Investigation of Oxygen Defect Formation in Supported Vanadium Oxide Catalysts by Impedance Spectroscopy

Vorgelegt von Diplom-Ingenieur
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Von der Fakultät III – Prozesswissenschaften
der Technischen Universität Berlin
zur Erlangung des akademischen Grades

Doktor der Ingenieurwissenschaften
- Dr. Ing. -

genehmigte Dissertation

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Tag der wissenschaftlichen Aussprache: 29.08.2012

Berlin 2013
D 83
Herrn Prof. Dr. H. Schubert möchte ich für die Möglichkeit danken, diese Arbeit am Institut für keramische Werkstoffe durchzuführen sowie für alle wissenschaftlichen Diskussionen. Herrn Prof. Dr. H.-D. Wiemhöfer und Prof. Dr. R. Schomäcker danke ich für das entgegengebrachte Interesse und die Übernahme des Koreferates. Ich danke Benjamin Beck und Carlos Carrero für die katalytische Charakterisierung und für viele Diskussionen. Weiterhin möchte ich allen Mitarbeitern herzlich danken, die durch ihre Unterstützung jeglicher Art zum Gelingen dieser Arbeit beigetragen haben.
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1. Introduction

Light olefins like ethene or propene are very important chemicals used for the synthesis of various polymers or solvents. In Europe the largest amount of propene is synthesized via steam cracking processes (70 – 75 %), followed by fluid catalytic cracking (28 %) and to a small amount (2 %) by catalytic dehydrogenation. But these processes require high temperature (above 800 °C) and show poor selectivity. The necessity of elevated temperature means high energy consumption and thus generation of large amounts of carbon dioxide. Another disadvantage is the formation of coke which leads to a deactivation of the catalyst and requires costly regeneration. Or worse, the catalysts deactivate permanently due to the high reaction temperature. Hence, it is desired to develop reactions that run at much lower temperature. An alternative might be the oxidative dehydrogenation (ODH) of alkane that depending on the educt and catalyst proceeds at temperatures in the range of 200 – 600 °C. It is an exothermal redox reaction that is running in an oxygen containing environment and is thus less prone to coking. [1]

Many transition metal oxides are active for the ODH but especially vanadium oxide has been investigated due to its high redox activity [2,3,4,5]. It is a heterogeneous catalytic reaction in which the surface of the VOₓ catalyst reacts with propane to form propene and water. This process follows a redox cycle known as Mars-van-Krevelen mechanism [6] (see Figure 1-1). In this mechanism donation of oxygen from VOₓ plays an important role. In the reduction cycle lattice oxygen accepts hydrogen from the alkane and desorbs as water leaving a vacancy in the catalyst. The role of oxygen as a hydrogen acceptor is the reason for the reaction to be exothermal and therefore energetically favourable in contrast to normal dehydrogenation reactions [7]. These vacancies are then refilled from the gas phase oxygen in the reoxidation cycle. In this part transport of oxygen ions through the lattice is assumed and thus the oxidation can occur at a different site than it was reduced.

For many reactions pure vanadium pentoxide is not very active or selective but it is found that vanadium oxide supported on different metal oxides shows improved performance. The type and dispersion of vanadia species depends on the loading and their catalytic properties are strongly altered by the support [2,3,8,4,9,10,11,12]. The nature of this effect is diversely
discussed in the literature. Some correlate the catalyst’s activity to the TPR reducibility \([8]\) or to the Sanderson electro-negativity \([9]\) and in theoretical investigation the oxygen defect formation enthalpy as a reactivity descriptor is tested \([13,14,15,16,17,18,19]\).

**Figure 1-1:** A Mars-van-Krevelen-like reaction mechanism. On reduction electrons are injected into the catalyst and are localized at nearby vanadia centres. Oxidation may occur through lattice diffusion. Thus, oxygen uptake may take place at a different site than it was reduced.

In this work impedance spectroscopic experiments are used to investigate the defect formation processes and to study the impact of solid state aspects on catalytic properties. This is possible because electronic and ionic charge carriers are exchanged on reduction and oxidation and thus enable us to use conductivity experiments as a probe.

At first in Chapter 4.1.1 the properties of the pure vanadium pentoxide are investigated and a method is developed that allows experimental determination of oxygen defect formation enthalpies \(\Delta H_f\). Then supported catalysts are examined in order to elucidate its effect on the solid state properties. For gaining deeper insight into transport paths, conduction mechanism, and the redox properties of the complex systems a systematic approach is chosen and starting at systems of very high loading (Chapter 4.1.2) the amount of vanadium pentoxide is successively lowered (Chapter 4.1.3) until monolayer coverage catalysts are investigated (Chapter 4.1.4). Then in Chapter 4.2 follows a discussion on the origin of the effect of the support on the solid state properties and finally, its impact on catalysis is discussed in Chapter 4.3.
2. Basics

2.1. Transport Properties

The total conductivity ($\sigma_t$) of a solid is the sum of all partial conductivities ($\sigma_a$):

$$\sigma_t = \sum_a (q_a \mu_a c_a)$$  \hspace{1cm} 2-1

The major charge carriers are ions ($i$), electrons ($e$) and electron holes ($h$). Therefore, equation (3-4) can be expressed as:

$$\sigma_t = \sigma_i + \sigma_e + \sigma_h$$  \hspace{1cm} 2-2

$$\sigma_t = \sum_i (z_i q_i \mu_i c_i) - q_e \mu_e c_e + q_h \mu_h c_h$$  \hspace{1cm} 2-3

The number of effective charges is $z$, $q$ the magnitude of electronic charge, $\mu$ the mobility and $c$ the carrier density. Therefore, two parameters, the carrier density and mobility, can be modified in order to enhance the conductivity. [20]

The mobility depends on several parameters. Examples are the potential barrier for ion migration, the polarizability of the lattice and electrostatic interactions of the moving charge carrier with its surroundings. There are different strategies to increase the carrier density:

(1) A classical approach is homogeneous doping with aliovalent ions that are dissolved in the matrix of the solid conductor. In order to maintain electrical neutrality, defects of opposite charge are formed and hence the concentration of charge carriers is increased. (2) Another possibility to generate defect is non-stoichiometry. Here, via a gas phase reaction the oxide is reduced or oxidized and excess vacancies or interstitials are formed. With this process ionic and electronic conductivity is modified. (3) Further influence on the charge carrier concentration have interface effects like space charge or chemical strain. [21]

In the following chapters the basics of defect chemistry is discussed and applied to the ionic and electronic conduction mechanism.

2.1.1. Defects in Solids

Every well ordered solid exhibits deviations from the perfect lattice structure when the temperature is raised above absolute zero. These irregularities are called defects and have a
significant influence on physical and chemical properties in particular on the transport of charge carriers and are therefore discussed in the following.

2.1.1.1 Ionic Disorder

The ionic disorder is shown and discussed for a model oxide MO$_2$ that forms predominantly anti-Frenkel type defects. This intrinsic defect structure is well known for ionic conducting oxides like ZrO$_2$, ThO$_2$ and CeO$_2$. By forming anti-Frenkel defects, the anionic sublattice equilibrates with anionic vacancies and interstitial positions [22,23,24,25,26].

Using the Kröger-Vink notation [27] this defect reaction can be written as:

$$M^+_M + O^{\cdot}_O \leftrightarrow M^+_M + O^-_i + U^{**}_O$$

$M^+_M$ is a neutral metal cation, $O^{\cdot}_O$ is a neutral oxygen on its lattice position, $O^-_i$ a twice negative charged (in respect to the lattice) oxygen interstitial and $U^{**}_O$ is a twice positive charged oxygen vacancy. Usually the symbol $V^{**}_O$ is used for the vacancy. But due to the vanadium investigated in this work, vanadium will be $V$ and a vacancy $U$. This defect reaction shows, that the cationic sublattice is not altered by the anti-Frenkel defects.

Usually the pure oxides do not exhibit high ionic conductivity but this can be altered by generating further defects. This is done by doping with cations of lower valence. These substitute the cations in the lattice and introduce large amounts of point defects. An example for doping MO$_2$ with a trivalent impurity is given in reaction 2-5:

$$M^+_3 + O_3 \leftrightarrow 2M^+_M + U^{**}_O + 3O^{\cdot}_O$$

For 2 $M^{3+}$ substituted for $M^{4+}$ a vacancy is formed in order to maintain electroneutrality.

