalysts.

A study of Mo-based mixed oxides showed that the thermodynamic redox properties of $\text{Al}_2(\text{MoO}_4)_3$, $\text{Zr}(\text{MoO}_4)_2$, $\text{Cr}_2(\text{MoO}_4)_3$, and $\text{MgMoO}_4$ at 873 K are nearly identical to each other but differ significantly from that of $\text{SrMoO}_4$. None of the mixed oxides exhibit thermodynamic properties similar to that of bulk MoO$_3$. The similarities and differences between these mixed oxides likely result from the presence of isolated MoO$_4^{2-}$ tetrahedra in the oxidized forms and two different types of Mo-O-Mo bonding in the reduced forms. However, the catalytic activities for methanol oxidation were much lower than that of bulk MoO$_3$. It appears that the low activity for the bulk mixed oxides is the result of the Mo$^{+6}$ cations within the MoO$_4^{2-}$ anions being inaccessible to reactants.
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Chapter 1. Introduction

1.1 Background

The world’s production of chemicals relies heavily on catalysis to produce a wide variety of materials. Typically, these catalysts are subdivided into two groups: homogeneous and heterogeneous. In the former, catalytic reactions happen in one phase, while in latter catalytic reactions happen on a boundary between two phases, typically between a solid and a gas (or liquid). A difficulty with homogeneous catalysts is that they usually need to be separated from the products at the end of reaction in order to be recycled. Since separation of the catalyst from the products is much simpler, heterogeneous catalysts are used whenever possible in most large-scale industrial processes. Therefore, heterogeneous catalysts are responsible for the production of many commodity chemicals.

The focus of this thesis is on metal-oxide catalysts, a sub-group of heterogeneous catalysts, which often are used for partial oxidation of hydrocarbons. Typically, these catalysts are complex heterogeneous mixtures of the active component, along with various additives and inert materials, and are designed to achieve the best catalytic performance, stability, and surface area available for catalytic reaction. The active component itself can be a highly engineered system made up by several metals forming mixed oxides or solid solutions. Some examples of metal-oxide catalysts and the oxidation processes for which they are used are given below:

- Iron oxide; water gas shift (WGS) reaction: \(\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2\)
- Iron molybdates; \(\text{CH}_2\text{O}\) from \(\text{CH}_3\text{OH}\).
- Bi-Mo mixed oxides; acrolein \((\text{C}_3\text{H}_4\text{O})\) from propylene \((\text{C}_3\text{H}_6)\).
- Vanadium pyrophosphate; butane \((\text{C}_4\text{H}_{10})\) to maleic anhydride \((\text{C}_4\text{H}_2\text{O}_3)\).
- Vanadium oxide dispersed on titania; o-xylene \((\text{C}_6\text{H}_4(\text{CH}_3)_2)\) to phthalic anhydride \((\text{C}_6\text{H}_4(\text{CO})_2\text{O})\).

The selective oxidation of hydrocarbons and inorganic compounds on oxide catalysts usually proceeds via a Mars-van Krevelen mechanism. Illustrated in Figure 1.1, this mechanism employs lattice oxygen rather than gaseous oxygen as an oxidizing agent; the oxidation of the reactant reduces the catalyst and leads to an oxygen vacancy in
the metal-oxide structure. This vacancy is later filled via reaction with gaseous oxygen in a separate step to complete the catalytic cycle. Since removing lattice oxygen from the catalysts during a reaction involves breaking oxygen-metal bonds, the strength of those bonds is expected to influence the selectivity and activity of the catalyst. For example, it might be difficult to oxidize a hydrocarbon using lattice oxygen if the metal-oxygen bond is too strong; analogously, a very weak metal-oxygen bond might result in complete oxidation of the hydrocarbon and/or slow reoxidation of catalysts which could be rate-limiting.

**Figure 1.1:** Schematic diagram of the Mars-van Krevelen mechanism

Even though the Mars-van Krevelen mechanism is commonly invoked, there are other possible oxidation-reaction pathways on the surface of a catalyst which do not involve lattice oxygen\(^3,7\). In the Eley-Rideal mechanism, a reaction takes place between adsorbed \(\text{O}_2\) and gaseous or weakly adsorbed reactants, i.e. a reactant strikes adsorbed oxygen on a surface and gets oxidized. In the Langmuir-Hinshelwood mechanism, both oxygen and reactant adsorb on a surface and react on a surface, followed by product desorption\(^8\). In addition, even if the Mars-van Krevelen mechanism applies, there is no guarantee that the rate-limiting step for the reaction will be removal of an oxygen from the lattice; therefore the effect of changing oxygen binding energies on kinetic behavior
might be more subtle or not even present. For example, such a situation has been reported for partial oxidation of methanol to formaldehyde over supported molybdenum oxide catalysts\(^9\) where rate limiting step of reaction is breaking of C-H bond in methanol and reaction rates show weak dependence on the nature of the support.

Catalysts based on metal oxides have been a subject of research for over 100 years since use of magnetite (Fe\(_3\)O\(_4\)) in the famous Haber-Bosch process to produce ammonia from atmospheric nitrogen\(^2\). Consequently, vast amounts of information have been published about their structures and catalytic properties. Paradoxically, even though importance of the Mars-van Krevelen mechanism has been overwhelmingly acknowledged in the literature, there is a lack of information available about lattice-oxygen binding energies on the surface and in the bulk of catalysts. Hence, characterization of metal-oxygen bond strengths is essential to determine the cause for the unique reactivity of these materials. The goal of the thesis is to determine precisely metal-oxygen bond energies in metal oxide catalysts and investigate fundamental relationship between these energies, the structure and catalytic activity.

Estimation of oxygen removal energies is typically qualitative and indirect. Temperature-programmed reduction (TPR), a measurement of the temperature at which a sample is reduced by a specific reactant in a flow reactor, is often used to determine relative reducibility of an array of materials\(^10\). TPR is essentially a reaction rate measurement; therefore, it is difficult to quantify the energetics of reduction from a TPR experiment. Badlani et al.\(^{(ref)}\) have characterized an extensive list of bulk metal oxides using H\(_2\)-TPR, yet no correlation between redox thermodynamic data and temperature at which reduction starts to occur has been shown. Figure 1.2 illustrates the point by plotting thermodynamic quantities for a reduction reaction to the next stable phase calculated using accepted literature data\(^11\) versus the temperature of initial reduction in H\(_2\)-TPR\(^{11-13}\): The Gibbs free energy is shown in part a) and enthalpy in part b). It is obvious from the graph that there is no obvious correlation between thermodynamic quantities and H\(_2\)-TPR data within even one study. Moreover, Bosch et al\(^{(ref)}\) have shown that pretreatment and the experimental procedure of H\(_2\)-TPR can significantly affect observed results over bulk V\(_2\)O\(_5\). For example, the onset temperature of the reduction for bulk V\(_2\)O\(_5\) can change from 530°C to 630°C depending on pretreatment. Therefore,
H$_2$-TPR data is unique to a particular catalyst from a particular study and cannot be used to compare catalysts across different studies.

In principle, energies of oxidation and reduction can be measured using calorimetric measurements of O$_2$ adsorption, but data from these experiments tend to be unreliable. In addition to difficulties associated with heat losses in microcalorimetry, oxidation reactions tend to be irreversible so that measured heats on high-surface-area sample will be, at best, an average value if the adsorption enthalpies are a function of stoichiometry. If bulk and surface oxidation are different, an O$_2$ pulse can easily saturate the external part of the sample before beginning to oxidize deeper parts of the sample. Finally, because the entropy of oxidation cannot be determined in the absence of equilibrium data, a complete set of thermodynamic redox properties for the material cannot be obtained from calorimetry.

![Figure 1.2: a) $\Delta G$ as a function of the onset temperature of reduction in H$_2$-TPR](image)
Figure 1.2: b) $\Delta H$ as a function of the onset temperature of reduction in $H_2$-TPR

In the ceramic literature, thermodynamic data for bulk oxides are often obtained by measuring equilibrium oxygen fugacities, or $P(\text{O}_2)$, as function of the equilibrium composition of the bulk oxide and temperature, usually at temperatures higher than $800^\circ C$, at known sample compositions by using gravimetric measurements or coulometric titration\textsuperscript{14-16}. For example, if the reaction $\text{MO}_4(s) + \text{O}_2(g) \rightleftharpoons \text{MO}_6(s)$, where $M$ is transition metal, is at equilibrium, the equilibrium constant is given by $P(\text{O}_2)^{-1}$ and the thermodynamic properties can be calculated from the following equations:

\[
\Delta G = RT \ln(P(\text{O}_2)^{-1}) \quad (1.1)
\]

\[
\Delta S = \frac{\partial \Delta G}{\partial T} \quad (1.2)
\]

\[
\Delta H = \Delta G + T\Delta S \quad (1.3)
\]

Therefore, a complete thermodynamic description of the oxidation of a solid oxide can be obtained by measuring equilibrium $P(\text{O}_2)$ as a function of the oxygen stoichiometry in the oxide.

As part of this work, an improved technique of coulometric titration was used to measure equilibrium $P(\text{O}_2)$ at lower temperatures and is described in detail in chapter
two. Redox thermodynamic properties have been measured for catalysts based on iron oxide, vanadium oxide, and molybdenum oxide. These catalysts are of interest because there is evidence for an effect of support and effect on catalytic behavior of these catalysts.

1.2 Iron oxide catalysts

Iron-based catalysts are used for a number of reactions including Fischer-Tropsch synthesis (FTS), Water-Gas Shift (WGS) and ammonia synthesis. In particular, the WGS reaction is currently a major reaction in the pathway to produce hydrogen on an industrial scale using methane gas or some other hydrocarbon as a starting material. The feedstock is reacted with H₂O in a steam reforming reaction to produce CO and H₂. Then the gases are fed with additional H₂O to WGS reactors to produce more H₂ from H₂O by oxidation of remaining CO to CO₂. The WGS reaction on iron oxide catalysts is generally thought to proceed via the following Mars-van Krevelen mechanism:

\[
Fe_2O_3 + H_2O \leftrightarrow Fe_3O_4 + H_2 \quad (1.4)
\]

\[
Fe_3O_4 + CO \leftrightarrow Fe_2O_3 + CO_2 \quad (1.5)
\]

In order to fully use reactants, minimize separation costs, and/or avoid catalyst poisoning downstream, it is important to have very low CO concentrations in the outlet stream. The upper limit on conversion of feed gases to H₂ and CO₂ is determined by thermodynamics and the composition of inlet gases. In general, the equilibrium conversion is inversely proportional to the temperature. In order to produce H₂ with low CO levels, the WGS reaction needs to be performed at low temperatures to achieve high CO conversion. Industrially, this is done by performing WGS in two stages. The high temperature stage is carried out over an iron-oxide catalyst in the presence of steam, with a final conversion of ~95%, while the low temperature stage takes place over a copper/zinc oxide catalyst to achieve >99% conversion. Any residual CO can be later scrubbed with selective adsorbent to the required concentrations.

It is unclear how the thermodynamic redox properties of the catalyst affect reactivity of the catalyst. Therefore, ΔG for the redox reactions of bulk iron oxide and several different loadings of iron oxide supported on ZrO₂ have been measured at 973 K via equilibrium partial pressure of oxygen. The rates for the WGS reaction on bulk iron
and on the supported iron catalysts are also reported in order to investigate the correlation between the redox properties and reactivity.

1.3 Vanadia based catalysts

Vanadium is one of the most abundant and widely used metals in the earth’s crust. Approximately 80% of the vanadium that is produced is used in metallurgy. The rest of the vanadium is used either in catalysis, as a ceramic or glass additive/sintering aid, or for other uses\textsuperscript{1,18,19}. The main form of vanadium used in catalysis is either supported vanadium oxide or a mixed oxide such as Mg\textsubscript{3}(VO\textsubscript{4})\textsubscript{2}, CeVO\textsubscript{4}, V\textsubscript{2}P\textsubscript{2}O\textsubscript{7}. In the former, vanadium oxide is usually dispersed, i.e. supported on another oxide such as TiO\textsubscript{2}, ZrO\textsubscript{2}, CeO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, etc to achieve maximum surface area per gram of catalyst and to avoid mass transport limitations in a gas phase. Some examples of reactions catalyzed by vanadia-based catalysts are listed in Table 1.1\textsuperscript{2}.

**Table 1.1: Reactions catalyzed by vanadium-based catalysts**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of NO\textsubscript{x} with NH\textsubscript{3}</td>
<td>V\textsubscript{2}O\textsubscript{5} supported on WO\textsubscript{3}/TiO\textsubscript{2}</td>
</tr>
<tr>
<td>Oxidative dehydrogenation of C\textsubscript{3}H\textsubscript{8} to C\textsubscript{3}H\textsubscript{6}</td>
<td>V\textsubscript{2}O\textsubscript{5} supported on Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>Oxidation of alcohols to aldehydes</td>
<td>Supported V\textsubscript{2}O\textsubscript{5}, mixed oxides of V</td>
</tr>
<tr>
<td>Oxidation of o-xylene to phtalic anhydride</td>
<td>V\textsubscript{2}O\textsubscript{5} supported on TiO\textsubscript{2}</td>
</tr>
<tr>
<td>Ammoxidation of aromatics</td>
<td>V\textsubscript{2}O\textsubscript{5}, mixed oxides of V and Mo</td>
</tr>
<tr>
<td>Oxidation of butane to maleic anhydride</td>
<td>(VO\textsubscript{2})P\textsubscript{2}O\textsubscript{7}</td>
</tr>
<tr>
<td>Oxidation of SO\textsubscript{2} to SO\textsubscript{3} (industrial)</td>
<td>V\textsubscript{2}O\textsubscript{5}</td>
</tr>
</tbody>
</table>

**Bulk Vanadates**

Mixed oxides of vanadia, such as Mg\textsubscript{3}(VO\textsubscript{4})\textsubscript{2}, (VO)\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, CeVO\textsubscript{4}, etc., have been shown to improve the activity and selectivity over bulk vanadia for partial oxidation reactions such as oxidative dehydrogenation of C\textsubscript{3}H\textsubscript{8} to C\textsubscript{3}H\textsubscript{6} and ammoxidation of propene to acrylonitrile\textsuperscript{20-22}. In all of the mixed oxides listed above, only vanadium atoms are cycling through their oxidation states, but the reaction pathways and ultimately selectivity of hydrocarbon-oxidation reactions are different for different oxides.
The variation of selectivity is likely to be related to the structure of these catalysts. The VO₃ species in these catalysts, which can be assumed to be active sites, have different environment due variations in crystal structures and presence of cations of other metals. Even bulk vanadium oxide is a system with complex redox behavior. It forms stoichiometric oxides (i.e. V₂O₅, VO₂, V₂O₃ and VO) and mixed-valence phases (i.e. Magnelli phases) between some of these stoichiometric oxides. In Mg₃(VO₄)₂, all of the oxygen ions are shared between V and Mg ions (Mg-O-V bonds); while for Mg₂V₂O₇, the active sites are V₂O₇ tetrahedra, where at least one of the oxygen atoms is shared between vanadium ions. In (VO₂)₂P₂O₇ catalysts, vanadium forms V₂O₈ units made of two V₂O₅ square pyramids which share one edge, i.e. two oxygen atoms are shared between two vanadia ions. It has been suggested that the probable reason for different selectivities on these mixed-oxide catalysts might be related to the strength with which the oxygen is bound to the lattice, which is expected to be different from bulk vanadia due to the unique lattice structure of each material. Although some attempts have been made to correlate oxygen binding energies of bulk vanadates to reaction kinetics, it is still not clear how those two are connected. In previous work by Shah et al²³, thermodynamic redox data was gathered for V₂O₅, Mg₃(VO₄)₂, CeVO₄, ZrV₂O₇, CrVO₄, and AlVO₄. It was shown that the oxygen binding energy depended strongly on the identity of the other cation in the mixed oxide as well as the structure of the mixed oxide. In materials with a structure in which every two vanadium cations share an oxygen anion, the reduction of vanadia proceeds in stepwise fashion, from V⁵⁺ to V⁴⁺ to V³⁺, over a wide range of energies for reduction and oxidation. Such structures occur in polymeric supported vanadia, bulk vanadia, and zirconium vanadate. Bulk vanadia and zirconium vanadate showed very similar thermodynamic properties, while polymeric supported vanadia was harder to reduce by over 100 kJ/mole of O₂. In materials with structures for which the vanadium cations do not share an oxygen anion, the reduction of vanadia proceeds in a single step from V⁵⁺ to V³⁺. Such structures occur in cerium, aluminum, chromium, and magnesium vanadate, as well as isolated supported vanadia. In mixed oxides having this structure, the reduction thermodynamics depended strongly on the identity of the other cation in the mixed oxides. The free energy of oxidation was -300 kJ/mol of O₂ for supported vanadia, which is much higher than that observed for bulk vanadia.
Furthermore, the free energy of oxidation did not change with the support used. In spite of all those differences, the reaction rate of methanol to formaldehyde showed little variation on all materials. 