2.1.1.1.2 Electronic Disorder

Many ionic conductors exhibit partial electronic conduction. This can be an intrinsic property of the material. Electrons are thermally activated to the conduction band generating a hole in the valence band:

$$0 \leftrightarrow e^- + h^*$$

But due to the large band gap of ionic oxides (above 2 eV) the contribution of intrinsic conduction is negligible.
Electronic conduction due to extrinsic disorder is more common. This may arise due to
impurities generating donor or acceptor states as known from semiconductors. But
electronic defects can also evolve due to deviations from stoichiometry. Therefore, in oxides,
it can be altered due to changes of the chemical potential of oxygen in the atmosphere [28].

**Partial Pressure Dependency**

At high oxygen partial pressure, oxygen will be incorporated into the lattice filling oxygen
cavancies. In order to maintain electroneutrality, electron holes are formed:

\[
\frac{1}{2}O_2 + U_o^{**} \rightarrow O_o^5 + 2h^* 
\]

In reducing conditions (low oxygen partial pressure) oxygen is extracted from the lattice
forming an oxygen vacancy and two electrons:

\[
O_o^5 \rightarrow \frac{1}{2}O_2 + U_o^{**} + 2e^* 
\]

The activity of lattice defects in a solid solution is approximately identical to the
concentration because it is considered as dilute species [29]. Due to the highly
 disordered
lattice, large amounts of point defects are present (reactions 2\textsuperscript{-7} and 2\textsuperscript{-8}). Thus, the
concentration of \([O_o^5]\) or \([U_i^\chi]\) is taken as constant when the oxygen partial pressure is
changed. Therefore, following equilibrium constants result for reaction (2\textsuperscript{-7}) and (2\textsuperscript{-8}):

\[
K_h = \frac{[h^*]^2}{p_o^{1/2} [U_o^{**}]} 
\]

\[
K_e = p_o^{1/2} [e^*] [U_o^{**}] 
\]

The defects that are formed are strongly partial pressure dependent. Only the concentration
of the defects formed by substitution doping is virtually partial pressure independent
because their quantity is so large, that the concentration change is negligible. Thus, their
concentration is assumed to be constant:

\[
[U_o^{**}] \approx const. 
\]

The electronic defect concentration is a function of the partial pressure and these are usually
illustrated in a Kröger-Vink-diagram diagram (Figure 2\textsuperscript{-1}).
At high partial pressure a p-type dominated region according to equation 2-7 is found and in this pressure range, the electroneutrality condition is:

$$2\left[ U_{O}^{\ast\ast} \right] = -\left[ h^{\ast} \right]$$

This gives with equation 2-9 a partial pressure dependency of the defect electron concentration of +1/6:

$$K_{h} = -1/2\left[ h^{\ast} \right] p_{O_{2}}^{-1/2}$$

$$\left[ h^{\ast} \right] \propto p_{O_{2}}^{1/6}$$

At low oxygen partial pressure the n-type conductivity dominates and the electroneutrality condition is:

$$2\left[ U_{O}^{\ast\ast} \right] = \left[ e^{\ast} \right]$$

Using equation 2-8 for the formation of electronic defects a partial pressure dependency of -1/6 is found.
\[ K_e = \frac{1}{2} [e^+]^{1/2} p_{O_2}^{1/2} \]  
\[ [e^+] \propto p_{O_2}^{-1/6} \]

At intermediate partial pressure the ionic defects exhibit the highest concentration and as already discussed their concentration is partial pressure independent. Thus, the equations 2-13 and 2-16 change to:

\[ K_h = -\frac{1}{2} [h^+]^{1/2} p_{O_2}^{-1/2} \]

\[ K_e = \frac{1}{2} [e^+]^{1/2} p_{O_2}^{1/2} \]

Hence, in the ionic conducting domain, the concentration of electrons and defect electrons are proportional to +1/4 and -1/4, respectively.

According to equation 2-1 the conductivity is directly proportional to the charge carrier concentration and therefore at constant mobility the conductivity exhibits the same pressure dependency as discussed above.

2.2. Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a versatile method that allows investigation of dynamic processes of charged particles. Material properties like conductivity, mobility and dielectric constants can be investigated and the method gives the possibility to characterize transport mechanisms in the volume or at interfaces like redox and diffusion processes. Using EIS the frequency dependent conductivity can be investigated over a broad bandwidth (mHz to MHz) giving thus the possibility to resolve transport processes exhibiting different time constants. Detailed information can be found in [31].

Impedance spectroscopy uses an alternating voltage \( U^* \) and the resulting alternating current \( I^* \) is analysed in respect to phase difference \( \varphi \) and amplitude. This is used to calculate the frequency dependent impedance \( Z \) of the system. For the interpretation the resulting impedance plot is modelled by using an adequate equivalent circuit in order to gain insight into the electrochemical processes. The most commonly used elements are resistive \( (R) \), capacitive \( (C) \) and inductive \( (L) \) elements. These are connected in series or parallel and can be completed using further elements for the description of e.g. diffusion processes.
If an alternating voltage $U^*$

$$U^* = U_0 \exp(j \omega t + \varphi_u) \quad 2-20$$

is applied to an electrochemical cell an electrical current $I^*$ flows through the sample:

$$I^* = I_0 \exp(j \omega t + \varphi_i) \quad 2-21$$

Current and voltage are described by the amplitude, $I_0$ and $U_0$, the complex number $j$, the pulsatance $\omega = 2\pi \nu$, with the frequency $\nu$, and the phase difference $\varphi_u$ and $\varphi_i$. The phase difference between voltage and current is given by $\varphi_u - \varphi_i = \varphi$. According to Ohm’s law the complex impedance is

$$Z = \frac{U_0}{I_0} \exp(j(\varphi_u - \varphi_i)) = Z_0 \cos \varphi + Z_0 j \sin \varphi = Z' + jZ''. \quad 2-22$$

$Z'$ is the real and $Z''$ is the imaginary part. Some elements have a frequency dependent impedance and thus the characteristics of the three basic elements are depicted in Table 2-1:

<table>
<thead>
<tr>
<th>Impedance Element</th>
<th>Resistance</th>
<th>Capacity</th>
<th>Inductance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>$Z = R$</td>
<td>$Z = (j \omega C)^{-1}$</td>
<td>$Z = j \omega L$</td>
</tr>
<tr>
<td>Nyquist Plot</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>$\varphi = 0^\circ$</td>
<td>$\varphi = -90^\circ$</td>
<td>$\varphi = 90^\circ$</td>
</tr>
</tbody>
</table>

The ohmic resistance is a frequency independent element and takes only real values. While the capacity and inductance take only imaginary values. This gives for the capacity a phase difference of $-90^\circ$ and for the inductance a value of $+90^\circ$.

Usually the equivalent circuits consist of several elements connected to a network and the overall impedance is calculated according to Kirchhoff’s laws. Hence, the impedance of a
Basic connection is the sum of all elements while for a parallel connection it is the sum of the reciprocal values. But real samples contain inhomogeneities and thus show a deviation from the perfect behaviour of the equivalent circuit elements. Responsible is a distribution of macroscopic material properties like a rough electrode that shows behaviour different from a perfect capacitor and can be modelled using a constant phase element (CPE). The impedance of the CPE is

\[ Z_{\text{CPE}} = A(j \omega)^m \]  

The distribution of the properties is modelled by the variables \( A \) and \( \alpha \). For \( m = 1 \) and \( A = 1/C \) the CPE corresponds to an ideal capacitor. For \( m = 0 \) and \( A = R \) it is equal to a resistance and for \( m = -1 \) and \( A = L \) it describes an inductive element. For \( m = 0 \) it is the Warburg diffusion impedance. [32,33].

The frequency dependent impedance can be shown in a Nyquist plot (Figure 2-2). In this diagram the imaginary and real part are depicted for every frequency. Therefore the frequency information is lost but the arrow indicates the direction of increasing frequency.

![Nyquist plot and equivalent circuit](image)

**Figure 2-2**: (a) Nyquist plot for parallel RC-circuit with a series resistance \( R_v \). (b) Corresponding equivalent circuit.

In Figure 2-2 the Nyquist plot for a parallel RC-circuit with a resistance in series is depicted and the impedance of this equivalent circuit is calculated as follows:

\[ Z(\omega) = R_v + (1/R + j\omega C)^{-1}. \]  

For an increase of the pulsatance \( \sigma \to \infty \) the second term vanishes and the impedance takes only real values:

\[ Z(\sigma \to \infty) = R_v. \]
If the frequency takes very small values \((\sigma \to 0)\), then, as shown in Figure 2-2, the impedance is the sum of \(R_v\) and \(R\):

\[
Z(\sigma \to 0) = R + R_v.
\]

The maximum of the imaginary part is found at the pulsatance:

\[
\sigma_{\text{max}} = (RC)^{-1}
\]

Another diagram for the impedance is the Bode plot (Figure 2-3). It shows the absolute value of the impedance \(|Z|\) and the pulsatance as a function of the frequency. This diagram contains the same information but the frequency information is not lost. But the interpretation in respect to choosing the equivalent circuit is easier in the Nyquist plot.

2.3. Physical Properties of the Vanadium Oxides

In this chapter the structural and electrical properties of vanadium pentoxide are be briefly reviewed.

2.3.1. Structure of the Vanadium Oxides

Vanadium pentoxide \((V_2O_5)\) has a layered orthorhombic structure of the type \(Pmmn\). The lattice parameters are \(a = 11.512(3)\ \text{Å}, \ b = 3.564(1)\ \text{Å}\) and \(c = 4.368(1)\ \text{Å}\) [34]. Figure 2-4 depicts the bulk structure of \(V_2O_5\). There are three differently coordinated oxygen atoms: the vanadyl oxygen \(O^1\), \(O^2\) linking chains along the a-axis and \(O^3\) connecting chains in the a-b plain. The layers are connected via weak van der Waals bonds along the c-axis. Due to the
easy change of valence from $V^{5+}$ to $V^{4+}$ and $V^{3+}$ many phases exist in the system $V_2O_5$-$VO_2$ and the compounds $V_2O_5$, $V_3O_7$, $V_4O_9$, $V_6O_{13}$, and $VO_2$ are known [35].

![Figure 2-4: The structure of vanadium pentoxide [34]. Red is oxygen and grey vanadium. The coordination of the oxygen atoms is indicated by the numbers.](image)

2.3.2. Electrical Properties of Vanadium Pentoxide

The electrical properties of vanadium pentoxide have been extensively investigated, but often in a temperature range where the defect concentration is independent of temperature or partial pressure [35,36,37,38,39,40,41]. Vanadium pentoxide is an n-type semiconductor with low electron mobility and the electronic transport at low temperature occurs via small polarons [36,37,38,42,43]. There are some investigation at higher temperature, but often the surface area of the sample (often a sintered body or single crystal) restricted the equilibration of the partial pressure of oxygen in the sample with the surrounding atmosphere because the surface reaction is usually the rate determining step [44,45]. Some authors found a hysteresis in the conductivity on heating and cooling at higher temperature which was attributed to the presence of lower oxides [46] or interactions with oxygen in the gas phase [47]. Allersma et al. [43] investigated the conductivity of molten vanadium pentoxide, which exhibits faster equilibration kinetics. The authors investigated the dissociation of vanadium pentoxide as a function of partial pressure and determined the enthalpy of formation for an oxygen vacancy to 1.3 eV. They found an apparent activation energy of the vanadium pentoxide melt of 0.63 eV and ascribed it to a combination of dissociation and migration enthalpy. By using the migration enthalpy $\Delta E_m$ of a single crystal they were able to calculate the defect formation enthalpy according to following approach:
The oxygen vacancy formation reaction \(2V^x + O^+_O \xrightarrow{\text{reduction}} 2V^+ + \bigcup^*_O + 1/2O_2\) exhibits for the conductivity a partial pressure dependency of \(-1/6\) as already discussed on page 11.

\[
2V^x + O^+_O \xrightarrow{\text{reduction}} 2V^+ + \bigcup^*_O + 1/2O_2 \quad \text{(2-28)}
\]

\(V\) is vanadium and \(V^+\) is a \(V^{4+}\) ion that is formed on reduction. Experiments on the melt confirmed the partial pressure dependency and thus following mass action law for the reduction reaction was used [43]:

\[
K = \left[ V^+_v \right] \cdot \bigcup^*_O \cdot P_{O_2}^{1/2} \quad \text{(2-29)}
\]

As \(\left[ V^+_v \right] = 2[\bigcup^*_O]^{1/2}\):

\[
K = \frac{1}{2} \left[ V^+_v \right]^2 \cdot P_{O_2}^{1/2} \quad \text{(2-30)}
\]

and \(\left[ V^+_v \right] = (2K)^{1/2} \cdot P_{O_2}^{-1/2}\).

From \(K = K_0 \cdot \exp \left( -\Delta H^0 / RT \right)\), where \(\Delta H^0\) is the enthalpy of formation of the \(\bigcup^*_O\) defect follows with equation (2-31):

\[
\left[ V^+_v \right] = K_1 \cdot \exp \left( -\Delta H^0 / 3kT \right) \cdot P_{O_2}^{-1/6} \quad \text{(2-32)}
\]

The conductivity of vanadium pentoxide depends on the concentration of \(\left[ V^+_v \right]\):

\[
\sigma = \left[ V^+_v \right] \cdot \exp \left( -\Delta E_m / kT \right) \quad \text{(2-33)}
\]

\(\Delta E_m\) is the ionization energy for the localized electron at the \(\left[ V^+_v \right]\) site. Substituting \(\left[ V^+_v \right]\) in equation (2-33) with equation (2-32), the conductivity is described by equation (2-34) with a pressure dependence of \(-1/6\):

\[
\sigma = K_2 \cdot \exp \left( -\left( \Delta H^0 / 3kT + \Delta E_m / kT \right) \right) \cdot P_{O_2}^{-1/6} \quad \text{(2-34)}
\]

\[
\sigma = K_2 \cdot \exp \left( -\Delta E^* / kT \right) \cdot P_{O_2}^{-1/6} \quad \text{(2-35)}
\]

Therefore at constant \(P_{O_2}\), the enthalpy of formation for an oxygen vacancy \(\Delta H^0\) can be calculated using equation (2-36):

\[
\sigma = K_2 \cdot \exp \left( -\Delta E^* / kT \right) \quad \text{(2-36)}
\]

where \(\Delta E^*\) is the measured activation energy derived from the conductivity data. As \(\Delta E^*\) is

\[
\Delta E^* = \Delta H^0 / 3 + \Delta E_m \quad \text{(2-37)}
\]

the value of \(\Delta H^0\) can be derived from the Arrhenius-plot if \(\Delta E_m\) is known.
2.4. Catalytic Properties of Vanadium Oxide Catalysts

In this chapter the catalytic properties of vanadium pentoxide are reviewed.

2.4.1. The Oxidative Dehydrogenation of Propane

The Oxidative Dehydrogenation of Propane (ODH) is a heterogeneous catalytic reaction and in this kind of reaction alkanes react with oxygen to form water and alkenes:

\[ C_3H_8 + \frac{1}{2}O_2 \rightarrow C_3H_6 + H_2O \]  

The reaction enthalpy is \( \Delta H_{298}^0 = -105 \text{kJmol}^{-1} \) and is thus thermodynamic favourable and allows high conversion in contrast to the catalytic dehydrogenation:

\[ C_3H_8 \rightarrow C_3H_6 + H_2 \]  

that exhibits an enthalpy of \( \Delta H_{298}^0 = +136 \text{kJmol}^{-1} \) and is thus endothermic. However, selectivity problems may arise for the ODH because the products of the total oxidation are more stable than the desired alkenes. [48]

The ODH follows a Mars-van-Krevelen mechanism [6] which is a redox reaction with contribution of lattice oxygen from the catalyst. It is called a redox mechanism because the reduction and oxidation cycle can be described as separate steps. In the reduction cycle the catalyst releases oxygen and oxidizes the alkane. In this step an oxygen vacancy is formed at the surface. This vacancy is refilled in the oxidation cycle but the reoxidation may occur at a
different site that the catalyst was reduced because transport of oxygen through the lattice is assumed (see Figure 2-5).