**Supported Vanadates**

Catalyst supports are used to increase the mechanical stability of the catalyst and the surface area of the active compound. In the case of supported vanadia, it has been reported that the selectivity and activity of the catalyst are also strongly influenced by the support material\(^{21,24-38}\). Depending on the support, the activity can be better or worse than that of bulk vanadia.

One of the proposed reasons for enhanced activity of supported vanadia might be due to structural effects. A large number of studies have been performed to elucidate the structure of vanadia dispersed on various materials using techniques such as Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Reflectance (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, etc. Although there is much debate on the exact structure of the surface vanadates, there is agreement that the structure is a function of vanadia loading on the surface. The most commonly accepted structures on a surface are shown in Figure 1.3. The effect of the vanadia surface concentration on the structure of the vanadia is similar across most of the materials, with an exception of SiO\(_2\). At low loadings, isolated VO\(_4\) species are present with three V-O-S (support cation) bonds and a single V=O bond. As the loading is increased, one-dimensional and two-dimensional polymeric VO\(_x\) chains are formed having V-O-V, V-O-S, and V=O bonds. Once the surface is saturated (at approximately 7-8 VO\(_x\)/nm\(^2\), the loading corresponding to a monolayer of vanadia) any additional vanadia leads to formation of bulk vanadium oxide, which can be either crystalline or amorphous. In the case of SiO\(_2\), crystalline bulk vanadia will form at much lower vanadia loading, because polymeric vanadia is not stable. Also, with some supports, vanadium oxide can react with the support and form a layer of mixed metal oxide (e.g. formation of AlVO\(_4\) or ZrV\(_2\)O\(_7\) at temperatures greater than 823 K).
Furthermore, not much is known about the distribution of vanadium oxidation states under reducing conditions. TPR and TPO studies have suggested that, upon reduction, the average oxidation state of the vanadium is between 3 and 4. Using electron spin resonance (ESR) spectroscopy, XPS, and UV-Vis diffuse reflectance spectroscopy (DSR), it has been reported that supported vanadia may exist in the +4 oxidation state in addition to the +5 state under ambient conditions.

As mentioned earlier, the selectivities and activities of supported vanadia catalysts are reported to be influenced by the support material. In particular, Deo et al. have studied partial oxidation of methanol to formaldehyde over vanadia supported on various metal-oxides. They reported that the turnover frequencies for CH$_2$O production (i.e. rate of reaction in molecules of CH$_2$O per vanadia reaction site) changed significantly with composition of the support, as shown in Table 1.2. Interestingly, the reported TOFs reported in a later study by the same group changed significantly, as shown in Table 1.2. However, while the TOF varied by several orders of magnitude on the different supports, the activation energies were similar and essentially independent of support in all of the studies. Bronkema and Bell also reported differences in methanol oxidation activity for V$_2$O$_5$ supported on ZrO$_2$, TiO$_2$, and SiO$_2$, but their results contradicted other studies in that they found that vanadia on zirconia was 8 times less active than vanadia on titania. In the propane to propene oxy-dehydrogenation reaction, Khodakov et al. have reported that the activity of the supported vanadia catalyst is essentially independent of support, but that the selectivity for propene changes significantly with the loading of vanadia.

**Figure 1.3:** (A) isolated (B) polymeric structures of supported vanadium oxide adopted from Shah et al.
Though multiple sources confirm that the support can influence the reactivity of vanadia catalysts, there are still conflicting reports on the magnitude of that effect and its origin. To explain their results, Deo et al\textsuperscript{30} proposed that variations in the TOF are due to the differences in the strength of the V-O-S bonds, which they infer from H\textsubscript{2}-TPR data. One possible reason for changes in the V-O-S bond strengths has been proposed by Zhao, et al, who have argued that the observed support effect is due to changes in the electron density on the V-O-S bond, a result of differences in the electronegativity of support cations\textsuperscript{48}.

**Table 1.2:** TOF of methanol oxidation over supported vanadia.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF for CH\textsubscript{3}OH oxidation to CH\textsubscript{2}O, s\textsuperscript{-1}, @230\degree C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deo et al\textsuperscript{30}</td>
</tr>
<tr>
<td>20% V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.068</td>
</tr>
<tr>
<td>5% V\textsubscript{2}O\textsubscript{5}/Si\textsubscript{2}O\textsubscript{5}</td>
<td>0.0015</td>
</tr>
<tr>
<td>6% V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}</td>
<td>1.1</td>
</tr>
<tr>
<td>4% V\textsubscript{2}O\textsubscript{5}/ZrO\textsubscript{2}</td>
<td>1.7</td>
</tr>
<tr>
<td>3% V\textsubscript{2}O\textsubscript{5}/CeO\textsubscript{2}</td>
<td>10</td>
</tr>
</tbody>
</table>

Since partial oxidation over vanadia-based catalyst likely takes place via a Mars-van Krevelen mechanism, supported vanadia offers three types of oxygen for reaction: oxygen associated with V-O-S, V=O, or V-O-V bonds. The possibility of a role for each of these types of oxygens has been discussed in the literature. While some of the earliest literature suggested the involvement of oxygen associated with the V=O bond as the active site for methanol oxidation, its involvement has been discounted based on in-situ RAMAN O\textsuperscript{18} exchange measurement, which also provided evidence that the oxygen from the V=O bond is not involved in the methanol oxidation reaction\textsuperscript{29}. Most recent reports favor the idea that oxygen associated with V-O-S bonds are primarily responsible for oxidation of methanol\textsuperscript{40}.

Support effects may be very different for propane ODH. Unlike the situation for methanol oxidation, the TOF for ODH has been shown to increase with loading, implying that either the V-O-V bond or the V=O bond may be involved in the reaction. DFT
studies suggest that oxygen from the V=O bond is the likelier candidate. Oxygen from the V-O-V bonds has been commonly thought to be inactive for methanol oxidation because lack of dependence of activity with vanadia loading\textsuperscript{30}.

Although a significant amount of research has been done to understand the activity of supported vanadia, there is no coherent explanation to rationalize how support interactions affect the vanadium species and influence their catalytic activity. Clearly, there is much to be learned about supported vanadia and vanadia catalysts. The goal is to determine effect of support on thermodynamic and catalytic properties of supported vanadia.

### 1.4 Molybdenum based catalysts

Molybdenum catalysts exhibit a number of similarities to vanadia. Both Mo and V are transition metals with multiple stable oxidation states. Both Mo- and V-based catalysts tend to be used in the form of complex mixtures with other oxides. The mechanisms for catalytic partial-oxidation reactions are typically classed as Mars-van Krevelen. Molybdenum mixed oxides are catalysts for a number of selective oxidation reactions and are used in industry for various processes, several of which are shown in Table 1.3\textsuperscript{2}. At least in part because pure MoO\textsubscript{3} is relatively volatile, molybdena is essentially always used in the presence of a second oxide, either on an oxide support such as alumina, titania, or zirconia\textsuperscript{1,49-54}, or in the form of a mixed oxide, such MgMoO\textsubscript{4} \textsuperscript{55,56}. For both types of catalyst, the second oxide component is reported to significantly alter catalytic properties. For example, molybdena catalysts supported on titania or zirconia have been reported to be six times more active than their alumina- or silica-supported counterparts for methanol oxidation\textsuperscript{9}. The CH\textsubscript{3}OH TOF of the various catalysts has been reported to correlate with peak temperature in TPR which has been interpreted as indicating the support affects the strength of the oxygen bonds\textsuperscript{9}.

However, quantitative information on how the presence of other metal cations influences the reducibility of a Mo cation and how this in turn affects catalytic activity is not available. Again, as in the case of vanadium mixed oxides, a correlation between catalytic activity for ethane ODH and electronegativity has been reported\textsuperscript{52}. If
electronegativity is the critical parameter, it may suggest that reactivity is related to how covalent or ionic the Mo-O bond is.

**Table 1.3:** Reactions catalyzed by molybdenum-based catalysts

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene to Acrylonitrile ammoxidation</td>
<td>Bi:Mo mixed oxides promoted with Fe, P, K and other metals</td>
</tr>
<tr>
<td>(SOHIO process)</td>
<td></td>
</tr>
<tr>
<td>Hydrogenation and hydrodesulfurization</td>
<td>Sulfided Co-Mo supported on Al₂O₃</td>
</tr>
<tr>
<td>Oxidation of alcohols to aldehydes</td>
<td>Fe₂(MoO₄)₃</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>Co-Mo and MoO₃ on solid acid support</td>
</tr>
<tr>
<td>Acrolein to acrylic acid oxidation</td>
<td>Mixed oxides of V and Mo</td>
</tr>
<tr>
<td>Selective reduction of NOₓ with NH₃</td>
<td>MoO₃, MoO₃/Pd supported on Al₂O₃</td>
</tr>
<tr>
<td>Alkanes to alkene oxi-dehydrogenation</td>
<td>Supported MoO₃</td>
</tr>
</tbody>
</table>

In the case of vanadium mixed oxides, the importance of electronegativity of the second cation to bonding in mixed oxides has been quantitatively demonstrated from the thermodynamic data. For mixed oxides of vanadium with only V-O-M bonds, ΔG of oxidation was found to scale with electronegativity of the Mⁿ⁺ cations and vary by up to 250 kJ/mol-O₂. Whether a similar correlation would exist for Mo-based mixed oxides is not known.

**Supported Molybdates**

Mo-based supported catalysts are highly complex materials. In most cases, molybdenum is dispersed on the support surface together with other metals and promoters in order to obtain desired catalytic characteristics. These materials exhibit catalytic properties similar or better than bulk oxides of molybdenum and are used for various reactions.

As with supported vanadia catalysts, structural effects, not just oxygen binding, may be a primary factor behind the enhanced properties. A large number of studies have been performed to elucidate the structure of the surface molybdena on various supports using techniques such as RAMAN, XPS, FTIR, etc. The exact structure of the surface molybdates is a highly researched topic in the literature; the only concretely
established fact is that the structure depends on molybdena loading and the method of preparation. The most commonly accepted structures on a surface are shown on Figure 1.4. Prevalence of one or another species depends on molybdena loading and preparation route, especially the temperature of calcination. Typically, the surface is saturated at \(~4 \text{ MoO}_x/\text{nm}^2\), i.e. a monolayer of molybdena is formed. Any additional molybdena leads to the formation of 3-dimensional molybdenum oxide which can be either crystalline or amorphous. The exception, as in the vanadia case, is molybdena on SiO\(_2\), since crystalline MoO\(_3\) was observed at loading above \(~1 \text{ MoO}_x/\text{nm}^2\). On some supports, molybdenum oxide can react with the support and form a layer of mixed metal oxide, i.e. formation of Al\(_2\)(MoO\(_4\))\(_3\) was observed at temperatures as low as 573 K and formation of Zr(MoO\(_4\))\(_2\) at 873 K.

Furthermore, not much is known about the distribution of molybdenum oxidation states under ambient and reducing conditions. Using XPS and RAMAN measurements, it has been reported that supported molybdena may exist in +5 state and even in +4 state in addition to +6 state under ambient conditions.

\[ \text{Figure 1.4: Possible molecular structures of supported MoO}_x: (A) mono-oxo MoO}_5^{4+} \text{ monomers (B) di-oxo MoO}_4^{2-} \text{ monomers (C) dimeric Mo}_2O}_6^{3-} \text{ (D) Polymeric MoO}_x \text{ species, adapted from} \]
As mentioned before, selectivity and activity of supported molybdenas are influenced by the support material. For example, Tsilomelekis et al.\textsuperscript{52} have studied in detail the oxidative dehydrogenation of ethane to ethene over various supported molybdenas. The reported TOF and selectivity are shown in Table 1.4. The activity of catalysts did not vary significantly but the support had a tremendous effect on selectivity with variation between 30\% and 90\% depending on a support. One important point about selectivity, which is also shown in Table 1.4, is that selectivity can strongly depend on the extent of conversion. Another reaction for which support effect has been reported is the partial oxidation of methanol to formaldehyde over supported molybdena\textsuperscript{51,53,61}. It is widely accepted that C-H bond breaking is a limiting step in the oxidation of methanol to formaldehyde over molybdenum oxide catalysts;\textsuperscript{51} therefore, a possible effect of the redox thermodynamics on reactivity is more subtle. Hu et al.\textsuperscript{9} reported that the turnover frequencies and selectivity of formaldehyde production, which are shown in Table 1.5, do not change significantly with the nature of the support, except in the case of molybdena on alumina. In the latter case, aluminum molybdate might have formed which might alter reaction mechanism and thus affect both selectivity and activity.

**Table 1.4:** \( \text{C}_2\text{H}_6 \) to \( \text{C}_2\text{H}_4 \) reaction over monolayer supported Molybdena at 500\(^\circ\text{C}.\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF, ( \times 10^3, \text{s}^{-1} )</th>
<th>Selectivity, %C(_2)H(_4) 5% Conversion</th>
<th>Selectivity, %C(_2)H(_4) 20% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 wt% MoO(_3)/ZrO(_2)</td>
<td>2.5</td>
<td>75</td>
<td>73</td>
</tr>
<tr>
<td>15 wt% MoO(_3)/Al(_2)O(_3)</td>
<td>1.2</td>
<td>92*</td>
<td>73</td>
</tr>
<tr>
<td>9 wt% MoO(_3)/TiO(_2)</td>
<td>.6</td>
<td>75</td>
<td>36*</td>
</tr>
<tr>
<td>2 wt% MoO(_3)/SiO(_2)</td>
<td>0.2</td>
<td>30*</td>
<td>0 @ conv. Of 8%</td>
</tr>
</tbody>
</table>

*extrapolated
Table 1.5: CH$_3$OH to CH$_2$O reaction over monolayer supported Molybdena at 230°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF, s$^{-1}$</th>
<th>Selectivity, % CH$_2$O at 5% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 wt% MoO$_3$/ZrO$_2$</td>
<td>0.55</td>
<td>78</td>
</tr>
<tr>
<td>20 wt% MoO$_3$/Al$_2$O$_3$</td>
<td>0.01</td>
<td>20</td>
</tr>
<tr>
<td>5 wt% MoO$_3$/TiO$_2$</td>
<td>0.58</td>
<td>85</td>
</tr>
<tr>
<td>6 wt% MoO$_3$/Nb$_2$O$_5$</td>
<td>0.19</td>
<td>80</td>
</tr>
</tbody>
</table>

Despite extensive experimental investigations, which established that partial oxidation over molybdena-based catalyst takes place via the Mars-van Krevelen mechanism$^{62,63}$, the mechanisms of oxidation are not well understood. Supported molybdena, similarly to supported vanadia, has many oxygen ions available for the oxidation reaction due to the variability of its structure; an oxygen ion can come from either various M-O-S, M=O, or M-O-M bonds. Depending on the oxygen ion used, the mechanism of oxidation might be different, thus catalysts would show different selectivity and activity behavior. For example, the mechanism of the oxidation of methanol to formaldehyde is different for di-oxo and mono-oxo monomers on silica$^{64}$.