2.4.2. The Support Effect

Many authors found an influence of the support material on the catalytic performance [2,3,8,4,9,10,11,12] but the role of the support is still a matter of discussion. Often a high reducibility of the support is correlated with a higher activity of the catalyst which is ascribed to the properties of the V-O-support bridging bonds [2,49,50]. Others propose, that the support determines only the structure of the resulting vanadium species (crystallites, polymers and monomers) [11] or that a complex interaction of supporting oxide and vanadia surface species are the origin of the support effect [4]. At low coverage isolated monomeric VO₄ species are found and with increasing loading the extent of polymerization rises [51,52,53,54] forming finally 3 dimensional crystalline vanadium pentoxide. The vanadium species exhibit different reducibility [10,55] and the support influences the speciation and dispersion of the VO₄ species and thus the catalytic performance [11,12,56,50]. Several models are proposed for the mono- and polymeric vanadia structures and are displayed in Figure 2-6:

![Figure 2-6: Structural models for the supported vanadia species on silica support. Left: monomers, middle and right represent polymeric structures. [57,58,59]](image)

In [60,61,62,63,64] the redox properties of vanadia-based mixed bulk oxides and supported catalysts are investigated using coulometric titration. Redox isotherms are determined and it is shown, that the transition to lower oxidation states proceeds at different oxygen partial pressures. Moreover, for mixed bulk oxides different oxidation enthalpies are found. However, supported catalysts of low loading showed nearly identical properties.
3. Methods

3.1. Catalyst preparation

3.1.1. High Loading

The powder catalysts were obtained by thermal spreading of vanadium pentoxide (GfE Materialien GmbH) over the supporting oxides (Table 3-1). The support and vanadium oxide was mixed in a ball mill (Retch, type PM4, 30 min, 120 Umin⁻¹, 30 Al₂O₃ balls) in cyclohexane and then subsequently dried at 70 °C for 1 day. The dried powder was calcined in a quartz furnace at 500 °C for 4 hours in a stream of synthetic air (AirLiquide N50, 20 ml/min) passing through the powder bed (Appendix, Figure 7-4). The heating and cooling rate was 3 Kmin⁻¹. Table 3-2 shows the composition of the differently supported catalysts.

Table 3-1: Manufacturer information for the metal oxides used as support and active compound.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Manufacturer</th>
<th>Lot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₅</td>
<td>GfE Materialien GmbH</td>
<td>92393</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Alfa Aesar</td>
<td>K207006</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Sumitomo</td>
<td>AKP50, HD881</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Alfa Aesar</td>
<td>H29T027</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Kronos</td>
<td>GL102/10827</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesia</td>
<td>Magnesia 298, 4309298</td>
</tr>
</tbody>
</table>

Table 3-2: Nomenclature and composition of supported catalysts. W is the mass fraction and x the molar fraction of vanadium pentoxide. Additionally the BET surface area is shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V₂O₅ (mol%)</th>
<th>V₂O₅ (m%)</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₅</td>
<td>100</td>
<td>100,0</td>
<td>2,01</td>
</tr>
<tr>
<td>VOₓ/TiO₂</td>
<td>30</td>
<td>49,8</td>
<td>4,63</td>
</tr>
<tr>
<td>VOₓ/m-ZrO₂</td>
<td>30</td>
<td>38,8</td>
<td>2,38</td>
</tr>
<tr>
<td>VOₓ/SiO₂</td>
<td>30</td>
<td>56,5</td>
<td>1,73</td>
</tr>
<tr>
<td>VOₓ/MgO</td>
<td>30</td>
<td>65,9</td>
<td>10,40</td>
</tr>
<tr>
<td>VOₓ/α-Al₂O₃</td>
<td>30</td>
<td>43,3</td>
<td>9,04</td>
</tr>
</tbody>
</table>
3.1.2. Percolation Catalysts

The percolation catalysts were prepared with the same method as used above. Mixtures of different composition were prepared for m-ZrO$_2$ and SiO$_2$ supports (Table 3-3 and Table 3-4).

<table>
<thead>
<tr>
<th>Name</th>
<th>SiV56</th>
<th>SiV43</th>
<th>SiV35</th>
<th>SiV25</th>
<th>SiV20</th>
<th>SiV14</th>
<th>SiV7</th>
<th>SiV0</th>
</tr>
</thead>
<tbody>
<tr>
<td>w (%)</td>
<td>56.5</td>
<td>43.1</td>
<td>34.8</td>
<td>25.2</td>
<td>19.7</td>
<td>13.7</td>
<td>7.2</td>
<td>0</td>
</tr>
<tr>
<td>x (%)</td>
<td>30</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>ZrV39</th>
<th>ZrV27</th>
<th>ZrV21</th>
<th>ZrV14</th>
<th>ZrV10</th>
<th>ZrV7</th>
<th>ZrV4</th>
<th>ZrV0</th>
</tr>
</thead>
<tbody>
<tr>
<td>w (%)</td>
<td>38.8</td>
<td>27.0</td>
<td>20.7</td>
<td>14.1</td>
<td>10.7</td>
<td>7.2</td>
<td>3.6</td>
<td>0</td>
</tr>
<tr>
<td>x (%)</td>
<td>30</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>7.5</td>
<td>5</td>
<td>2.5</td>
<td>0</td>
</tr>
</tbody>
</table>

3.1.3. Amorphous Catalysts

The amorphous monolayer catalysts were obtained by a thermal spreading method. The supports (Table 3-5) were calcined at 750 °C for 4 hours in a quartz rotary furnace in a flow of synthetic air (50 ml/min, 20% O$_2$/Ar) and then mixed with a precursor (vanadyl acetylacetonate) in an agate mortar. The mixture was again calcined at 500 °C for 4 hours.

<table>
<thead>
<tr>
<th>Name</th>
<th>Support manufacturer</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Surface density (V at/nm)</th>
<th>w (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_x$/TiO$_2$</td>
<td>Saint-Gobain Norpro</td>
<td>17.1</td>
<td>3.5</td>
<td>0.6</td>
</tr>
<tr>
<td>VO$_x$/m-ZrO$_2$</td>
<td>Saint-Gobain Norpro</td>
<td>52.1</td>
<td>3.1</td>
<td>1.4</td>
</tr>
<tr>
<td>VO$_x$/γ-Al$_2$O$_3$</td>
<td>Saint-Gobain Norpro</td>
<td>200.9</td>
<td>3.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

3.2. Impedance Spectroscopy

For the impedance spectroscopic experiments, the powder catalysts were compacted into discs of 10 mm or 6 mm using an uniaxial press. These discs were isostatically redensified at 2.5 kbar. Then platinum contacts with a diameter of 5 mm were sputter coated (Balzers, SCD 050) on both sides at 44 mA and 240 s.
The electrochemical measurements were done using a Zahner IM6ex with the software package Thales 3.13. The measurement setup enables experiments in different atmospheres and temperature up to 1100 °C (Figure 3-1).

For the experiments, the sample chamber was equilibrated at a starting temperature of 350 °C for about 5 hours. Then with a heating rate down to 0.1 K/min was used for the temperature dependent experiments on heating and cooling. Due to the low heating rate the experiments take up to 3 days (Figure 3-2).

Figure 3-1: Setup for electrochemical impedance spectroscopy.

Figure 3-2: Temperature profile for the conductivity experiments. Due to the low heating rate, one experiment runs up to 3 days.
Methods

Usually, an amplitude of 50 mV was applied and the frequency range was adapted to the required measurement range (e.g. 100 mHz to 3 MHz). The modelling of the impedance spectra was done using the Thales software and the conductivity $\sigma$ was calculated using the equation:

$$\sigma = \frac{d}{A \cdot R}$$  \hspace{1cm} 3-1

d is the sample thickness, $A$ the cross section and $R$ the resistance.

3.2.1. Conductivity Relaxation Experiments

The system was equilibrated at a certain oxygen partial pressure and temperature. Then the gas in the sample chamber was exchanged. For this purpose the chamber was evacuated (300 mbar) and rinsed with the new gas composition 3 times. Then the impedance spectra were taken for a certain time. For the evaluation of the data, an exponential dependency of conductivity and time was assumed and the data was fitted with the function:

$$\sigma = \sigma_0 + A \cdot \exp(rt)$$  \hspace{1cm} 3-2

$\sigma$ is the conductivity at time $t$, $\sigma_0$ is the conductivity at $t = 0$ s, $A$ is the pre-exponential factor and $r$ the rate constant.

3.2.2. Partial pressure Dependent Conductivity

The samples were heated in oxygen to the final temperature and then equilibrated for 5 days. Then the partial pressure was lowered and again equilibrated to 2 – 3 days. Equilibration was verified by observing the change of conductivity as a function of time. Then an impedance spectrum was taken.

Table 3-6: Gas mixtures for the partial pressure dependent experiments. $D$ is the gas flow in l/min.