Although significant amounts of effort have been put towards understanding the activity-structure relationship of supported molybdena catalysts, there remains uncertainty as to how and why these catalysts work. Similarly to vanadium oxide, the goals of molybdenum oxide studies are to determine thermodynamic properties of these compounds and relate them to structure and catalytic activity.

1.5 Scope of the Thesis

As the introduction above states, mixed and supported metal oxides display catalytic behavior in oxidation reactions which is a complex function of structure and composition and is different from their parent oxide. It has been hypothesized that one of the reasons for such behavior is that binding energy of the lattice’s oxygen, exposed on a catalytic surface, varies with composition and structure. Despite the widely accepted idea of support affecting the oxygen binding energy, mostly unreliable measurements of oxygen binding energies via H$_2$-TPR or calorimetry have been made to examine this
hypothesis. Detailed thermodynamic characterization of oxygen binding energies has never been done for any catalyst. Therefore, this dissertation is focused on measuring the redox thermodynamic properties of important catalysts and then correlated these to structure, composition, and catalytic activity for oxidation reactions. The catalysts examined were supported iron oxide, supported vanadium oxide, mixed oxides of molybdenum, and supported molybdenum oxide. The reactions used were water gas shift, methanol to formaldehyde partial oxidation, and propane to propene oxidative dehydrogenation.

This dissertation is partitioned into six chapters. The experimental techniques and methods used are described in chapter two. The work done with supported vanadia is described in chapter three, exploring the influence of preparation route on redox properties, stability, and reaction rates. In addition, a novel technique for estimating the number of redox sites on a catalytic surface and its application to supported vanadia is described in chapter three. The thermodynamic properties of supported iron oxide are explored in chapter four along with how they influence the water-gas-shift reaction. In chapter five, the redox properties of bulk mixed oxide of molybdenum are reported and compared to the mixed oxide of vanadium, pointing to the importance of structure in redox properties. Conclusions and insights are summarized at the end.
Chapter 2. Experimental techniques

The experimental techniques used for the work in this thesis are described below. Theory and practical implementation of the coulometric titration technique are described in detail due to the novelty of the method to catalysis sciences. Preparation and characterization of employed catalysts are described afterwards. Steady state and transient measurements of reaction rates over the materials are described last.

2.1 Theory of equilibrium $P(O_2)$ measurements

The most direct way to determine thermodynamics of any reaction is to measure equilibrium concentrations, or fugacities, of species involved in a reaction. If such information is available, then an equilibrium constant can be easily computed. Using thermodynamic identities, the Gibbs free energy change for the reaction can be calculated. By measuring the Gibbs free energy at various temperatures, enthalpy and entropy of the reaction of interest can be deduced. For example, consider the reaction of A and B to form C and two D:

$$A + B = C + 2D$$  \hspace{1cm} (2.1)

$$K_{eq} = \frac{\alpha_c \alpha_D^2}{\alpha_A \alpha_B}$$ \hspace{1cm} (2.2)

$$\Delta G = RT \ln(K_{eq}) = \Delta H - T\Delta S$$ \hspace{1cm} (2.3)

$$\Delta S = \frac{\partial \Delta G}{\partial T}$$ \hspace{1cm} (2.4)

$$\Delta H = \Delta G + T\Delta S$$ \hspace{1cm} (2.5)

In this study, most materials are oxides of metals and their interaction with oxygen can be described through the following reaction, where M denotes a metal:

$$MO_x(s) + O_2(g) \rightleftharpoons MoO_{x+2}(s)$$ \hspace{1cm} (2.6)

Because the oxides of metals examined are solids at the temperatures of interest, their activity by definition is 1. Therefore, the equilibrium constant for a reaction (2.6) is simply the reciprocal fugacity, i.e. pressure of oxygen $K_{eq} = P(O_2)^{-1}$. If the equilibrium of $P(O_2)$ can be measured, fundamental thermodynamic quantities can be obtained using equation 2.2 through 2.5.
For most oxides at relevant temperatures, the equilibrium fugacity of oxygen is very low, e.g. \(<10^{-6}\) atm of P(O\(_2\)); thus, a material cannot establish equilibrium with gas-phase oxygen directly in a reasonable time due to a very low flux of O\(_2\) molecules from the gas phase to the surface. For example, consider a reduced metal oxide that is held at P(O\(_2\)) of \(10^{-13}\) atm and 1000 K; and, assume that the sample would be oxidized under those conditions based on the bulk thermodynamics. Using kinetic theory of gases, the flux of O\(_2\) molecules to the surface can be computed and it is so small that it would take 12 hours for the surface to at least absorb one Langmuir of oxygen, i.e oxidize the first atomic layer of the material, assuming sticking coefficient of one. In addition, at partial pressures of oxygen below \(10^{-20}\) atm and 973 K, the experimental apparatus used in this study would contain less than one molecule of oxygen. Therefore, equilibrium must be established via an interaction with a redox couple, or buffer gas, such as CO\(_2\)/CO or H\(_2\)/H\(_2\)O. If the system described above contained at least 0.1 atm of H\(_2\)O initially, the flux of H\(_2\)O to the surface at 1000 K would be \(10^{12}\) langmuirs/second. H\(_2\)O can oxidize the surface and thus bring it to equilibrium at a much faster rate. The amount of H\(_2\)O oxidized/reduced can be calculated from the equilibrium equation, provided the initial conditions are known, e.g. P(H\(_2\)O):

\[
H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O
\]  

(2.7)

\[
\log(P(O_2)) = -2\log(K_{eq}) + 2\log\left[\frac{P(H_2O)}{P(H_2)}\right]
\]  

(2.8)

The oxygen stoichiometry of the solid at a given P(O\(_2\)) is an important variable, because it can help assign thermodynamic data to a particular oxidation reaction that a metal oxide is going through. The stoichiometry of a solid at a given P(O\(_2\)) can be determined using techniques like gravimetry or flow titration. Both gravimetry and flow titration \(^{13,65,66}\) are limited in regards to their accessible P(O\(_2\)) range, because they are essentially an open system where P(O\(_2\)) is set using precise quantities of inlet gases. Therefore, the precision with which one can establish the P(O\(_2\)) above the sample is set by the ability to control the partial pressures of H\(_2\) and H\(_2\)O. Another option in determining oxygen stoichiometry of a sample is keeping track of oxygen transferred to a closed system. If the size of the system, the initial state of the sample, the initial and final equilibrium P(O\(_2\)), and the amount of oxygen added to the system are known, then by using mass balance the final oxygen stoichiometry can be computed:
\[ O_{\text{total}} = O_{\text{sample}} + O_{\text{gas phase}} + O_{\text{redox couple}} \]  \hspace{1cm} (2.9)
\[ O_{\text{total, final}} = O_{\text{total, initial}} + O_{\text{added}} \]  \hspace{1cm} (2.10)

The amount of the oxygen in the gas phase and in the redox buffer gases can be determined from the \( P(O_2) \) measurement using the ideal gas law, the initial amounts of buffer gases, and equation (2.8). If the initial oxygen stoichiometry of the sample and the amount of added oxygen is known, the final oxygen stoichiometry can be easily solved.

### 2.2 Coulometric titration

Coulometric titration is an electrochemical technique for the measurement of equilibrium \( P(O_2) \) above a sample of interest. The design adheres to the theory outlined in section 2.1; it is performed with a closed system, with the ability to quantitatively add or remove oxygen via an \( O^{2-} \) conducting membrane such as yttria-stabilized zirconia. The same membrane is also used to measure the fugacity of oxygen inside the system.

Coulometric titration has been used extensively to determine the redox properties of oxides at temperatures above 1273 K, and many designs have been described in the literature\(^{15, 16, 67} \). In most designs, the experimental configuration is a closed system with a yttria-stabilized zirconia (YSZ) membrane. YSZ is a chemically inert material and an electric insulator, known to conduct \( O^{2-} \) ions at temperatures above 200\(^\circ\)C. Because of that, the electric potential across the membrane can be related to the \( P(O_2) \) difference across the membrane via the Nernst equation:

\[
V = -\frac{RT}{4F} \ln \left( \frac{P(O_2)_{\text{inside}}}{P(O_2)_{\text{outside}}} \right) \]  \hspace{1cm} (2.11)

Therefore, the \( P(O_2) \) inside the system can be estimated if the outside \( P(O_2) \) is known, which is typically atmospheric \( P(O_2) \). Second, oxygen can be added or removed from the system by applying a voltage across the membrane and passing current through an external circuit, which forces oxygen to flow across the membrane. Recording the amount of charge that is passed enables determination of the amount of \( O^{2-} \) pumped, since passing one oxygen atom through the membrane requires two electrons to move from one electrode to the other through an external circuit, with 1 coulomb of charge passed corresponding to \( 2.59 \times 10^{-6} \) mol of \( O_2 \).
The experimental setup used to collect thermodynamic data in all studies in this thesis is shown in Figure 2.1. The main element of the coulometric titration setup is the YSZ tube (McDaniels ceramics) with dimensions of 0.3048 m x 0.0127 m x 0.0238 m, corresponding to the length, the outer diameter, and the inner diameter respectively. The tube served both as a structural element and as a YSZ membrane. In this design, the seals are placed outside of the heating zone, which allowed for the use of robust Swagelok fittings with Viton O-rings. In addition, this design makes it possible to examine samples with a large volume, which is very important with supported materials where active component can be less than 5 wt%. Using a supporting tube as a membrane also allows the use of electrodes with large surface areas which help to improve oxygen pumping. Silver electrodes were painted in the middle of the tube, on the inside and outside, using silver paste supplied by Alfa Aesar and platinum wires (SRI supplies) glued to the electrodes using the same silver paste. The tube was then baked in ambient air at 500°C to oxidize the solvent used in the silver paste. Then, the inside Pt wire was attached to the Swagelok ultra-torr fitting by spot-welding.

![Figure 2.1: Schematic of Coulometric Titration apparatus](image)

The tube was then inserted into a horizontal furnace (0.1524 m x 0.0381 m L x ID, Omega Engineering) in such a way that the outer ends of the tube were outside of the furnace. The furnace was insulated and the ends of the tube were supported. The sample was inserted into the tube using a ceramic sample holder made from an alumina tube with a 0.635 cm outer diameter (McDaniel Ceramics). Swagelok fittings (1.27 cm to 0.635 cm...
reducing union) were then fixed to the ends of the tubes. The temperature rate of the oven was set to 5°C/min or lower then heating to the desired temperature. The starting mixture of gases was allowed to flow over the sample for approximately 4 hours. For measurements from the oxidized state, either a mixture of 50% CO₂, 5% O₂, and 45% Ar or 33.4% H₂O, 6.6% O₂, and 60% Ar was used. For the measurement from the reduced state, either 5% CO/45%CO₂ or 5% H₂/45%H₂O in He was flown over the sample. Finally, glass stoppers were used to seal the system.

In all experiments, a Gamry Instruments potentiostat was used to apply a potential across the cell for pumping oxygen across the YSZ membrane and simultaneously measuring the current to determine the amount of O₂ pumped. To measure open-circuit voltages, either the Gamry Instruments potentiostat or an Agilent 34401A digital multimeter, in >10 GΩ impedance mode, were used.

Coulometric titration was validated by measuring the heats of transition of bulk CuO⇌Cu₂O⇌Cu^{6+}, bulk V₂O₅⇌V₂O₄⇌V₂O₃^{6'}, and bulk Fe₂O₃⇌Fe₃O₄⇌FeO^{70}. All values obtained were within the experimental error of the data published in the literature.

2.3 Synthesis of materials

Most of the materials used in this study were prepared in-house using wet chemical techniques. The only exceptions were alumina (γ phase, Alfa-Aesar) and titania (anatase, Degussa P-25).

Mixed oxides were prepared by the Pechini Method. This method provides a thorough mixing of precursors, therefore eliminating the need to fire samples at temperatures above 800 °C, which produces sintered materials with a low surface area. To prepare a mixed oxide by this method, precursor salts of the oxides, typically nitrates, were dissolved in an aqueous solution with citric acid or oxalic acid. The amount of acid added was 10% more than molar equivalence of the metal ions to completely chelate the solution. The excess water was evaporated until dry powder was formed. The material was then dried overnight in ambient air at 400 K, ground with a mortar and pestle, fired at 748 K to decompose the nitrates, reground again, and finally fired at the desired temperature to yield the required mixed oxide. The details of the preparation such as
ingredients and firing temperatures for particular mixed oxides are described in corresponding chapters.

In this work, the main method of preparation for supported catalysts was incipient wetness impregnation. Ammonium metavanadate, ammonium hepta-molybdate, or iron nitrate was dissolved in water acidified by oxalic acid. The support of choice was added to the solution and stirred vigorously for at least 4 hours. The amount of precursor and support were carefully chosen to obtain the desired weight loading. The slurry was then dried, ground, and calcined in hot air at 748 K to decompose the precursors and obtain a catalyst in an oxidized state. Details of preparation for a catalyst based on an oxides of particular metals are described in the subsequent chapters.

Section 2.4 Characterization techniques

The materials that were synthesized were characterized with one or more of the methods discussed below. The results of the characterization studies are discussed in subsequent chapters.

BET Surface area measurement

Measuring the specific surface area of a catalyst is important, because the reaction takes place on a phase boundary between the solid and gas phase, e.g. surface of catalyst. In this work, all surface areas were measured by the Brunauer-Emmett-Teller (BET) method using N$_2$ as the adsorbent. The theory behind the measurement is well described in the literature$^{71}$. The method takes advantage of well-described equilibrium between the gas phase (i.e. partial pressure) and adsorbed N$_2$ on the surface of a material at the boiling temperature of N$_2$. By measuring the amount of adsorbed N$_2$ and the equilibrium pressure of N$_2$ above the sample at several points, an isotherm can be fitted to the data, and surface area extracted from it, given that the size of the N$_2$ molecule is known. Prior to taking measurements, the samples were pretreated by evacuating them at ~450 K for at least 1 hour to desorb impurities from the surface of the sample.

X-Ray Diffraction

X-ray diffraction (XRD) techniques are used to determine the crystalline structure at an atomic level and to characterize crystalline materials. X-rays have wavelength of ~0.1 nm and therefore are scattered by molecules. For molecules in ordered arrays such
as crystals, X-ray scattering produces diffraction patterns. The patterns are unique to the crystal structure and act as a fingerprint of the material. In the case of materials having the same crystal structure and similar atoms sizes, the XRD patterns are very similar. An XRD can provide other important information such as lattice parameters using Bragg’s Law and grain size using Scherrer’s equation.