<table>
<thead>
<tr>
<th>$pO_2$</th>
<th>$N_2$ flow (%)</th>
<th>$O_2$ flow (%)</th>
<th>$D$ (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>2</td>
<td>3</td>
<td>0.05</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>0.04</td>
</tr>
<tr>
<td>0.4</td>
<td>3</td>
<td>2</td>
<td>0.05</td>
</tr>
<tr>
<td>0.33</td>
<td>4</td>
<td>2</td>
<td>0.06</td>
</tr>
</tbody>
</table>
3.3. Neutron diffraction

Supported catalysts comprising 10 mol% of vanadium pentoxide were used for the diffraction experiments. As support α- and γ-alumina, titania and zirconia were used and the catalysts were prepared according to chapter 3.1.1.

Neutron diffraction measurements were done at instrument E6 at BENSC/HZB Berlin, Germany. 5 mg of catalyst were applied to the quartz glass crucible (diameter = 10 mm) and the experiments were done in a flow of oxygen (0.05 ml/min, Linde, purity 5.0). Measurements were done at following temperatures: 30 °C, 300 – 500 °C in 50 K steps. Each temperature increase was done in a single step and then equilibrated during repeated neutron diffraction. (Wave length 2.439 nm, range 10 ≤ 2Θ ≤ 130°, measuring time 50 min).

Equilibrium was achieved after 20 min (thermo couple) and the according measurement was used for evaluation. The lattice parameters were calculated using the software Full Prof.

3.4. X-ray Diffraction

The XRD experiments at 500 °C at different oxygen partial pressure were done in a D5000 with a Cu-anode (λ = 0.1542 nm) in a range 10 ≤ 2Θ ≤ 70°. A Buehler heating chamber (Pt-resistance heater) and a scintillator detector was used in this setup. The time for a single measurement was 24 hours.

| Table 3-7: Program for the partial pressure dependent XRD experiments at 500 °C. |
|-----------------|---------|-----------------|
| Atmosphere      | T (°C)  | Comment         |
| 1 Air           | 10      | Reference measurement |
| 2 O₂            | 500     | 24 hour equilibration |
| 3 O₂            | 500     | measurement |
| 4 Synt. Air     | 500     | 24 hour equilibration |
| 5 Synt. Air.    | 500     | measurement |

Slurry of Vanadium pentoxide and alcohol was applied on the heating band and dried at room temperature. After the alcohol was evaporated, the sample chamber was heated at 1 K/min in a flow of oxygen to 500 °C. Then, after 24 hours for equilibration, the first
Methods

measurement was done and after that the partial pressure was changed and again after 24 hours the second measurement was done (see Table 3-7). The lattice parameters were calculated using the software Full Prof.

XRD phase analysis was done using a Philips PW 1070 with a Cu-anode ($\lambda = 0.1542$ nm) and monochromator in a range $10 \leq 2\Theta \leq 90^\circ$ and was analyzed using the software package DiffracPlus.

3.5. UV-vis Spectroscopy

UV-Vis spectroscopy was done with a Perkin Elmer Lambda 900 UV/VIS/NIR-Spectrometer in reflection geometry on pressed powder pellets. The measurements were calibrated using BaSO$_4$ and performed in a range of 300 to 900 nm with a resolution of 1 nm. The spectra were transformed into the Kubelka-Munk function ($F(R_s)$) with the OPUS software (Bruker). The optical band gap ($E_g$) was determined from the intersect of a linear function of $(F(R_s) \times h\nu)^{0.5}$ against $h\nu$ with the x-axis.

In order to investigate thermally induced defect formation the band gap of temperature pretreated samples was determined. For this purpose powder pellets were tempered for 8 days at different temperatures in air. They were taken from the hot furnace and stored in nitrogen atmosphere. The measurements were done in ambient air at room temperature.

3.6. Rutherford backscattering

In order to investigate the non-stoichiometry in the system V$_2$O$_x$, RBS (Rutherford Backscattering) was used. For these experiments, protons with a primary energy of $E_0 = 300$ keV were used. In the setup the ion beam passed an aperture and a beam monitor and then irradiated the sample with an area of 1 mm in diameter. The proton yields are all related to an incident ion charge of 10 $\mu$C and the analysis of backscatter ions is done by an electrostatic cylinder capacitor analyser (ESA). The acceptance solid angle was equal to $7.5 \times 10^{-4}$ sr, the energy resolution $\Delta E_{res}/E = c1 = 7.3 \times 10^{-3}$. For the detection of protons a CsI:Tl scintillator and a photo multiplier was used. The experiments were done at normal incidence and the scattering angle $\phi_2$ corresponds to the angle between incident beam and outgoing beam and was $45^\circ$ for these experiments.
Methods

Figure 3-3 depicts the energy spectra of backscattered protons for vanadium pentoxide single crystals, polycrystals, vanadium trioxide polycrystals and a sample of unknown oxygen content V$_2$O$_x$.

![RBS spectra of V2O5 poly and single crystals](image)

Specific threshold energies are found at 280 keV and 242 keV due to scattering at vanadium and oxygen atoms, respectively. Evaluation of the ratio of proton yield for oxygen and vanadium allows calculation of the oxygen concentration. The measured spectrum for the single crystal agrees with the simulation of a function with $x = 5$.

Taking into account the roughness of the sample surface [65], the RBS energy spectra were simulated for polycrystals. In order to verify the RBS method to determine the oxygen concentration, a V$_2$O$_5$ was reduced by CO to V$_2$O$_3$ at a 500 °C. The atom concentrations N$_O$/N$_V$ are determined by the ratio of the proton yield at 240 keV and 280 keV for oxygen and vanadium, respectively. Taking the intensities of V$_2$O$_5$ as a reference for V$_2$O$_x$ then it follows:

$$x = 5 \times \frac{I_O(V_2O_5)}{I_O(V_2O_3)} \frac{I_V(V_2O_3)}{I_V(V_2O_5)}$$

3-3

This gives for polycrystalline V$_2$O$_3$ a good agreement with $x = 3.1 \pm 0.2$. 
3.7. TG-FTIR

The thermogravimetric experiments were done in a reducing gas atmosphere (CRYSTAL gas mixture, Air Liquide) consisting of O$_2$/Propane/N$_2$ (2.18 % / 7.97 % / 89.85 %) using a Netzsch STA409PC/PD and a Bruker Equinox IFS55 FTIR setup. Alumina crucibles were used and a gas flow of 80 ml/min was chosen.

3.8. Scanning Electron Microscopy

The EDX mappings and micrographs were done at the Hahn-Meitner-Institut (Berlin Wannsee) using a Zeiss FIB 1540 EsB Cross Beam and the specimens were evaporated with carbon.

3.9. Transmission Electron Microscopy

Transmission electron microscopy (TEM) investigation were done in a Zeiss LIBRA 200 FE operated at 200 kV accelerating voltage. Bright field micrographs were recorded while using the in-column energy filter to obtain zero energy loss filtered images. Samples for the TEM experiments were obtained by crushing the material and dispersing it onto copper grids covered with carbon film.

3.10. Catalytic Testing

Catalysts at High Loading

The powder was compacted at 30 MPa and then granulated and sieved to the fraction 100 – 200 µm.

The catalytic measurements were performed at ambient pressure in U-shaped fixed bed quartz reactors (Ø6 mm). The catalyst particles were diluted with inert silicon carbide in the mass ratio 1:2 (catalyst/SiC). The feed had a composition of C$_3$H$_8$/O$_2$/N$_2$ = 2/1/4. The experiments were performed in the temperature range from 350 to 500 °C under differential reaction conditions. The feed and the product components were analyzed by an on-line gas chromatograph.

Due to the high loading of the catalysts excess vanadium pentoxide not in contact with the support is present and thus it was not possible to calculate the loading of the surface. Hence,
the apparent propane activation energy $E_{a, app}$ was determined from the temperature dependent propane conversion $X$ using the function:

$$X = X_0 \cdot \exp\left(-\frac{E_{a, app}}{RT}\right)$$ 3-4

**Amorphous Monolayer Catalysts**

Catalytic testing was done in a stainless steel fixed bed reactor with a diameter of 8 mm. The inside of the tube is catalytic inactive due to a SilcoTek™ silicon coating. The kinetic experiments were done under differential conditions using a standard stoichiometric feed composition of 6 kPa oxygen and 12 kPa ethanol with a total flow rate of 220 Nml/min. The temperature was varied in a range of 140 to 200 °C. The products were analyzed by a Shimadzu GC-2014 equipped with a methanizer, TCD, FID, and packed HayeSep Q and Molsieve 13X columns.