XRD patterns were collected using a Rigaku Geigerflex diffractometer with a Cu(Kα) radiation source (\( \lambda = 1.5405 \text{ Å} \)). Diffraction patterns from the Powder Diffraction File, International Center for Diffraction Data, along with research literature, were used as references.

**RAMAN Spectroscopy**

Raman Spectroscopy is a technique used to study the vibrational motions of molecules in molecular systems. It is based on the RAMAN effect; when photons impinge onto a molecule, most photons interact elastically with the electron cloud, i.e. the molecule becomes excited and then goes back to the original state or light is scattered at the same wavelength as incident light via Raleigh Scattering. However, in some excitation events, the molecule does not come back to the original state. There are two scenarios to describe this: Stokes Raman Scattering or Anti-Stokes Scattering. In Stokes Raman Scattering, molecules return to a state of higher energy then the original state, which results in light being scattered at a lower frequency. In Anti-Stokes Scattering, the final state has a lower energy than the original state, resulting in light being scattered at a higher frequency. Typically, the former is much more intense than the latter, since most molecules are initially in the ground state. The difference in the frequencies of the incident photon and the photon scattered by the Stokes process is called the Raman shift.

RAMAN spectroscopy was used mainly to characterize supported catalysts, because it can discern supported atoms in different coordination environments, i.e. polymeric versus isolated species. Raman spectroscopy was performed at two locations: the Materials Characterization Facility at Drexel University, where RAMAN spectra were obtained at room temperature under ambient conditions using a Renishaw RM1000 VIS Raman Microspectrometer with 514.5 nm Ar laser as an excitation source. The second facility was a home-made setup located in the Physics department at the University of Pennsylvania, provided through the courtesy of Professor Jay Kikkawa. In
the latter setup, Raman spectra of powders were collected in air. Powders were excited by a 532 nm diode-pumped solid state laser off-angle from the collection axis. Excitation light was filtered in three steps to remove spectral content in the region of interest. A prism and iris provided the separation of the 532 line from a broadband background, followed by two 532 laser line filters (Semrock LL01-532, 2 nm bandpass around 532 nm). Scattered light was filtered through a long-pass step-edge filter (Semrock RazorEdge LP03-532-RS), and dispersed across a CCD array (PI-Acton Pixis 256E) by a 0.5 m spectrometer (Acton 2500i) and 1200 groove/mm holographic grating.

Catalytic site counting via transient reaction rate measurements

A flow reactor equipped with an online gas chromatograph (SRI-8610C) and a TCD detector was used to measure transient reaction rates using the following procedure. After oxidizing the catalyst in air and then flushing with He, a gas mixture consisting of He and CH$_3$OH in a 95.5:4.5 molar ratio was passed over the catalyst at a total flow rate of 50 or 100 cm$^3$/min depending on the reaction rate and amount of catalyst. The temperature and mass of the catalyst were chosen such that the sample would be completely reduced within 3-5 minutes of flow. The instantaneous conversion of methanol was then measured at a set time after the sample was exposed to the methanol-He mixture. A plot of the instantaneous conversion as a function of time was then constructed by repeating this experiment for different times. Integrating the area under the curve allowed for calculating the amount of oxygen that was removed from the sample via reaction with methanol. If the material has reducible bulk, performing experiments at these sufficiently low temperatures insured that only the surface of the material was reduced, because oxygen flux from bulk to surface was much slower than the reduction of the surface. Assuming that one oxygen atom was removed per site and knowing the mass of the catalyst, the number of catalytic sites could be calculated.

2.5 Reaction Rate Measurements

The flow reactor equipped with an online gas chromatograph (SRI-8610C) and a TCD detector was used to measure transient reaction rates using the following procedure. For the water-gas shift reaction, the feed composition was fixed at 25 torr for both CO and H$_2$O in the He carrier gas, while the total flow rate was varied between 120 and 155 cm$^3$/min. For methanol oxidation, the gas mixture consisting of He, O$_2$ and CH$_3$OH in a
22.5:2:1 molar ratio was passed over a catalyst at a total flow rate of 50-130 cm$^3$/min, which was varied to keep conversion below 15%. The feed for propane ODH consisted of He:O$_2$:C$_3$H$_8$ in 7.6:1.6:1 ratio with a total flow rate of 100 cm$^3$/min. In all cases, the conversion was kept below 15% so that differential reaction conditions could be assumed. The reaction rates were normalized to the amount of active component on the surface of each catalyst. For supported catalysts of vanadia, molybdena, and iron with coverages below a monolayer, all metal was assumed to be accessible. For supported catalysts with coverages over a monolayer, the surface densities of the bulk compounds were assumed, which were 4, 6 and 7 atoms per nm$^2$ for Mo, Fe and V respectively. For mixed oxides, the bulk surface densities were assumed to be the bulk surface density of the pure active components multiplied by a ratio of active metal ions to total metal ions in the compound. For example, AlVO$_4$ would have a 3.5 V/nm$^2$ surface density for vanadium according to the calculations.
Chapter 3. Vanadia catalysts

3.1 Introduction

The selective oxidation of methanol to formaldehyde and propane to propene has been widely studied with vanadium-oxide catalysts. The reactions are believed to occur through a Mars-van Krevelen mechanism, in which the water produced in the overall reaction is formed using lattice oxygen from the solid. Past work comparing specific rates for both reactions over vanadia catalysts on different supports have indicated that the effect of support can be dramatic in both reaction rates and selectivity to desired products\textsuperscript{72, 73}. Therefore, many theoretical and experimental studies have been performed to understand how the local environment affects the oxygen bonding in these catalysts and how that in turn might affect rates.

In this chapter I expand upon previous studies of vanadia catalysts from our group\textsuperscript{23, 36, 39, 69} to include vanadia supported on alumina. The thermodynamic properties of an alumina-supported vanadia were studied as a function of loading and preparation procedure. The impact of redox properties on catalytic activity was studied by measuring reaction rates of methanol partial oxidation to formaldehyde and propane oxidative dehydrogenation (ODH) to propene.

\begin{equation}
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (4.1)
\end{equation}

\begin{equation}
\text{C}_3\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} \quad (4.2)
\end{equation}

It will be shown that the local environment of the vanadium cations dramatically affects oxygen binding, but the effect is different for reactions (4.1) and (4.2). Specific rates for methanol oxidation on each of the bulk mixed oxides and supported-vanadia catalysts are similar, indicating that oxygen binding does not affect the rate limiting step in this reaction. In the case of propane ODH to propene, thermodynamic properties significantly affect both the selectivity and the overall reaction rate.

3.2 Experimental

The supported-vanadia catalysts were synthesized using incipient wetness. Vanadia was deposited onto an alumina support by impregnation of a solution of ammonium metavanadate (NH\textsubscript{4}VO\textsubscript{3}, Sigma) and oxalic acid (C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}, Aldrich). A series
of vanadia loadings were prepared from 3.6 to 15 wt%. After drying in hot air at 400 K, the samples were ground with a mortar and pestle and calcined at 753 K in ambient air for 4 hours. All of the catalysts were characterized using BET isotherms and Raman spectroscopy. 5wt% and 15wt% samples were characterized in detail using coulometric titration and XRD. The reaction rates of methanol and propane oxidation over these catalysts were measured.

A central assumption in the Mars-van Krevelen mechanism is that the reaction of methanol with the oxidized catalyst is distinct and separate from the re-oxidation of the solid. Taking advantage of this, a novel method for counting redox catalytic sites on the surface was devised. The reaction of methanol was carried out over a catalyst in the absence of oxygen; in other words, the catalyst was reduced with a probe molecule. By observing the amount of oxidation product formed, the number of sites could be estimated by assuming that one oxygen removed equalled one site. Bulk vanadia and magnesium vanadate were studied in the temperature range of 443 K to 623 K. 2.5-wt% \( \text{V}_2\text{O}_5/\text{TiO}_2 \) (prepared and characterized by Shah et al\textsuperscript{36}) and 5-wt% \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) catalysts were studied at 443 K. It was found that only the surface reduction occurred on all materials at 443 K, and that the number of sites was consistent with the literature\textsuperscript{74, 75}. The kinetics of reduction were found to be consistent with the steady state reaction rate measurements.

3.3 Results and Discussions

The surface areas of prepared \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) catalysts as determined using the BET method are listed in Table 3.1. The surface areas were measured for both the as-prepared samples that were calcined in air at 753 K. Each sample was then calcined in ambient air at 973 K for 10 days. This latter treatment was chosen to induce a reaction between the vanadia and the alumina support in order to form a surface layer of AlVO\textsubscript{4}. The calculated vanadia coverage for each sample, assuming that the vanadia forms a film on the surface, is also given in Table 3.1. For the samples calcined at 753 K, the surface areas were slightly less than that of the bare support (180 m\textsuperscript{2} g\textsuperscript{-1}) and decreased with increasing vanadia weight loading. The 15 wt% \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) sample had a vanadia coverage of 7.3 V nm\textsuperscript{-2}, a value close to that reported for the monolayer coverage of
polyvanadates in the literature. The surface area of the 15 wt% \( V_2O_5/Al_2O_3 \) was \( 137 \, m^2 \, g^{-1} \), which is 24% less than that of the bare alumina support. This decrease is primarily due to the added mass of the sample, indicating that the overall morphology of the alumina support is preserved.

Upon calcination at 973 K for 10 days, the BET surface areas of all the samples decreased, with the larger decreases observed for the higher weight loading samples. For example, for the 3.6 wt% \( V_2O_5/Al_2O_3 \) sample, the surface area decreased by only 15%, while surface area of the 15 wt% sample decreased by 84%. Obviously, major structural changes occurred upon calcination of the high vanadia coverage samples at high temperatures, while the low vanadia coverage samples remained largely unchanged. These differences between the low and high vanadia coverage samples are also reflected in the XRD data presented in Figure 3.1 and 3.2.

**Table 3.1:** BET surface areas and vanadia coverage in alumina supported samples

<table>
<thead>
<tr>
<th>wt% of ( V_2O_5 ) supported on alumina</th>
<th>Surface area, ( m^2/\text{gram} ), Calc. at 753 K</th>
<th>Calcined at, ( m^2/\text{gram} ), calc. at 973 K for 10 days,</th>
<th>% reduction in area</th>
<th>Coverage, #V/nm(^2), calc. at 753 K</th>
<th>Coverage, #V/nm(^2), calc. at 973 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>180</td>
<td>163</td>
<td>9.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.6</td>
<td>151</td>
<td>128</td>
<td>15.3</td>
<td>1.6</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>124</td>
<td>31.2</td>
<td>1.8</td>
<td>2.7</td>
</tr>
<tr>
<td>6.36</td>
<td>139</td>
<td>80</td>
<td>42.4</td>
<td>3.0</td>
<td>5.3</td>
</tr>
<tr>
<td>8.3</td>
<td>132</td>
<td>75</td>
<td>43.7</td>
<td>4.2</td>
<td>7.4</td>
</tr>
<tr>
<td>14.5</td>
<td>131</td>
<td>35</td>
<td>73.4</td>
<td>7.3</td>
<td>28</td>
</tr>
<tr>
<td>15</td>
<td>137</td>
<td>22</td>
<td>83.6</td>
<td>7.3</td>
<td>44</td>
</tr>
</tbody>
</table>
Figure 3.1 displays XRD data for the 5 wt % vanadia sample. The XRD pattern for the bare alumina support is also shown for reference. Note that the XRD pattern for the 5 wt % vanadia sample after calcining at 753 K contains only features indicative of the alumina support. This is consistent with the vanadia being present as a well dispersed surface species. It is also worth mentioning that the calcination at 973 K did not cause any significant changes in the XRD pattern. Figure 3.2 displays XRD data for the 15 wt % vanadia sample. For the 15 wt % sample calcined at 753 K, small peaks at 20.4, 26.3, and 31.2 2θ, which can be attributed to bulk V$_2$O$_5$, are present in the XRD pattern in addition to the features indicative of γ-Al$_2$O$_3$. This demonstrates the presence of V$_2$O$_5$ crystallites and that the vanadia coverage was slightly greater than one monolayer. After calcination at 973 K, the 15 wt% sample transforms into a new highly crystalline phase whose XRD pattern resembles that of the monoclinic phases of alumina. Diffraction peaks indicative of AlVO$_4$ or V$_2$O$_5$ could not be identified for this sample, but the surface is presumably covered with an AlVO$_x$ species. Vanadia has a relatively low melting point of only 963 K and is a well known sintering aid$^{18}$. It is likely that this may have
contributed to the dramatic loss of surface area and recrystallization of the 15 wt % \(V_2O_5/Al_2O_3\) sample upon calcination at 973 K.

Analogous trends were observed using Raman spectroscopy. Raman spectra of the 5 and 15 wt % vanadia samples as a function of pretreatment conditions are shown in Figures 3.3 and 3.4, respectively. The Raman spectra for the 5 wt % vanadia catalyst after calcination at 753 and 973 K were nearly the same and contained broad peaks at 810 cm\(^{-1}\) and 950 cm\(^{-1}\), which can be assigned to polymeric vanadia. Peaks indicative of monomeric vanadia species were not observed, but this may be due to the fact that the spectra were collected in air and the surfaces were likely to be hydrated. Like the XRD results, these results indicate that high-temperature calcination had little effect on the structure of the catalyst. A Raman spectrum of this sample collected after the catalyst had been used for methanol oxidation kinetic studies was also similar to those reported in Figure 3.4.

Consistent with the XRD results, the Raman spectrum of the 15 wt % sample calcined at 753 K, shown in Figure 3.4, is dominated by peaks indicative of bulk \(V_2O_5\). The features associated with polymeric dispersed vanadia were not observed but could be obscured by the more intense peaks due to the crystalline vanadia. Calcination at 973 K resulted in significant changes in the Raman spectrum, including a large decrease in the intensity of the peaks associated with bulk \(V_2O_5\) and a broad peak at 760 cm\(^{-1}\).
origin of this feature is not clear. As shown by the reference spectra of AlVO$_4$, which is also included in the figure, they do not correspond to aluminum vanadate.

![Figure 3.3: Raman spectra of 5 wt% V$_2$O$_5$ on alumina](image)

Redox isotherms were measured for each sample at 748 K. The isotherms for the 5 wt % sample calcined at both 748K and 973 K are displayed in Figure 3.5. The isotherm for the 753 K calcined sample shows that reduction from V$^{+5}$ to V$^{+4}$ is gradual and occurs for P$_{O_2}$ values between 10$^{-4}$ and 10$^{-19}$ atm ($\Delta$G = 57 to 272 kJ/mol). A sharper transition is observed for the reduction from V$^{+4}$ to V$^{+3}$ which occurs at a P$_{O_2}$ of 10$^{-24}$ atm ($\Delta$G = 401 kJ/mole). A similar isotherm was obtained for the sample calcined at 973 K, except that the reduction of V$^{+4}$ to V$^{+3}$ occurred at a lower P$_{O_2}$ of 10$^{-28}$ atm ($\Delta$G = 344 kJ/mole), suggesting that some structural changes in the catalyst may have occurred during high-temperature calcination.
Figure 3.4: Raman spectra of 15 wt% V$_2$O$_5$/Al$_2$O$_3$

Figure 3.5: Redox isotherms for 5wt% V$_2$O$_5$/Al$_2$O$_3$ obtained at 748 K: ■ calc at 753K and □ at 973K for 10 days
The isotherms for the 5 wt % sample were significantly different from those observed for bulk V$_2$O$_5$. Previously measured redox isotherms for bulk V$_2$O$_5$, corrected to 748 K, show stepwise reduction from V$_2$O$_5$ to VO$_2$ and then to V$_2$O$_3$ with the transitions occurring at P$_{O_2}$ values of 10$^{-12}$ and 10$^{-26}$ atm, ($\Delta G = -83$, and -183 kJ/mole), respectively. A gradual transition from V$^{+5}$ to V$^{+3}$ like the one observed here for 5 wt % vanadia on alumina has been observed, however, for vanadia on zirconia. In that case, the lack of a sharp transition in the isotherm was attributed to the presence of polyvanadates with a distribution of cluster sizes as well as some isolated species. This is also likely to be the case for the 5 wt % V$_2$O$_5$/Al$_2$O$_3$ sample. It is worthy to note that for the 973 K calcined sample that the reduction from V$^{+4}$ to V$^{+3}$ occurred at a P$_{O_2}$ lower than 10$^{-27}$ atm ($\Delta G = -386$ kJ/mole). At such a low oxygen pressure, one needs to consider whether reduction of the YSZ electrolyte is starting to occur. Nonetheless, the redox isotherm clearly shows that for the 5 wt % V$_2$O$_5$/Al$_2$O$_3$ sample it is very difficult to reduce V$^{+4}$ to V$^{+3}$.