The apparent propane activation energy $E_{a, app}$ was determined from the temperature dependent ODP rate $r$ at differential reaction conditions (conversion $X < 10\%$) using the function:

$$r = \frac{\dot{n} \cdot X \cdot M}{m \cdot w}$$ 3-5

$\dot{n}$ is the flux of propane, $X$ the conversion, $M$ the molar mass of vanadium, $m$ the mass of the catalyst and $w$ is the mass fraction of vanadium in the catalyst.
4. Results and Discussion

First the transport properties of vanadium pentoxide based catalysts are investigated and discussed in Chapter 4.1. Then, in Chapter 4.2 micro-structural influences on the conductivity are shown and finally in Chapter 4.3 the impact of transport properties on the catalytic reaction is discussed.

4.1. Transport Properties

4.1.1. The Method – Pure Vanadium Pentoxide

In this Chapter the transport properties of pure vanadium pentoxide are characterized and a method is developed that allows the experimental determination of the oxygen defect formation enthalpy.

4.1.1.1. Impedance Spectroscopic Investigations

The samples for conductivity measurements consist of pressed powder pellets. These exhibit a strong orientation along the c-axis due to the anisotropic lattice of vanadium pentoxide. A less pronounced orientation is present in the direction of the a-axis. These results - determined by XRD – are shown in Figure 4-1.

![Figure 4-1: Experimental pole figure of compressed V2O5 pellet, (a) (001)-reflex, (b) (200)-reflex](image)

\[
\text{max.} = 4.00 \quad \text{max} = 3.40
\]
As the electrical properties are anisotropic [36,37,38,39,66], the measurements are governed by the properties parallel to the c-axis.

A typical plot of the impedance spectroscopic measurements is shown in Figure 4-2. This plot can be approximated by a single semi circle, and hence the electrical behavior of the investigated sample is described by a parallel RC-circuit.

![Nyquist plot of V2O5 at room temperature.](image)

**Figure 4-2:** Nyquist plot of V2O5 at room temperature.

**Charge carriers – polarization experiments and conduction path**

For the determination of the contributing charge carriers, polarization experiments in the temperature range of 300 to 500 °C were carried out in synthetic air. As no polarization was detected, the charge transfer was concluded to be of electronic nature. In order to distinguish between bulk, grain boundary and electrode effects, the sample thickness and grain size was varied. Because no change of the capacitive element with sample thickness was observed and electrode effects were excluded the variation of grain size (see Figure 4-3) due to sintering had no effect on the capacitive element in the RC-circuit. Therefore, grain boundary conduction was also excluded. Hence the derived values can be attributed to bulk properties. Further indication results from the value of the capacitive element with C ≈ 250 pF which is in the order of magnitude of a bulk mechanism [67].
Figure 4-3: SEM micrograph of compressed V$_2$O$_5$. 5k magnification. (a) original material and (b) annealed in air for 7 days 610 °C. The grain size is 0.13 and 8.8 µm, respectively.
Conductivity and Redox State

In this chapter a connection between conductivity and the redox state of vanadium pentoxide is shown with special focus on formation of oxygen vacancies.

![Arrhenius plot of V₂O₅ of different samples. Measurements were performed under synthetic air. (a) Untreated sample. (b) Annealed in air at 610 °C and quenched to room temperature.](image)

In Figure 4-4 Arrhenius plots of conductivity $\sigma$ vs. temperature $T$ are shown. The heating direction of the temperature profile is given by an arrow. During heating of the untreated sample, in Figure 4-4 curve (a), two linear domains can be observed (no. 1 and no. 3). One at low temperature ending above 100 °C and one at higher temperature starting at about 380 °C. During cooling a different behaviour is observed (no. 4). At 209 °C a drop in conductivity is present (no. 2) which is more distinct, when a thermally reduced sample is used (curve (b)).

Figure 4-5 shows 3 Arrhenius plots of vanadium pentoxide samples heated at different rates. Heating at 3 Kmin$^{-1}$ results into a non-linear conductivity increase above 380 °C. And a heating rate of 0.5 or 0.2 Kmin$^{-1}$ gives a linear conductivity dependency.
Results and Discussion - Transport Properties

Figure 4-5: Arrhenius plot of conductivity for different heating rates. At 3 K/min a non-linear temperature dependency is observed. At 0.5 and 0.2 K/min a linear change with temperature is observed above 380 °C.

Figure 4-6 displays 4 cycles of the same specimen at 3 K/min are depicted. In the first cycle using a pristine sample, a large hysteresis is observed. In the subsequent cycle (2) the conductivity on heating and cooling follows the cooling curve of cycle 1. After the 2nd cycle the sample was annealed for 7 days in air at 200 °C. A 3rd cycle was run and the hysteresis behaviour reappears. The 4th cycle, directly after run 3, shows again like cycle 2 heating and cooling on the same curve.
Figure 4-6: 4 cycles of the same vanadium pentoxide sample in synthetic air. A fast heating rate of 3 Kmin⁻¹ was chosen. Therefore the conductivity increase above 380 °C is non-linear. 1st cycle: pristine sample shows hysteresis. 2nd cycle: heating and cooling follow the same line. 3rd cycle: after annealing the sample at 200 °C in air the hysteresis behavior reappears. 4th cycle: again heating and cooling is equal to the cooling conductivity of the 3rd cycle.

The variation of heating rate (Figure 4-5) shows that a heating rate of 0.5 Kmin⁻¹ is sufficient to attain equilibrium. The results of the cycling experiment in Figure 4-6 display the reversibility of the process but shows that the time on cooling is not sufficient. Prolonged heating at 200 °C is necessary. The features in the Arrhenius plots can be correlated to redox processes. When reaching the Tammann-temperature of 209 °C [68] (no. 2), surface species are activated and reduced sites are reoxidized. Therefore donor centers are eliminated and the conductivity drops to lower values with rising temperature. This effect is more distinct in the thermally reduced sample in Figure 4-4 (b) as it exhibits more point defects. The freezing of defects up to a certain temperature is known and is responsible for the semi-conductive properties at lower temperatures for several oxides [69] (no. 1). Then, starting at 380 °C (no. 3) the conductivity exhibits an activation energy of 0.66±0.04 eV which is in good agreement with the value of 0.63 eV found by Allersma et al. for liquid vanadium pentoxide in air [43], where vanadyl oxygen is released with formation of an oxygen vacancy \( V'_O \) left with two electrons. Again, this is supported by the Tammann rule, that predicts at \( 2/3T_m \) (369 °C) an
avalanche of point defects leading to a breakdown of the structure, as discussed by Merkle [70]. The defect reaction for oxygen vacancy formation and electron generation is:

\[
\text{O}_2^\text{reduction} \rightarrow \text{U}_0^{\text{reduction}} + 2\text{e}^- + 1/2 \text{O}_2
\]  

These electrons are then localized at two adjacent V\textsuperscript{5+} centers, creating two V\textsuperscript{4+} centers [71,72]. The V\textsuperscript{4+}-ions act as donor centers where the electrons can be thermally activated. The electrical conductivity of V\textsubscript{2}O\textsubscript{5} is assumed to be due to hopping of localized electrons from V\textsuperscript{4+} to V\textsuperscript{5+} [37,40,43]:

\[
\text{V}^{4+} - \text{O} - \text{V}^{5+} \xrightarrow{\Delta E} \text{V}^{5+} - \text{O} - \text{V}^{4+}
\]  

With the conductivity for V\textsubscript{2}O\textsubscript{5} as an n-type semiconductor given by

\[
\sigma = C \cdot [V^4] \exp(-\Delta E/kT)
\]  

the conductivity is directly related to the amount of reduction (see equation 4-1). [V\textsuperscript{4}] is the concentration of V\textsuperscript{4+}, \Delta E the activation energy, k the Boltzmann factor and T the temperature. During cooling a different activation energy is found (no. 4) in the same temperature region (500 – 380 °C) with a value of 0.23±0.01 eV. As it is very similar to the values found for the conduction in poly- and single-crystals (0.23 eV, 0.19 – 0.21 eV) [38,43] it is concluded that during cooling no further reduction or reoxidation occurs. This is also in agreement with calculations done on the stability of the reduced sites in [73].

For comparison, experiments under reducing conditions were performed: Conductivity experiments under vacuum (2*10\textsuperscript{-4} bar) led to the formation of lower oxides (V\textsubscript{6}O\textsubscript{13} and VO\textsubscript{2}).
**Results and Discussion**

**Transport Properties**

Starting at about 380 °C ((no. 3) in Figure 4-7, graph (b)) a strong reduction with phase transformation takes place, so that no activation energy can be determined. As many charge carriers by formation of oxygen vacancies are generated, the conductivity raises up to 2 orders of magnitude. During cooling a less pronounced temperature dependency of the conductivity is observed. At about 67 °C (no. 5) the characteristic metal to semiconductor transition of VO$_2$ can be identified [74]. The reduction of V$_2$O$_5$ proceeds via V$_2$O$_5$ $\rightarrow$ V$_4$O$_9$ $\rightarrow$ V$_6$O$_{13}$ $\rightarrow$ VO$_2$ $\rightarrow$ V$_2$O$_3$ [72,45] and because XRD phase analysis revealed the presence of small amounts of V$_2$O$_5$ and V$_6$O$_{13}$ the reduction was not complete (Figure 4-8).

**Figure 4-7:** Arrhenius plot of vanadium pentoxide in synthetic air (a) and vacuum (b).
4.1.1.2. Evolution of Defects (UV-vis and RBS)

UV-vis Spectroscopic Experiments

In Figure 4-9 UV-Vis spectra of untreated and annealed (T = 500 and 610 °C) samples are displayed. The band gaps are 2.27 eV and 2.23 eV, respectively, which is in good agreement with literature values in [43,75,76,77,78]. In Figure 4-10 the pretreatment temperature dependent change of the band gap with respect to untreated vanadium pentoxide is displayed. With rising temperature the energy shifts to higher values with a maximum of 2.27 eV at 200 °C. Above 400 °C the gap shifts to lower energies.
Results and Discussion - Transport Properties

Figure 4-9: UV-Vis spectroscopic experiments on thermally treated vanadium pentoxide in air. Analysis of band gap according to Tauc’s law.

The shift of the band gap is an evidence for a redox process as donor states are generated or eliminated in the forbidden zone by the formation or filling of oxygen vacancies as seen in reaction 4-1 [45,78,79]. Therefore in Figure 4-10 oxidation below 400 °C is observed and reduction above that temperature. The temperature dependency of the redox process correlates with the conductivity experiments.

Figure 4-10: UV-Vis spectroscopic experiments on thermally treated vanadium pentoxide in air. Difference of band gap in respect to pristine sample is shown.
Rutherford Backscattering Experiments

The conductivity experiments indicate close to 200 °C fully oxidized vanadium pentoxide (V\(^{5+}\), x = 5) and for temperature above 400 °C an oxidation state of V\(^{4+}\) (x = 4). In order to confirm those hypotheses RBS was used to determine the oxygen content x.

Figure 4-11 depicts the RBS energy spectra and the open squares correspond to the pristine vanadium pentoxide, the full squares to an annealed sample (200 °C) and the stars correspond to 2 different samples heat treated for 1 week at 500 °C in air. The fit parameters for the different spectra are shown in Table 4-1.

Table 4-1: Parameter for the fitted RBS-spectra. \(\sigma_{\text{rough}}\) is the surface roughness and x the oxygen content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\sigma_{\text{rough}}) [(\mu\text{m})]</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed at 200 °C</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>Annealed at 500 °C</td>
<td>0.3</td>
<td>4.2 ± 0.2</td>
</tr>
</tbody>
</table>

The samples annealed at 200 °C and the pristine sample are fully oxidized. These were calculated using an average grain diameter of \(\sigma_{\text{rough}} = 0.3 \mu\text{m}\) which is confirmed by SEM micrographs which are shown in Figure 4-12.
Annealing at 500 °C results into a lowered oxygen content $x < 5$ and the oxygen concentration can be calculated using equation 3-3. Analysis of the intensities at 280 keV and 240 keV gives $x \approx 4.1$. From the simulation of the whole energy spectrum as described in [65], follows $x = 4.2 \pm 0.2$. The value $x = 4.2$ is between $x = 4.33$ (V$_6$O$_{13}$) and $x = 4$ (VO$_2$). Hence, for temperatures $T > 400^\circ$C a reduction is observed from V$_2$O$_5$ to VO$_2$, with the reduction to VO$_2$ being not complete.

*Figure 4-12: SEM images of V$_2$O$_5$ (a) treated at 200 °C and (b) treated at 500 °C for 7 days in air.*

4.1.1.3. Defect Equilibrium and Defect Formation Enthalpy

We have studied the defect equilibrium with oxygen partial pressure via conductivity measurements. As it was determined by [71,72], the electrons after formation of an oxygen vacancy $O^*_{\text{o}}$ are localized at two adjacent $V^{3+}(V^{4+})$ centers forming two $V^{4+}(V^{4+})$:

$$2V^x_v + O^*_o \xrightarrow{\text{reduction}} 2V^*_v + O^*_{\text{o}} + 1/2O_2$$  \hspace{1cm} 4-4

This is in agreement with DFT calculations done from [80], where the localization of electrons leads to the formation of a new covalent bond between two a-b layers accompanied by a relaxation of the lattice in c-direction [13]:
Results and Discussion - Transport Properties

A mass action law for this case was given by [43] resulting into an oxygen partial pressure dependence of the conductivity of -1/6. The mass balance for the reduction reaction (4-4) is [43]:

\[
K = \left[ \frac{V}{V_{0}} \right]^{3} \cdot U_{0}^{\alpha} \cdot P_{O_{2}}^{\beta}
\]

Using van’t Hoff’s law (as discussed on page 16) it is possible to derive following connection of the measured apparent activation energy \( \Delta E^{*} \), the defect formation enthalpy \( \Delta H_{0}^{f} \) and the migration enthalpy \( \Delta E_{m}^{m} \):

\[
\Delta E^{*} = \Delta H_{0}^{f} / 3 + \Delta E_{m}^{m}
\]

The value of \( \Delta H_{0}^{f} \) can be derived from the Arrhenius-plot if the migration enthalpy is known.

The conductivity of a V₂O₅ sample was measured in an oxygen partial pressure range of \( p(O_{2}) = 1.00 - 0.22 \) bar at 508 °C starting with high oxygen pressure and lowering it subsequently. A re-equilibration after each pressure step was achieved in 1 to 2 days. Figure 4-14 displays the data of the conductivity measurements exhibiting a slope of -0.170 ± 0.003.
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Figure 4-14: Oxygen partial pressure dependency of V$_2$O$_5$ at 510 °C. The slope of -1/6 supports defect equilibrium describe in equation 4-4.

Therefore the mechanism in equation 4-4 is valid for our samples. Further evidence for this model gave x-ray diffraction experiments at 500 °C. Lattice parameters were determined for different oxygen partial pressures and are summarized in Table 4-2.

Table 4-2: Lattice parameters determined by high temperature XRD of V$_2$O$_{5-x}$ at 500 °C in oxygen and synthetic air.

<table>
<thead>
<tr>
<th>p(O$_2$) [bar]</th>
<th>lattice parameter [Å]</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>1.00</td>
<td>11.5439 ± 0.0003</td>
<td>3.5620 ± 0.0001</td>
</tr>
<tr>
<td>0.21</td>
<td>11.5447 ± 0.0004</td>
<td>3.5624 ± 0.0001</td>
</tr>
<tr>
<td>extension</td>
<td>7.2E-05</td>
<td>1.2E-04</td>
</tr>
</tbody>
</table>

When lowering the oxygen partial pressure from 1.00 to 0.21 bar the lattice contracts along the c-axis and extends in a- and b-direction. This is in agreement with lattice relaxation on reduction of the vandyl oxygen site as derived from DFT calculations done by Ganduglia-Pirovano and Sauer [80].
As the defect equilibrium is known, the enthalpy of formation for an oxygen vacancy can be calculated using equation 4-6. $\Delta E^*$ was derived from an Arrhenius-plot, like depicted in Figure 4-15, using the linear slope starting at about 400 °C. For this purpose the average of 6 measurements was taken giving a value of $\Delta E^* = 0.66 \pm 0.04$ eV which comprises activation of electrons and formation of oxygen vacancies. The mobility term $\Delta E_m$ can be determined from the slope during cooling, resulting in a value of $\Delta E_m = 0.23 \pm 0.01$ eV. This can be attributed to the ionization of localized electrons, as the re-equilibration reaction during cooling proceeds very slowly and can be neglected. Using relation 4-6 a value of $\Delta H_f^0 = 1.3 \pm 0.1$ eV was calculated, which is in good agreement with results from experiments on molten $V_2O_5$ (1.3 eV) [43] and quantum-chemical calculations 1.17 eV [13].