Different redox behavior was observed for the 15 wt % sample as shown in Figure 3.6. For the 753 K calcined sample, the isotherm is similar to that obtained for the 5 wt % sample, although there is a significantly lower fraction of easily reduced species. The isotherm shows that approximately 25 % of the V$^{+5}$ cations undergo reduction to V$^{+4}$ at P$_{O_2}$ values between 10$^{-4}$ and 10$^{-19}$ atm, with the remaining V$^{+5}$ cations undergoing reduction to V$^{+4}$ at a P$_{O_2}$ of 10$^{-20}$ atm ($\Delta G = -286$ kJ/mole). Recall that the XRD and Raman results for this sample indicate that the vanadia coverage is slightly above one monolayer. Thus, the redox properties of the dispersed monolayer and the V$_2$O$_5$ crystallites should be observed in the redox isotherm for this sample. Since the reduction of bulk V$_2$O$_5$ to VO$_2$ at 753 K occurs at a P$_{O_2}$ of ~10$^{-12}$ atm, some of the 25 % vanadium cations that undergo reduction between 10$^{-4}$ and 10$^{-19}$ atm of O$_2$ may be in the V$_2$O$_5$ crystallites, with the remaining cations that undergo reduction to V$^{+4}$ at 10$^{-20}$ atm of O$_2$ being associated primarily with the dispersed polymeric species. The sharper reduction transition in the 15 wt % sample compared to 5 wt % sample may be a result of the higher vanadia coverage producing a more uniform polymeric species.
Steady-State Methanol Oxidation

The methanol-oxidation TOF for the three supported-vanadia catalysts are shown in Figure 3.7 as a function of temperature. As reported previously, the titania-supported catalyst was the most active, followed by zirconia-supported vanadia and alumina-supported vanadia; however, the TOFs were again similar on each of the supports and within a factor of three. Interestingly, the TOFs on the supported catalysts were also similar to those obtained on the bulk oxides. With the supported catalysts, there is no ambiguity regarding whether the sites observed in reaction are the same as those probed by coulometric titration, because all sites are present on the surface. If methanol-oxidation rates depend on oxygen binding strength, the surface vanadia species in the bulk oxides must not be resolvable in the coulometric titration data.

The steady state methanol oxidation rates and the coulometric titration data raise interesting questions about what controls the reactivity of supported vanadia catalysts. For the bulk oxides, if one assumes that the coulometric titration data is representative of the catalytically active vanadia species, then these results demonstrate that there is little to no correlation between the oxygen binding strengths and reactivity. Even if the
catalytic activity of the bulk vanadates is dominated by surface species that were not resolvable in the coulometric titration experiments, the results of this study still have important implications for understanding the reactivity of supported mono-vanadates. Note that, in the bulk mixed vanadium oxides, the bonding strength of an oxygen atom that bridges between a V cation and a second non-reducible cation is a strong function of the identity of this second cation. This difference, however, does not appear to manifest itself in the V-O-support bonds of the supported mono-vanadate species. The coulometric titration data shows that the $\Delta G$ of oxidation of $V^{+3}$ to $V^{+5}$ for the majority of the vanadium cations in these samples were similar, with a value of $375 \pm 25$ kJ/mol at 748 K. This result is consistent with a recent theoretical study of supported vanadates and the reactivity data for the supported vanadia samples, which show that the steady state TOF only varied by a factor of 3.

![Figure 3.7: TOF of CH$_3$OH partial oxidation to CH$_2$O over ▲5wt% V$_2$O$_5$ calc at 753K, ■ 15wt% V$_2$O$_5$ calc at 753K, Δ 5wt% V$_2$O$_5$ calc at 973K, □ 15wt% V$_2$O$_5$ calc at 973K](image)

The other interesting question is how to explain the observation that TOF for methanol oxidation does not depend strongly on the support, given previous reports that the support can have a strong effect on reactivity. A closer examination of the earlier literature indicates that the supports, which show the largest differences, are silica and ceria. Since TOFs on silica-supported vanadia are dramatically lower than those on bulk V$_2$O$_5$ or any of the supports used in the present study, one should probably view this support as causing deactivation of the vanadia. The case of ceria is more interesting, since TOF on
ceria-supported vanadia catalysts are reported to be somewhat higher than those obtained with the supports examined here. Given that ceria is well known to enhance other oxidation reactions because of its oxygen storage properties, this research suggests that it is this property, rather than changes in the vanadia, that lead to higher rates with ceria.

**Steady-State Propane to Propene oxidative dehydrogenation**

The results for propane ODH are interesting as shown in Figure 3.8. For this reaction, the more reducible form of vanadia on the high-temperature vanadia/alumina was completely unselective for the production of propene. We suggest that surface species formed after abstraction of hydrogen on this sample are probably oxidized quickly to CO\(_2\) and H\(_2\)O by the loosely bound oxygen present in this catalyst. This in turn suggests that researchers looking for more selective vanadia catalyst for ODH consider investigating additives which strengthen the oxygen binding. In light of the ease of reduction of the high-temperature vanadia/alumina sample, it is reasonable to expect the catalyst also to exhibit higher oxidation rates. Instead, ODH activities on this catalyst were significantly lower. A possible explanation for the lower rates is that the working catalyst may be in a more highly reduced state under reaction conditions, with reoxidation of the catalyst being rate limiting.

![Figure 3.8: C\(_3\)H\(_8\) consumption rate for following catalysts: ▲ 5wt% V\(_2\)O\(_5\) calc at 753K, ■ 15wt% V\(_2\)O\(_5\) calc at 753K, ∆ 5wt% V\(_2\)O\(_5\) calc at 973K, □ 15wt% V\(_2\)O\(_5\) calc at 973K.](image-url)
Obviously, vanadia catalysts are not simply oxygen donors; oxygen bond strengths are only one aspect of these materials. There are significant differences in the geometry of the sites and in the accessibility of the vanadium cations for the vanadia on the various supports and for the low- and high-temperature forms of vanadia/alumina. More work is required to understand the mechanisms for partial oxidation reactions and the results highlight only one aspect of these materials.

*Transient Reaction Rate measurements for quantification of available sites*

The reaction rate of transient methanol oxidation over bulk vanadia in the absence of gas phase oxygen was measured and results are shown in Figure 3.9. At 443 K, the reaction rate declines to zero exponentially in 300 sec which indicates that only the surface of vanadia is reduced, while at 503 K and 523 K, the reaction rate stabilizes at a particular rate which indicates reduction of bulk vanadia. The reaction rate stabilized faster at 523K than at 503 K, because the surface reaction rate is faster at a higher temperature. At 443 K, the amount of oxygen used in the reaction was determined to be 7.4 O per nm$^2$ of surface. Therefore, there are 7.4 V sites per nm$^2$ of bulk vanadia, which agrees with the accepted values from the literature for surface monolayer coverage of vanadia$^{75}$. Because of interference from the reduction of bulk vanadia at a higher temperature, the number of sites was slightly higher at 473 K (not shown in Figure 3.9 for clarity) and 503 K, making surface reduction too fast to measure at 523 K and above.

Assuming that methanol oxidation over bulk vanadia is pseudo-1$^{st}$ order in the oxygen of vanadia, the TOF of the reaction can be computed. The TOF is simply the time constant of the fitted exponential function. For data taken at 503 K and below, the initial observed reaction rate over vanadia was successfully fitted to the exponential function. The TOFs at different temperatures are plotted in Figure 3.10, along with the TOF values for steady state CH$_3$OH oxidation from the previous work$^{36,39}$. The reaction rates from both transient and steady state measurements are within a factor of 2. The activation energy is 36 kJ/mol for transient reaction, while it is 69 kJ/mol for steady state reaction. Even though it is not clearly understood what causes such difference, conditions of reaction are different under each regime, which might explain the observed data.
**Figure 3.9:** Normalized oxidation rate of CH$_3$OH over bulk vanadia at ■ 443 K △ 503 K and □ 523 K

**Figure 3.10:** CH$_3$OH oxidation rate over V$_2$O$_5$ under ■ transient and □ steady state conditions
A summary of data for bulk vanadia and bulk magnesium vanadate is shown in Table 3.2. The number of sites on both vanadia and magnesium vanadate matches the literature for lowest temperature. The number of sites per surface area is significantly lower for magnesium vanadate, since magnesium occupies part of the surface. Importantly, the number of sites is constant for magnesium vanadate from 443 K to 503 K, indicating that only surface is reduced in that range of temperatures. Bulk vanadia is available for reduction at 503 K and above, while in magnesium vanadate, this transition occurs at a much higher temperature of ~ 573 K. This phenomenon can be explained by the thermodynamics of reduction, where the Gibbs free energies of the reduction of bulk vanadia and magnesium vanadate are 86 kJ/mol O$_2$ and 250 kJ/mol O$_2$, respectively. Because the oxygen anion is bound with more energy in the lattice of magnesium vanadate than in the lattice of bulk vanadia, oxygen diffusion in the latter is significantly faster. Therefore, oxygen from the bulk of the sample can be accessed at a lower temperature using CH$_3$OH in bulk vanadia.

Table 3.2: Number of sites and bulk reduction of vanadia and magnesium vanadate

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Surface V/nm$^2$</th>
<th></th>
<th></th>
<th>Bulk Reduction, 10$^6$*Mol/sec</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V$_2$O$_5$</td>
<td>Mg$_3$(VO$_4$)$_2$</td>
<td>V$_2$O$_5$</td>
<td>Mg$_3$(VO$_4$)$_2$</td>
<td></td>
</tr>
<tr>
<td>443</td>
<td>7.4</td>
<td>2.1</td>
<td>Not Observed</td>
<td>Not Observed</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>12</td>
<td>2.1</td>
<td>Not Observed</td>
<td>Not Observed</td>
<td></td>
</tr>
<tr>
<td>503</td>
<td>13</td>
<td>2.2</td>
<td>0.2</td>
<td>Not Observed</td>
<td></td>
</tr>
<tr>
<td>523</td>
<td>N/A</td>
<td>3.7</td>
<td>1</td>
<td>Not Observed</td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>N/A</td>
<td>6</td>
<td>1.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>

The transient reaction rate of the oxidation of methanol over sub-monolayer vanadia supported on titania and alumina was measured at 443 K. Transient reaction rate exhibited exponential decline over both catalysts, and the reaction stopped completely by the third minute. From exponential fitting, TOFs were calculated to be 0.037 s$^{-1}$ and
0.031 s\(^{-1}\) over vanadia supported on titania and alumina, respectively. The ratio of vanadia available for the reaction to loaded vanadia was 0.85 and 0.40 on vanadia supported on titania and alumina, correspondingly. Such a significant decrease in available vanadia on 5 wt% V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) can be explained by the solid state reaction between the catalyst and support. Vanadia is known to react with alumina at lower temperatures and dissolve in bulk;\(^{76}\) therefore, the amount of vanadia on the surface decreases, while no solid state reaction is observed between vanadia and titania. Using obtained data of the number of sites per surface, steady state oxidation rates over both catalysts measured here and in previous work\(^{36}\) could be adjusted. Reaction rate per site over both catalysts is almost identical.

3.4 Conclusions:

Redox isotherms for V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts were measured as a function of the vanadia weight loading and calcination temperature. 5 wt % V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts were found to be thermally stable and their redox isotherms at 748 K showed that a reduction from V\(^{+5}\) to V\(^{+4}\) occurred for P\(_{O_2}\) values between 10\(^{-4}\) and 10\(^{-19}\) atm and that a reduction from V\(^{+4}\) to V\(^{+3}\), which occurred at a P\(_{O_2}\) of 10\(^{-28}\) atm. The 748 K redox isotherm for a 15 wt % V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalyst, which was calcined at 753 K, showed a sharper transition for reduction from V\(^{+5}\) to V\(^{+4}\) which occurred P\(_{O_2}\) of 10\(^{-20}\) atm. This sharper transition compared to the lower vanadia coverage sample may be the result of a more uniform polyvanadate species on this sample. In contrast to the 5 wt % sample, the 15 wt % sample was not thermally stable and underwent recrystallization upon calcination at 973 K, resulting in a low surface area material whose surface was covered with a highly reducible AlVO\(_x\) species. In spite of the differences in redox properties, all of the V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalysts were found to exhibit similar activity for the selective oxidation of methanol to produce formaldehyde, suggesting that oxygen removal from the surface is not the rate limiting step for this reaction. For propane ODH, larger differences between the catalysts were observed. While the 5 wt % vanadia samples and the 15 wt % vanadia sample calcined at 753 K, all exhibited similar activity for the ODH reaction. The highly reducible 15 wt % V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) sample that was calcined at 973 K was active only for the complete oxidation of propane to CO\(_2\) and water.
Transient reduction of vanadia catalysts by CH$_3$OH was used to determine the number of redox sites per surface area, as well as transient kinetics and accessibility of bulk oxygen. By performing measurements at sufficiently low temperatures (below 443 K), only the surface of the vanadia catalyst is reduced, while bulk stays oxidized. The number of sites on bulk vanadia and magnesium vanadate was determined to be 7.4 and 2.1 V/nm$^2$, respectively. The bulk reduction was observed above 473 K for bulk vanadia and 573 K for magnesium vanadate. In the case of supported vanadates, a majority of vanadium was available for reaction in 2.5 wt% V$_2$O$_5$/TiO$_2$, while in 5 wt% V$_2$O$_5$/Al$_2$O$_3$, only 40% of vanadium was available for surface reaction due to the solid state reaction between vanadia and alumina. The reaction rate per site over both supported catalysts was determined to be essentially the same in both transient and steady state reaction.
Chapter 4. Iron Oxide catalysts

4.1 Introduction

Iron-based catalysts are an interesting example where the thermodynamic properties of the catalyst are important. In the water-gas shift (WGS) reaction used for the production of H₂, the catalyst is in a form of unsupported iron oxide, promoted by chromia, which exists as Fe₃O₄ under reaction conditions. The reaction is thought to proceed via a redox mechanism, in which the catalyst cycles between the +3 and +2 oxidation states via oxidation by steam and then reduction by carbon monoxide. Based on this mechanism, one would expect a close relationship between WGS activity and the thermodynamic properties of the catalyst.

In this chapter, the study of a series of Fe catalysts supported on zirconia, alumina, and ceria is presented. While the catalytic properties of all catalysts were measured, only iron oxide supported on zirconia and alumina was characterized in detail using thermodynamic measurements and other techniques. It was observed that the equilibrium constant for the catalytically relevant reaction $3\text{Fe}_2\text{O}_3 \leftrightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2$ was shifted to significantly higher $P(\text{O}_2)$ on the supported catalysts, a result that helps explain a dramatically lower WGS activity for the supported catalysts compared to their bulk counterparts.

4.2 Experimental techniques

The supported iron oxide catalysts were synthesized using incipient wetness. Iron oxide was deposited onto a support by impregnation of a solution of iron nitrate (Fe(NO₃)₃·9H₂O, Fisher) and oxalic acid (C₂H₂O₄, Aldrich). A series of iron oxide loadings was prepared from a theoretical monolayer coverage of up to 6 monolayers. After drying in air at 400 K, the samples were ground with a mortar and pestle and calcined at 773 K in hot air for 4 hours. The redox properties of the catalysts were characterized using the coulometric titration technique described in Chapter 2. It is important to note that all redox isotherms were taken in a water/hydrogen atmosphere, so iron catalysts were equilibrating not with oxygen but with water/hydrogen mixture above it, as performed under industrial reaction conditions. The structure of the iron oxide
catalysts used was characterized by XRD and N\textsubscript{2} BET. The WGS reaction rate measurements were done in a flow reactor equipped with an on-line gas chromatograph (SRI-8610C) and a TCD detector. The feed composition was fixed at 25 torr of CO and H\textsubscript{2}O, balance He, while total flow rate was varied between 125 and 155 sccm.

4.3 Results and Discussion

The BET surface areas of the supported iron catalysts before and after the reaction experiments are shown in Table 4.1.

Table 4.1: Surface areas of zirconia-supported iron oxide

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area, m\textsuperscript{2}/gram</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before WGS</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>53.5</td>
</tr>
<tr>
<td>5 wt% Fe/ZrO\textsubscript{2}</td>
<td>--</td>
</tr>
<tr>
<td>20 wt% Fe/ZrO\textsubscript{2}</td>
<td>--</td>
</tr>
<tr>
<td>30 wt% Fe/ZrO\textsubscript{2}</td>
<td>21.8</td>
</tr>
</tbody>
</table>

Surface areas measured before and after the reaction study experiments are significantly less than the surface area of the bare support, which implies that iron aggregates on the surface and plugs pores of zirconia.

X-ray diffraction patterns of the zirconia-supported samples before and after catalytic experiments are displayed in Figure 4.1. Patterns are easily identified as body-centered cubic Fe\textsubscript{2}O\textsubscript{3} for fresh catalyst, and as cubic Fe\textsubscript{3}O\textsubscript{4} for catalyst after the reaction study as expected, while zirconia is in a tetragonal phase. Note that the peaks associated with Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} are very intense on 20wt% and 30wt% catalysts but non-existent on the 5wt% catalyst.

The absence of peaks associated with bulk iron oxide on a 5wt% sample suggests that iron oxide exists as very small crystallites, or a two-dimensional film. Additional evidence that iron oxide forms a film is shown in Figure 4.2, which is a plot of the ratio of the most intense peaks for iron oxide and zirconia lattices in the XRD data for fresh samples. The plot is nearly linear and intersects the x-axis near 5wt% Fe. At 5wt% of Fe, iron oxide film would be only one unit cell thick and would not have a XRD signal.
Figure 4.1: XRD of Fe/ZrO\textsubscript{2} catalysts; i) freshly made and ii) after WGS reaction; a) ZrO\textsubscript{2}, b) 5wt\% Fe/ZrO\textsubscript{2} c) 10 wt\% d) 20 wt\% e) 30 wt\% and f) bulk Fe\textsubscript{2}O\textsubscript{3}

Figure 4.2: Ratio of height of the most peaks of Fe\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2} as function of Fe loading
Figure 4.3 displays Raman spectra of the supported iron samples under ambient conditions from 100 to 1000 cm⁻¹ after the WGS reaction. The peaks at 269 cm⁻¹ and 650 cm⁻¹ in the spectrum of the support (spectrum d) is characteristic of the tetragonal phase of ZrO₂⁷⁷,⁷⁸; the peak at 181 cm⁻¹ is an attribute only to the monoclinic phase of ZrO₂⁷⁸. The support does not have any intense peaks between 700 and 1,000 cm⁻¹. The Raman spectra of 20 wt% and 30 wt% iron catalyst used in reaction studies contain a shoulder at 72 cm⁻¹, which is characteristic of high temperature treated Fe₃O₄⁷⁹. The intensities of the tetragonal phase of ZrO₂ for the supported samples used in WGS reaction are much less compared to the bare support, implying that all of the ZrO₂ surface has converted to the monoclinic phase. However, the XRD patterns of those samples still show only the tetragonal phase of ZrO₂, implying that only surface zirconia is affected. Therefore, if this can be attributed to the iron-zirconia interactions, iron oxide must wet the zirconia surface completely.

![Raman spectra](image)

**Figure 4.3**: Raman spectra of FeOₓ catalysts after WGS reaction: a) 30wt% Fe/ZrO₂, b) 20wt%, c) 5wt% and d) ZrO₂

Figure 4.4 shows the difference between 30 wt% iron on zirconia before and after the WGS reaction. In addition to the peaks characteristic of ZrO₂, the Raman spectra of fresh zirconia supported iron sample (spectrum b) contain peaks centered at 225 and 293 cm⁻¹ which are attributed to Fe₂O₃⁷⁹. In both samples, although the characteristic
monoclinic phase peak of ZrO$_2$ at 181 cm$^{-1}$ is present, peaks at 269 cm$^{-1}$ and 650 cm$^{-1}$ are suppressed in supported samples, which, with XRD evidence, is suggesting that iron oxide affects zirconia only on the surface. Therefore, it implies that iron oxide has to cover the surface completely before and after the WGS reaction independent of its redox state, though exact morphology of the surface could not be determined at the time.

Figure 4.4: Raman spectra of a) 30wt% Fe/ZrO$_2$ after WGS, b) 30wt% Fe/ZrO$_2$ fresh and ZrO$_2$

Figure 4.5 displays equilibrium isotherms for zirconia-supported iron catalysts at 973 K. For all three samples, the change in oxygen stoichiometry for the intermediate step corresponds to going from the Fe$_2$O$_3$ to Fe$_3$O$_4$ phase. In these sets of data, the amount of oxygen removed from each sample corresponded to an O:Fe ration of 1.5, implying that no oxygen was removed from the zirconia. For the 5wt% sample, the transition from the Fe$_3$O$_4$ to FeO phase is gradual, which might be associated with the structure of the monolayer species present. Overall, there is a significant difference in the equilibrium pressure of oxygen for the reaction Fe$_2$O$_3$ ↔Fe$_3$O$_4$ for bulk and supported
samples, which results in a factor of two change in Gibbs free energy. The free energy for other redox reactions was not affected, as shown in Table 4.2.

![Graph showing redox isotherms for Fe/ZrO₂ samples at 973 K](image)

**Figure 4.5:** Redox isotherms for Fe/ZrO₂ samples at 973 K: □ 30wt%, ◆ 20wt%, ◊ 5wt% and — bulk FeOₓ from¹¹

**Table 4.2:** Measured ΔG free energy of oxidation of FeOₓ/ZrO₂ at 973 K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ΔG of oxidation, kJ/mol O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe₂O₃↔Fe₃O₄</td>
</tr>
<tr>
<td>Bulk iron</td>
<td>-202.9</td>
</tr>
<tr>
<td>5 wt% Fe/ZrO₂</td>
<td>-114.9</td>
</tr>
<tr>
<td>20 wt% Fe/ZrO₂</td>
<td>-108.4</td>
</tr>
<tr>
<td>30 wt% Fe/ZrO₂</td>
<td>-109.3</td>
</tr>
</tbody>
</table>

Under the condition for the WGS reaction, P(O₂) at 973 K was calculated to be ~10⁻¹⁸ atm. A shift in ΔG values can be interpreted as that in supported catalyst, since it is easier to reduce Fe₂O₃ but harder to oxidize Fe₃O₄ due to the fact that the equilibrium P(O₂) for 2Fe₃O₄ + ½ O₂↔3Fe₂O₃ reaction is further away from the reaction condition of P(O₂). The oxidation of iron oxide by water in WGS has been confirmed to be a rate
limiting step in the WGS reaction in the literature (ref), which further supports this hypothesis.

In addition, the enthalpy and entropy of $\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}_2\text{O}_3$ reaction has been measured on 30 wt% Fe/ZrO$_2$, as shown in Table 4.3.

**Table 4.3:** Thermodynamic data for reaction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, 30 wt% Fe/ZrO$_2$

<table>
<thead>
<tr>
<th>O/Fe ratio</th>
<th>$\Delta G$, kJ/mole, 973 K</th>
<th>$\Delta H$, kJ/mole, 973 K</th>
<th>$\Delta S$, J/mole*K, 973 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.47</td>
<td>-109.1</td>
<td>-127.1</td>
<td>-18.4</td>
</tr>
<tr>
<td>1.43</td>
<td>-108.5</td>
<td>-148.0</td>
<td>-40.5</td>
</tr>
<tr>
<td>1.39</td>
<td>-108.8</td>
<td>-125.3</td>
<td>-16.7</td>
</tr>
</tbody>
</table>

In comparison, the $\Delta H$ for the same reaction in bulk iron oxide is -530 kJ/mole O$_2$, which is four times the value of $\Delta H$ for zirconia supported iron oxide. In support of these results, the entropy of the $\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}_2\text{O}_3$ reaction was calculated using observed $\Delta G$ for supported catalyst and literature values of $\Delta H$ for bulk oxide, essentially holding the latter constant. The calculated $\Delta S$ turned out to be -450 J/K*mole O$_2$, which was two times higher than any $\Delta S$ observed for metal redox reaction and four times the value of reaction which consumes one molecule of gas, typically -130 J/K*mole O$_2^{11}$. This supports an explanation that the effects observed are not only due to entropy but enthalpy as well, due to the physical constraint that the entropy value cannot be that large.

Therefore, the difference between $\Delta H$ of supported catalyst and bulk is observed. The reasons for such a drastic effect on the $\Delta H$ of the reaction $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and the role of the support or structure of iron oxide on the surface in determining redox thermodynamics is beyond the scope of this chapter.

A series of reaction experiments on supported iron were conducted. The results of which are displayed in Figure 4.6, and show that the WGS reaction rates over
zirconia-supported iron oxide catalysts are roughly 2 orders of magnitude slower than that of bulk. The WGS reaction rates were also measured and shown in Figure 4.6 for alumina-supported and ceria-supported iron catalyst. The activation energy of the WGS reaction for bulk and supported irons are shown in Table 4.4 and are in good agreement with the literature data\textsuperscript{80-82}.

![Graph showing reaction rates over supported iron oxide catalysts](image)

**Figure 4.6:** WGS rates over supported iron oxide catalyst: ■ bulk Fe\textsubscript{2}O\textsubscript{3} ▲ 5wt% Fe/CeO\textsubscript{2} ◊ 30wt% Fe/ZrO\textsubscript{2} □ 20wt% Fe/ZrO\textsubscript{2}, △ 5wt% Fe/ZrO\textsubscript{2} and ● 20wt% Fe/Al\textsubscript{2}O\textsubscript{3}.

**Table 4.4:** apparent activation energy of bulk and iron catalysts, kJ/mole

<table>
<thead>
<tr>
<th>Supported iron oxide</th>
<th>Al\textsubscript{2}O\textsubscript{3}-supported</th>
<th>ZrO\textsubscript{2}-supported</th>
<th>CeO\textsubscript{2}-supported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk iron oxide</td>
<td>41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 wt% Fe</td>
<td>122.3</td>
<td>75.3</td>
<td>75.2</td>
</tr>
<tr>
<td>20 wt% Fe</td>
<td>85.7</td>
<td>75.1</td>
<td>--</td>
</tr>
<tr>
<td>30 wt% Fe</td>
<td>75.6</td>
<td>77.0</td>
<td>51.7</td>
</tr>
</tbody>
</table>
The coulometric experiments were repeated for alumina-supported iron catalyst, but part of the iron on the surface was found to react with both alumina and lanthanum to form mixed oxide compounds. Iron on alumina was found to behave similarly to iron on zirconia\textsuperscript{70}, suggesting that observed changes cannot be attributed to catalyst-support interaction but rather to the structural effect. Iron oxide can form either a film or small particles on a surface of the support with periodic defects in the iron oxide lattice in both cases, caused by the lattice mismatch between the support and iron oxide, which has been observed under other conditions\textsuperscript{83-86}.

The fundamental question is why does iron oxide behave so differently on a surface from bulk? Though no direct evidence was found in these studies, there are reports suggesting that iron forms a different structure than that of bulk oxide by wetting the surface of the metal\textsuperscript{86, 87} or metal oxide\textsuperscript{84} support, forming a FeO-like structure with up to 6 ML coverage of iron on alumina\textsuperscript{84}. This hypothesis is supported by the Raman spectra of the 5 wt\% catalyst, where the characteristic peak of bulk magnetite or hematite could not be observed, because the iron oxide structure is different from that of the bulk. It has been determined that in thin films of iron oxide reaction \( \text{Fe}_2\text{O}_3 \leftrightarrow \text{Fe}_3\text{O}_4 \) proceeds via an intermediate phase not observed in a bulk oxide\textsuperscript{88}. This phase of iron oxide was formed and observed at \( 5\times10^{-8} \) atm at 900-1000 K, albeit on a Pt single crystal substrate, corresponding to \( \Delta G \) of -126 kJ/mole, which is close to the values we have measured, especially for 5 wt\% iron on zirconia. In addition, it was observed that this phase has a specific structure independent of support of up to a thickness of \( \sim 2 \) ML\textsuperscript{84}. From these experiments, there could be no support effect because close \( \Delta G \) for studied reactions are observed for vastly different supports – metal and metal oxide. Also, the surface-area
normalized reactivity and redox isotherms of iron supported on alumina or zirconia are almost identical. The only explanation of these results is that the iron oxide forms the same thin-film phase on all supports due to the geometrical constraints. The only major difference from previous studies that we observed is that properties of thin-film structure propagate for much higher loading of iron oxide, up to ~ 15 ML. As for the structure of this thin film, there are different explanations offered in the literature – it is either iron-deficient Fe$_2$O$_3$ with similarities to $\gamma$-Fe$_2$O$_3$(111) or a phase with FeO(111)-like in-plane parameters$^{85,88}$.

4.4 Conclusions

In this chapter, the redox isotherms for supported iron oxide were examined as a function of iron loading on zirconia. Zirconia supported iron had a redox isotherm that showed well-defined steps corresponding to transitions Fe$_2$O$_3$(hematite) → Fe$_3$O$_4$(magnetite), Fe$_3$O$_4$→FeO, and FeO→Fe. In the redox isotherm for supported iron oxide, the transition Fe$_2$O$_3$→Fe$_3$O$_4$ shifted to a significantly higher pressure of oxygen, compared to bulk iron, effectively making surface iron easier to reduce and harder to oxidize compared to bulk iron oxide. The rate measurements for the WGS reaction over supported iron catalysts and bulk iron showed that specific rates for supported samples were much slower than bulk iron and varied significantly among supports, correlating exponentially with electronegativity of metal cation of support oxide.
Chapter 5. Molybdena mixed oxide catalysts

5.1 Introduction

Mo-based catalysts exhibit good catalytic properties for a number of selective oxidation reactions. These oxidation reactions are believed to occur through a Mars-van Krevelen mechanism in which lattice oxygen bound to molybdenum is used to oxidize the hydrocarbon. In part because pure MoO₃ is relatively volatile, molybdena is almost always used in the presence of a second oxide, either on an oxide support such as alumina, titania, zirconia, or in the form of a mixed oxide, such MgMoO₄ or Fe₂(MoO₄)₂. Indeed, Fe₂(MoO₄)₂ is used commercially for the conversion of methanol into formaldehyde. The active phase of the iron-molybdate catalyst is reported to be a surface monolayer of MoOₓ on bulk, crystalline Fe₂(MoO₄)₂.

For both supported catalysts and bulk mixed oxides, the second metal component in the oxide can significantly alter catalytic properties. For example, molybdena catalysts supported on titania or zirconia have been reported to be six times more active than their alumina- or silica-supported counterparts for methanol oxidation. Even larger differences between various supported catalysts were reported for ethanol oxidation. The fact that turn-over frequencies (TOF) for both of those reactions have been shown to correlate with catalyst reducibility as measured by peak temperatures in Temperature Programmed Reduction (TPR) suggests that the support affects reactivity by changing the strength of the oxygen bonds. Indeed, in a study of oxydehydrogenation (ODH) over supported molybdena catalysts, it was suggested that differences in the TOF for that reaction are due to the oxygen site involved in the anchoring Mo-O-support bond.

How the support oxide affects the Mo-O bonding is not entirely understood, although a correlation has been reported between catalytic activity and the electronegativity of the support cations, which in turn has been suggested to affect the Mo-O bond strength. Indeed, the importance of the electronegativity of the second cation to oxygen bonding in mixed oxides has been quantitatively demonstrated for vanadium in a thermodynamic study. Considering only those vanadium mixed oxides
with V-O-M bonds (where M is the second metal cation), $\Delta G$ of oxidation was found to vary by as much as 250 kJ/mol-O$_2$, depending on the electronegativity of the M$^{n+}$ cations. Whether a similar correlation would exist for Mo-based mixed oxides is not known.

In order to understand the role of neighboring cations on the reducibility and catalytic activity of molybdena, a series of bulk mixed oxides, including MgMoO$_4$, Zr(MoO$_4$)$_2$, Al$_2$(MoO$_4$)$_3$, SrMoO$_4$, and Cr$_2$(MoO$_4$)$_3$ was chosen for examination. Because these are bulk crystalline compounds, the Mo-O sites are expected to be relatively homogeneous compared to normal, supported catalysts. The particular mixed oxides that were chosen for study have a second cation that is non-reducible under the experimental conditions that were used, so that the oxidation and reduction which are observed is only that of Mo. In addition to the fundamental aspects of understanding the properties of these mixed oxides, Zr(MoO$_4$)$_2$ and Al$_2$(MoO$_4$)$_3$ are also of interest because of their possible significance to zirconia- and alumina-supported catalysts; Cr$_2$(MoO$_4$)$_3$ is of interest because chromium is used as a dopant in Fe$_2$(MoO$_4$)$_2$ catalysts; MgMoO$_4$ and SrMoO$_4$ are of interest because of their use as oxidative dehydration catalysts and solid oxide fuel cell materials. The crystal structure of each of the mixed oxides is known. Similar to the case with the series of vanadium mixed oxides that were investigated previously (CeVO$_4$, LaVO$_4$, Mg$_3$(VO$_4$)$_2$ AlVO$_4$, and CrVO$_4$), the oxygens in each of the molybdenum mixed oxides are shared between dissimilar metal cations.

In this chapter, the redox properties of the mixed oxides of molybdena are examined and shown to differ in significant ways from that of bulk molybdena. Redox properties can change dramatically depending on the structure of the reduced phases. Unlike what was found with the vanadia mixed oxides, none of the molybdena mixed oxides showed significant catalytic activity for methanol oxidation.

5.2 Experimental

The samples were prepared by mixing stoichiometric amounts of (NH$_4$)$_2$Mo$_2$O$_7$ (Alfa Aesar), oxalic acid (Alfa Aesar), and the nitrate salt of the other metal cation together in distilled water. After evaporating the excess water, the residue was dried at 400 K and then calcined in ambient air at or above 873 K for as long as required to achieve the desired crystal structure. The crystal structure was determined by X-ray
diffraction (XRD) using a Rigaku Geigerflex Diffractometer with a Cu-K$_\alpha$ radiation source ($\lambda$=0.15406 nm).

The reduced phases, with the exception of that formed from Al$_2$(MoO$_4$)$_3$, were also characterized by XRD. It was found that the temperature required to rapidly reduce the samples was different for each sample. In each case, the samples were reduced in a flow system with 50% CO in He for 4 hours. The temperatures were 923 K for MgMoO$_4$ and Zr(MoO$_4$)$_2$, 973 K for Zr(MoO$_4$)$_2$, MgMoO$_4$, SrMoO$_4$ and Cr$_2$(MoO$_4$)$_3$, and 1023 K for Zr(MoO$_4$)$_2$. After cooling the samples to room temperature in the reducing gas mixture, the samples were characterized in air by XRD. The same samples were then reoxidized with ambient air at 923 K and again characterized by XRD to demonstrate the reversibility of the redox process.

Transmission Electron Microscopy (TEM) studies were conducted on the reduced MgMoO$_4$ using a JEOL-2000FX-II operating at 200 kV with a LaB$_6$ source. The reduced powder sample was ground and dispersed in a n-hexane. A drop of this suspension was deposited onto a 3 mm Cu grid (300-mesh with lacey carbon film) and dried for few minutes prior to mounting and insertion. Powder diffraction rings, along with a more finite assortment of diffraction spots, were observed from the MgMoO$_4$ reduction products. The smallest objective aperture (20 µm) was used to sample scattered electrons for dark-field (DF) imaging. These images showed particles illuminated selectively from one phase or the other, depending on the placement of the objective aperture on the rings or spots. The particle size distributions for the reduced phases were compared with the estimates of mean particle size obtained from the XRD data.

The equilibrium isotherms were measured using a coulometric titration experiment. The reaction rates, which are reported as turnover frequencies (TOF), were normalized to the molybdenum surface concentration, which was estimated from the sample surface areas, assuming that all samples had 4 Mo/nm$^2$.

5.3 Results and Discussion

Structural Characterization

The diffraction patterns for the MgMoO$_4$, Zr(MoO$_4$)$_2$, Al$_2$(MoO$_4$)$_3$, Cr$_2$(MoO$_4$)$_3$, and SrMoO$_4$ samples are shown in Figure 5.1. Each of the samples was highly crystalline
and the diffraction patterns were in agreement with published data\textsuperscript{99-104}. The XRD patterns for Al\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} and Cr\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} are similar, because these two mixed oxides are reported to have the same crystal structure and the cation radii for Al\textsuperscript{3+} and Cr\textsuperscript{3+} (0.052 and 0.0535 nm) are nearly the same\textsuperscript{105}. Each of the crystal structures is made up of (MoO\textsubscript{4})\textsuperscript{2-} tetrahedral building blocks, with oxygens shared between Mo\textsuperscript{6+} and the other cations from the mixed oxide. There are no Mo-O-Mo linkages in any of the structures.

\textbf{Figure 5.1:} XRD of a) MgMoO\textsubscript{4}, b) Cr\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}, c) Al\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}, d) Zr(MoO\textsubscript{4})\textsubscript{2} and e) SrMoO\textsubscript{4}. 
The diffraction patterns for reduced and re-oxidized MgMoO₄, Zr(MoO₄)₂, Cr₂(MoO₄)₃, and SrMoO₄ samples are shown in Figure 5.2. The products of reduction were unique to each compound. With MgMoO₄, the sample segregated into crystalline MgO and Mg₂Mo₃O₈ after reduction, while Zr(MoO₄)₂ segregated into MoO₂ and a mixture of monoclinic and tetragonal ZrO₂. The MoO₂ was amorphous when the sample was reduced at 873 K, but crystalline MoO₂ was observed after reduction at 973 K. Cr₂(MoO₄)₃ formed an unknown but simple crystalline phase upon reduction, without segregating chromium oxide. SrMoO₄ was only partially reduced to SrMoO₃ under similar treatment. In all cases, the samples returned to their initial, oxidized state upon exposure to air at 873 K.

In order to understand the morphology of the reduced samples, TEM measurements were performed on the reduction products from MgMoO₄. Powder diffraction rings from MgO and isolated diffraction spots from Mg₂Mo₃O₈ were observed, shown in Figure 5.3a. Particle size distributions were sampled from multiple DF images from both MgO and Mg₂Mo₃O₈ (Figure 5.3b); mean particle sizes for the MgO and Mg₂Mo₃O₈ phases were estimated to be 7±2 nm and 16±2 nm, respectively. Although the rings and spots could not be completely isolated, by shifting the location of the objective aperture, emphasis was shifted between predominantly powder ring contributions and contributions weighted toward the isolated diffraction spots. This allowed assignment of the particles to the appropriate distributions. Particle size analysis from the XRD data obtained from the MgMoO₄ reduction products using Scherrer formula is consistent with these size distributions. Mg₂Mo₃O₈ is characterized by the distorted, double-hexagonal packing of oxygen layers between alternate layers of magnesium and molybdenum atoms.
Figure 5.2: XRD of the following: a) Zr(MoO$_4$)$_2$ reduced at 923 K; b) Zr(MoO$_4$)$_2$ reduced at 1023 K; c) Zr(MoO$_4$)$_2$ reoxidized at 873 K after being reduced at 1023 K; d) MgMoO$_4$ reduced at 973 K; e) MgMoO$_4$ reoxidized at 873 K; f) Cr$_2$(MoO$_4$)$_3$ reduced at 973 K; g) Cr$_2$(MoO$_4$)$_3$ reoxidized at 873 K; h) SrMoO$_4$ reduced at 973 K and i) SrMoO$_4$ reoxidized at 873 K. The symbols +, *, X, O and Λ denote peaks of ZrO$_2$, MoO$_2$, Mg$_2$Mo$_3$O$_8$, MgO and SrMoO$_3$, respectively.
Figure 5.3: TEM results from MgMoO$_4$ reduction products: a) Selected area electron diffraction pattern showing powder diffraction rings from MgO and isolated diffraction spots from Mg$_2$Mo$_3$O$_8$; b) Dark-field image showing finely dispersed MgO particles and coarser grains of Mg$_2$Mo$_3$O$_8$.

Thermodynamic Properties

The redox isotherms for the MgMoO$_4$, Zr(MoO$_4$)$_2$, Al$_2$(MoO$_4$)$_3$, Cr$_2$(MoO$_4$)$_3$, and SrMoO$_4$ samples at 873 K, starting from the oxidized state, are shown in Figure 5.4. The solid line in the figure is the calculated isotherm for bulk molybdena$^{107}$, taking into account the presence of phases having mixed Mo valencies. When plotted as moles of oxygen per mole of Mo, the isotherms for each of the mixed oxides, with the exception of SrMoO$_4$, were nearly identical. Based on the oxygen stoichiometries, the equilibrium reactions involved a change in the formal Mo oxidation state from +6 to +4. The vertical lines at 10$^6$ atm imply that equilibrium exists between distinct reactants and products for each mixed oxide (e.g. MgO + Mg$_2$Mo$_3$O$_8$ + 1.5O$_2$ ⇌ 3MgMoO$_4$). Because the equilibrium constant is equal to exp(-ΔG/RT), ΔG for the oxidation of each of the reduced mixed oxides, again with the exception of SrMoO$_4$, can be calculated to be -100 kJ/mol O$_2$, at 873 K.
Figure 5.4: Redox isotherms at 873 K of □ Cr$_2$(MoO$_4$)$_3$, ◇ Zr(MoO$_4$)$_2$, △ Al$_2$(MoO$_4$)$_3$, ○ MgMoO$_4$ and ■ SrMoO$_4$. The solid line is bulk MoO$_3$ isotherm using data from the literature.$^34$

SrMoO$_4$ was different from the other mixed oxides in that reduction was negligible for P(O$_2$) greater than 10$^{-22}$ atm. Following the removal of approximately 0.5 oxygen atoms per Mo cation, the P(O$_2$) for SrMoO$_4$ was approximately 10$^{-26}$ atm, corresponding to $\Delta G$ of -375 kJ/mol O$_2$; it was not possible to reduce SrMoO$_4$ completely to SrMoO$_3$ due to limitations of the coulometric titration apparatus. (At P(O$_2$) below 10$^{-28}$ atm, corresponding to a CO:CO$_2$ ratio of 97.7:2.3, the structural elements of the apparatus could be damaged.) This result agrees with previous measurements that also showed SrMoO$_4$ as being difficult to reduce.$^{108}$ The earlier thermodynamic study of SrMoO$_4$ indicated that the equilibrium P(O$_2$) for the reaction between SrMoO$_4$ and SrMoO$_3$ is 3x10$^{-13}$ atm at 1473 K.$^{108}$ Using the thermodynamic relationship for the temperature dependence of the equilibrium constant (d lnK/d1/T = -\Delta H/R), the enthalpy of oxidation

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of SrMoO$_3$ to SrMoO$_4$ is determined to be -550 kJ/mol-O$_2$, compared to a standard enthalpy of oxidation for MoO$_2$ to MoO$_3$ of approximately -200 kJ/mol-O$_2$. From the equilibrium constants at 873 and 1473 K, the entropy of oxidation for SrMoO$_3$ to SrMoO$_4$ is -200 J/Kmol-O$_2$, which is typical of entropies reported for the oxidation of other reduced mixed oxides and nearly identical to the entropy of oxidation for the reaction of MoO$_2$ to MoO$_3$ at 873 K, -193 J/Kmol-O$_2$.

To demonstrate the reversibility of the isotherms, the P(O$_2$) was also measured while pumping oxygen back into the cells containing the reduced Zr(MoO$_4$)$_2$, Al$_2$(MoO$_4$)$_3$, SrMoO$_4$ and Cr$_2$(MoO$_4$)$_3$ samples. In each case, the P(O$_2$) equilibrated to the same value as that shown in Figure 4; however, in all samples except SrMoO$_4$, the amount of oxygen that could be added before the equilibrium P(O$_2$) became greater than $10^{-6}$ atm was less than one per Mo. For the Zr(MoO$_4$)$_2$, Al$_2$(MoO$_4$)$_3$, and Cr$_2$(MoO$_4$)$_3$ samples, the amounts of oxygen associated with the vertical steps in the isotherm during re-oxidation were 0.8, 0.55, and 0.75 O/Mo respectively. The reason less oxygen could be added during re-oxidation was due to the loss of Mo because of the sublimation of some MoO$_x$ species. MoO$_x$ vapor would transport and condense on colder parts of the coulometric-titration apparatus during the extended times (~3 to 4 months) required to measure each isotherm. The loss of Mo following the isotherm measurements was demonstrated by XRD, with results for Zr(MoO$_4$)$_2$ shown in Figure 5.5. After completing a reduction/re-oxidation cycle by coulometric titration, the sample was found to be a physical mixture of monoclinic ZrO$_2$ and Zr(MoO$_4$)$_2$. Similar results were found for both Al$_2$(MoO$_4$)$_3$, and Cr$_2$(MoO$_4$)$_3$. 

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While the high vapor pressure of MoO$_3$ (~10$^{-3}$ torr at 873 K) prevented the measuring of equilibrium data for bulk molybdena (MoO$_2$ + ½O$_2$ ⇌ MoO$_3$), the CRC handbook and literature data indicate that $\Delta G$ is equal to -220 kJ/mol O$_2$ at 873 K$^{105,107}$, compared to our measured value of -100 kJ/mol O$_2$ for molybdates of Zr, Cr, Al, and Mg and -375 kJ/mol O$_2$ for SrMoO$_4$. Obviously, oxygen binding is different in the mixed oxides compared to that of bulk molybdena. This is not surprising given that the oxygens are shared by two different types of cation in the mixed oxides in their oxidized states, and are therefore, in environments that are chemically different from that of oxygens in bulk molybdena. The surprising result is that $\Delta G$ of oxidation is the same for four of the mixed oxides in this study and so different for SrMoO$_4$.

*Methanol Oxidation Activity*

To investigate the relationship between oxygen binding in the mixed oxides and catalytic activity, differential reaction rates were measured for methanol oxidation to formaldehyde. A summary of the results is given in Table 5.1 and Figure 5.6.
reported rates were normalized to the surface areas measured by BET isotherms on the samples after they were removed from the reactor. For purposes of calculating a turnover frequency, the site concentrations were assumed to be 4 Mo/nm\(^2\). The data for a bulk MoO\(_3\) sample are included in Figure 5.6 for comparison purposes.

![Figure 5.6: CH\(_3\)O production from partial oxidation of CH\(_3\)OH over the following samples: \(\square\) Cr\(_2\)(MoO\(_4\))\(_3\), \(\Diamond\) Zr(MoO\(_4\))\(_2\), \(\triangle\) Al\(_2\) (MoO\(_4\))\(_3\), \(\bigcirc\) MgMoO\(_4\), \(\triangleup\) SrMoO\(_4\) and ■ bulk MoO\(_3\).](image)

Table 5.1: Catalyst properties for CH\(_3\)OH partial oxidation

<table>
<thead>
<tr>
<th></th>
<th>BET area after reaction, m(^2)/gram</th>
<th>Selectivity towards CH(_2)O at 523 K, %,</th>
<th>Activation energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrMoO(_4)</td>
<td>36</td>
<td>70, rest to DME</td>
<td>81</td>
</tr>
<tr>
<td>Al(_2)(MoO(_4))(_3)</td>
<td>36</td>
<td>35, rest to DME</td>
<td>59</td>
</tr>
<tr>
<td>Cr(_2)(MoO(_4))(_3)</td>
<td>21</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>Zr(MoO(_4))(_2)</td>
<td>30</td>
<td>79, rest to DME</td>
<td>61</td>
</tr>
<tr>
<td>MgMoO(_4)</td>
<td>31</td>
<td>58, rest to CO(_2)</td>
<td>31</td>
</tr>
<tr>
<td>MoO(_3)</td>
<td>3</td>
<td>100</td>
<td>69</td>
</tr>
</tbody>
</table>
Although each of the materials exhibited some activity, even the most active sample, \( \text{Cr}_2(\text{MoO}_4)_3 \), exhibited rates that were 10 times lower than that of bulk \( \text{MoO}_3 \) and nearly 100 times lower than that which has been reported in the literature for titania- and zirconia-supported \( \text{MoO}_3 \) at 503 K\(^9\). Since the low level of activity could well be due to small amounts of surface molybdena that are not part of the crystalline phases, the conclusion from the data in Figure 6 is that none of the mixed oxides are active for methanol oxidation. The selectivity data, measured at 523 K and reported in Table 5.1, also lead to that conclusion. The \( \text{Al}_2(\text{MoO}_4)_3 \) and \( \text{Zr}(\text{MoO}_4)_2 \) samples both show poor selectivity, forming significant amounts of the acid-catalyzed product, dimethyl ether. Although the other oxides were reasonably selective for formaldehyde formation, this is likely because their metal cations are less acidic.

It is interesting to notice that, based on the redox properties in Figure 5.4, \( \text{MgMoO}_4 \), \( \text{Zr}(\text{MoO}_4)_2 \), \( \text{Al}_2(\text{MoO}_4)_3 \), and \( \text{Cr}_2(\text{MoO}_4)_3 \) are significantly easier to reduce than bulk \( \text{MoO}_3 \), while \( \text{SrMoO}_4 \) is significantly less reducible. Since all of the mixed oxides show low activity compared to bulk \( \text{MoO}_3 \), it would appear that reducibility is not the main factor influencing methanol oxidation rates over these molybdena catalysts.

There are several interesting points that can be made from the results in this study. Most important, Mo-containing mixed oxides, at least the ones examined in this study, are not active for methanol oxidation compared to either bulk \( \text{MoO}_3 \). Furthermore, based on literature reports, supported-molybdena catalysts exhibit higher rates than the bulk oxide\(^9,50,54\). This low activity for the bulk mixed oxides is in sharp contrast to what was reported previously for vanadium-containing mixed oxides\(^23\). \( \text{V}_2\text{O}_5 \), \( \text{ZrV}_2\text{O}_7 \), \( \text{AlVO}_4 \), \( \text{Mg}_3(\text{VO}_4)_2 \), and \( \text{CeVO}_4 \) were found to exhibit nearly identical turnover frequencies with rates that were also similar to that of zirconia- and alumina-supported vanadia catalysts\(^98\).

For the vanadia case, it was argued that the binding energy for oxygen did not affect methanol oxidation, because the rate-limiting step did not involve V-O bond breaking\(^98\). Apparently, the site geometry in vanadia catalysts also has a modest effect on rates, since the surfaces on the various vanadia mixed oxides are clearly different.

While Mo-O bond breaking is not the rate-limiting step for methanol oxidation on molybdena catalysts\(^53,56\), it was surprising that the bulk mixed oxides exhibited such poor catalytic properties for this reaction. The reason for the low activity of the bulk
mixed oxides must be associated with the site geometry. On each of the mixed oxides, the Mo$^{6+}$ cations exist as (MoO$_4$)$_2^-$ anions with the mixed oxides essentially being salts of this (MoO$_4$)$_2^-$ anion. One possible explanation for the low activity of the Mo mixed oxides is that the Mo cations within the (MoO$_4$)$_2^-$ anions are simply inaccessible for reaction. The implication is that this site geometry must be avoided in supported catalysts, at least for the methanol-oxidation reaction. Clearly, the formation of the mixed oxides in supported molybdena should be viewed as a deactivation mechanism for methanol oxidation.

Considering only the redox properties, it is also interesting to note that the isotherms for molybdates of Zr, Cr, Al, and Mg are the same. This implies that, thermodynamically, the initial and final states for these mixed oxides must be nearly equivalent. Apparently, the critical parameter for the initial state in each of the mixed oxides is the structure surrounding the Mo cations, rather than the presence of the second type of cation. Unlike the case for mixed oxides of vanadium$^{65}$, the electronegativity of the second cation in the molybdena compounds does not influence the oxygen binding. The similarity of the oxygen environments in the reduced states for molybdates of Zr, Cr, Al, and Mg is less easy to rationalize, since the structures of the mixed oxides in their reduced states are all quite different. A common feature for the reduced samples with low $\Delta G$ of oxidation is that there are Mo$^{4+}$-O-Mo$^{4+}$ units in all cases. Assuming that bonding geometry does not affect the energy of these structures, the final states in all of the samples would be the same.

The reason that SrMoO$_4$ is so different from the other mixed oxides is that SrMoO$_3$ has a perovskite structure with a 3-dimensional network of corner-shared octahedral Mo-O-Mo linkages$^{108}$. This difference between SrMoO$_3$ and the reduced states of the other mixed oxides is additional evidence that the final state is important in establishing thermodynamic properties.

Finally, it is interesting to compare the isotherms in Figure 5.7 for the Mo-based mixed oxides to the analogous results for the V-based oxides (ZrV$_2$O$_7$, Mg$_3$(VO$_4$)$_2$, AlVO$_4$, and CrVO$_4$) in Figure 7$^{65}$. First, there is a fundamental difference between ZrV$_2$O$_7$ and the other vanadates in this grouping in that there are V-O-V linkages in ZrV$_2$O$_7$. In the isotherm for this material, the V-O-V bonds manifest themselves by
showing oxidation and reduction in two separate regions of P(O₂)⁴⁶,⁶⁵. With the removal of the first oxygens, two V⁺⁵ cations are reduced to V⁺⁴ and the ΔG for this process is different from that of the reduction of two V⁺⁴ to V⁺³. The effect of V-O-V bonds on thermodynamic properties appears to be a general phenomenon, found also with bulk V₂O₅⁶⁹ and with high-coverage, supported vanadia in which V-O-V linkages are observed³⁶,⁹⁸. However, even with vanadium mixed oxides, which do not have V-O-V bonds, the nature of the second cation affects the redox properties of the mixed oxide dramatically. Although the redox properties of AlVO₄ and CrVO₄ are similar, this is probably because Cr⁺³ and Al⁺³ have similar electronegativities and ionic radii, ΔG of oxidation for Mg₃(VO₄)₂ is different by 150 kJ/mol O₂ at 873 K. This strong effect of the second cation is not observed with the Mo-based oxides.

\[\text{Figure 5.7: Redox isotherms at 873 K for the following samples: } \square \text{CrVO}_4, \diamond \text{ZrV}_2\text{O}_7, \bigtriangleup \text{AlVO}_4, \text{and } \bigcirc \text{Mg}_3(\text{VO}_4)_2.\]
5.4 Conclusions

The thermodynamic redox properties of $\text{Al}_2(\text{MoO}_4)_3$, $\text{Zr}(\text{MoO}_4)_2$, $\text{Cr}_2(\text{MoO}_4)_3$, and $\text{MgMoO}_4$ at 873 K are nearly identical to each other but differ significantly from that of $\text{SrMoO}_4$. None of the mixed oxides exhibit thermodynamic properties similar to that of bulk $\text{MoO}_3$. The similarities and differences between these mixed oxides likely result from the presence of isolated $\text{MoO}_4^{2-}$ tetrahedra in the oxidized forms and two different types of Mo-O-Mo bonding in the reduced forms. However, the catalytic activity for methanol oxidation was much lower than that of bulk $\text{MoO}_3$. It appears that the low activity for the bulk mixed oxides is the result of the $\text{Mo}^{+6}$ cations within the $\text{MoO}_4^{2-}$ anions being inaccessible to reactants.
Chapter 6. Conclusions

Redox thermodynamic properties and catalytic activities of metal oxides have been studied to draw connections between these two properties and between the structure of catalysts. Catalysts based on iron oxides (Water-Gas-Shift reaction for H\textsubscript{2} production) on vanadium oxides and molybdenum oxides (hydrocarbon partial oxidation and oxidative dehydrogenation) were studied because of their industrial importance and because of the extensive research literature. The background information available on these materials allowed for the concentrating on the thermodynamic properties of the materials rather than elucidating their crystal structure.

Redox isotherms for V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} catalysts were measured as a function of the vanadia weight loading and calcination temperature. 5 wt % V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} catalysts were found to be thermally stable and their redox isotherms at 748 K showed that reduction from V\textsuperscript{+5} to V\textsuperscript{+4} occurred for P\textsubscript{O\textsubscript{2}} values between 10\textsuperscript{-4} and 10\textsuperscript{-19} atm and reduction from V\textsuperscript{+4} to V\textsuperscript{+3} occurred at a P\textsubscript{O\textsubscript{2}} of 10\textsuperscript{-28} atm. The 748-K redox isotherm for a 15 wt % V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} catalyst calcined at 753 K showed a sharper transition for reduction from V\textsuperscript{+5} to V\textsuperscript{+4} which occurred at P\textsubscript{O\textsubscript{2}} of 10\textsuperscript{-20} atm. This sharper transition compared to the lower vanadia coverage sample may be the result of a more uniform polyvanadate species on this sample. In contrast to the 5 wt % sample, the 15 wt % sample was not thermally stable and underwent recrystallization upon calcination at 973 K, resulting in a low surface area material whose surface was covered with a highly reducible AlVO\textsubscript{x} species.

In spite of the differences in redox properties, all of the V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} catalysts were found to exhibit similar activities for the selective oxidation of methanol to produce formaldehyde, suggesting that oxygen removal from the surface is not the rate limiting step for this reaction. For propane ODH, larger differences between the catalysts were observed. While the 5 wt % vanadia samples and the 15 wt % vanadia sample calcined at 753 K, all exhibited similar activities for the ODH reaction. The highly reducible 15-wt% V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} sample that was calcined at 973 K was active only for the complete oxidation of propane to CO\textsubscript{2} and water. This work has established that the influence of redox properties on catalytic properties of material depends on the particular reaction of interest and on the reaction mechanism.
The transient reduction of vanadia catalysts by CH$_3$OH was used to determine the number of redox sites per surface area, as well as to examine the transient kinetics and the accessibility of bulk oxygen. By performing measurements at sufficiently low temperatures (below 443 K), only the surface of vanadia catalyst is reduced while bulk stays oxidized. The number of sites on bulk vanadia and magnesium vanadate was determined to be 7.4 and 2.1 V/nm$^2$, respectively. Bulk reduction was observed above 473 K for bulk vanadia and 573 K for magnesium vanadate. In the case of supported vanadates, the majority of vanadium was available for reaction in 2.5 wt% V$_2$O$_5$/TiO$_2$, while in 5 wt% V$_2$O$_5$/Al$_2$O$_3$, only 40% of vanadium was available for surface reaction due to the solid-state reaction between vanadia and alumina. Reaction rates per site over both supported catalysts were determined to be essentially the same in both transient and steady state reactions. The transient reaction rate measurements were found to be a simple, yet powerful tool to quantify the number of redox sites per surface area in complex catalysts.

Redox isotherms for supported iron oxide were examined as a function of iron loading on zirconia. Zirconia supported iron had a redox isotherm that showed well-defined steps corresponding to transitions of Fe$_2$O$_3$ (hematite) to Fe$_3$O$_4$ (magnetite), Fe$_3$O$_4$ to FeO and FeO to Fe. In the redox isotherm for supported iron oxide, the transition of Fe$_2$O$_3$ to Fe$_3$O$_4$ shifted to a significantly higher pressure of oxygen, compared to that observed with bulk iron, effectively making surface iron easier to reduce and harder to oxidize compared to bulk iron oxide. The reaction rate measurements for the WGS reaction over supported iron catalysts and bulk iron showed that specific rates for supported samples were much slower than rates for bulk iron, which is expected, because re-oxidation of iron oxide by water is a rate limiting step in the WGS reaction.

The thermodynamic redox properties of Al$_2$(MoO$_4$)$_3$, Zr(MoO$_4$)$_2$, Cr$_2$(MoO$_4$)$_3$, and MgMoO$_4$ at 873 K are nearly identical to each other but differ significantly from that of SrMoO$_4$. None of the mixed oxides exhibit thermodynamic properties similar to that of bulk MoO$_3$. The similarities and differences between these mixed oxides likely result from the presence of isolated MoO$_4^{2-}$ tetrahedra in the oxidized forms and two different types of Mo-O-Mo bonding in the reduced forms. However, the catalytic activities for methanol oxidation on each of the mixed oxides were much lower than that found on
bulk MoO$_3$. It appears that the low activity for the bulk mixed oxides is the result of the Mo$^{+6}$ cations within the MoO$_4^{2-}$ anions being inaccessible to reactants.

The main contribution of this work is in confirming that the structure of metal oxides can have a profound effect on the thermodynamic redox properties, due to changes in the environment around metal cations. However, the impact of redox thermodynamic properties on reaction kinetics is more subtle and depends on the details of the reaction mechanism. If the rate limiting step depends on the oxygen binding, then the impact will be significant. On the other hand, if the rate limiting step is independent of oxygen binding energy, then the reaction rate will not be affected in any way. This was shown using vanadia catalysts with different redox thermodynamic properties and two oxidation reactions: methanol to formaldehyde and propane to propene.
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