### 4.1.2. Transport Properties of Supported Catalysts at High Loading

Pure $V_2O_5$ is used as a catalyst for several reactions [2]. But often supporting metal oxides are applied in order to improve the properties of the catalyst. These enhance the stability of the oxide by inhibiting sintering of the VO$_x$ particles [81], increase the performance, and may further more alter the metal oxide bond strength [82,83] (change of defect formation...
enthalpy at interface BaO/MgO and V$_2$O$_5$/TiO$_2$) and thus the reactivity of the catalyst. It is the goal of this chapter to investigate the defect formation in supported VO$_x$-catalysts of high loading. These are easier to investigate due to higher conductivity of V$_2$O$_5$ but not applied as catalyst, because they are unselective due to large amounts of bulk vanadium pentoxide not in contact to the support. The interpretation of the results is based on the assumption that these catalysts exhibit the same behaviour as pure V$_2$O$_5$. On the next pages the Arrhenius plots for the conductivity experiments of the different catalysts are depicted together with results from catalytic tests. The propane activation energies $E_a$ are calculated using an Arrhenius approach (equation (3-4)) for the temperature dependent propane conversion $X$(propane). Furthermore the XRD patterns of aged catalysts (500 °C for 5 days in air) are given for phase analysis. In Table 4-3 the results of the conductivity experiments and catalytic tests are summarized on page 50.
4.1.2.1. Hysteresis Characteristics

In this chapter the hysteresis characteristics are shown and the defect formation enthalpies are calculated. The results are summarized in Table 4-3 on page 50.

α-Alumina Supported Vanadium Oxide Catalyst

Figure 4-16 shows the conductivity results for the VO<sub>x</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst.

In the Arrhenius plot a large hysteresis of the conductivity on heating and cooling is visible. The thermal activated region starts at 400 °C and prevails up to 500 °C. On heating an apparent activation energy of $\Delta E^* = 1.4 \pm 0.1$ eV is measured. On cooling the migration energy is $\Delta E_m = 0.5 \pm 0.1$ eV. Using equation (4-6) a defect formation enthalpy of $\Delta H_f = 2.8 \pm 0.1$ eV is calculated. The x-ray diffractogram in Figure 4-17 shows the phases α-Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> after prolonged heat treatment at 500 °C in air.
Results and Discussion - Transport Properties

Magnesia Supported Vanadium Oxide Catalyst

In Figure 4-18 the results for the VOₓ/MgO catalyst are depicted.

Figure 4-17: VOₓ/α-Al₂O₃. XRD phase analysis (aged sample, 5 days at 500 °C in air). No phase transition is visible.

Figure 4-18: VOₓ/MgO. Arrhenius plot of the conductivity in oxygen (0.5 K/min) with the corresponding propane conversion. On heating above 450 °C a deviation from the linear behaviour is visible. The arrow shows the direction of heating.
Results and Discussion - Transport Properties

The conductivity shows stronger changes on heating than the VO\textsubscript{x}/\alpha-Al\textsubscript{2}O\textsubscript{3} catalyst. First the conductivity reaches a local maximum at about 325 °C and then drops into a minimum at 350 °C. With increasing temperature the conductivity rises linearly from 375 °C to 430 °C giving an apparent activation energy $\Delta E^* = 0.75 \pm 0.05$ eV. The conductivity reaches a global maximum at 475 °C and declines until 500 °C. On cooling no further deviation from linearity is observed down to 300 °C and a migration energy $\Delta E_m = 0.21 \pm 0.01$ eV results from linear regression. A defect formation enthalpy of $\Delta H_f = 1.62 \pm 0.09$ eV was calculated using these values. XRD phase analysis (Figure 4-19) of the aged sample gave evidence for MgO, V\textsubscript{2}O\textsubscript{5} and larger amounts of mixed compounds (MgV\textsubscript{2}O\textsubscript{6}, Mg\textsubscript{2}V\textsubscript{2}O\textsubscript{7} and Mg\textsubscript{3}(VO\textsubscript{4})\textsubscript{2}).

![XRD phase analysis](image.png)

**Figure 4-19**: VO\textsubscript{x}/MgO. XRD phase analysis (aged sample, 5 days at 500 °C in air). A transition to MgO spinel phases is observed that might be responsible for the non-linearity above 450 °C in the conductivity plot.

Silica Supported Vanadium Oxide Catalyst

The data for the VO\textsubscript{x}/SiO\textsubscript{2} catalyst is displayed in Figure 4-20. The conductivity shows a simple temperature dependency with reaching a linear region at 370 °C with an apparent activation energy of $\Delta E^* = 0.57 \pm 0.01$ eV. On cooling from 500 to 300 °C a migration energy of $\Delta E_m = 0.20 \pm 0.01$ eV is obtained. This results into a defect formation enthalpy of $\Delta H_f = 1.11 \pm 0.08$ eV.
Results and Discussion - Transport Properties

Figure 4-20: VOₓ/SiO₂. (a) Arrhenius plot of the conductivity in oxygen with the corresponding propane conversion. The arrow shows the direction of heating.

XRD phase analysis of the aged sample (Figure 4-21) shows the presence of V₂O₅ and SiO₂.

Figure 4-21: VOₓ/SiO₂. XRD phase analysis (aged sample, 5 days, 500 °C, air). No new phases evolve.

Titania Supported Vanadium Oxide Catalyst

Figure 4-22 depicts the conductivity results of the VOₓ/TiO₂ catalyst.
A thermally activated region is present at 350 to 450 °C with an apparent activation energy $\Delta E^* = 0.56 \pm 0.06$ eV. Above 450 °C a transition to a different activated region is visible that may exist above 500 °C. On cooling a linear slope is obtained in the same range as on heating (450 °C to 350 °C) resulting into a migration energy of $\Delta E_m = 0.25 \pm 0.02$ eV. The calculated defect formation enthalpy for this catalyst is $\Delta H_f = 0.55 \pm 0.06$ eV. V$_2$O$_5$ and the TiO$_2$ phases Anatase as well as Rutile are detected in the aged sample (Figure 4-23).
Results and Discussion - Transport Properties

Zirconia Supported Vanadium Oxide Catalyst

Figure 4-23 shows the conductivity hysteresis of the VO\textsubscript{x}/m-ZrO\textsubscript{2} catalyst.

**Figure 4-23**: VO\textsubscript{x}/TiO\textsubscript{2} XRD phase analysis (aged sample, 5 days, 500 °C, air). A transition to the rutile TiO\textsubscript{2} can be seen and may cause the transition region in the conductivity plot.

Figure 4-24 shows the conductivity hysteresis of the VO\textsubscript{x}/m-ZrO\textsubscript{2} catalyst.

**Figure 4-24**: VO\textsubscript{x}/m-ZrO\textsubscript{2}. (a) Arrhenius plot of the conductivity in oxygen with the corresponding propane conversion. The arrow shows the direction of heating.
On heating, the onset of the linear region is 400 °C and remains for the whole temperature range. The apparent activation energy is $\Delta E^* = 0.63 \pm 0.02$ eV. On cooling the conductivity shows linear behaviour down to 400 °C with a migration energy of $\Delta E_m = 0.35 \pm 0.02$ eV and results into a defect formation enthalpy of $\Delta H_f = 0.85 \pm 0.01$ eV. Ageing of VO$_x$/m-ZrO$_2$ gave XRD pattern for monoclinic ZrO$_2$ and V$_2$O$_5$ (Figure 4-25).

![XRD pattern](image)

Figure 4-25: VO$_x$/m-ZrO$_2$. XRD phase analysis (aged sample, 5 days, 500 °C, air). No new phases develop.

### Table 4-3: Activation energies (apparent activation energy $\Delta E^*$, migration energy $\Delta E_m$), defect formation enthalpies ($\Delta H_f$) and propane activation energy $E_a$ for supported VO$_x$-catalysts with high loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$\Delta E^*$ (eV)</th>
<th>$\Delta E_m$ (eV)</th>
<th>$\Delta H_f$ (eV)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$</td>
<td>380-500</td>
<td>0.66 ± 0.04</td>
<td>0.23 ± 0.01</td>
<td>1.3 ± 0.1</td>
<td>0.73 ± 0.04</td>
</tr>
<tr>
<td>VO$_x$/TiO$_2$</td>
<td>350-450</td>
<td>0.56 ± 0.06</td>
<td>0.25 ± 0.02</td>
<td>0.55 ± 0.06</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>VO$_x$/m-ZrO$_2$</td>
<td>400-500</td>
<td>0.63 ± 0.02</td>
<td>0.35 ± 0.02</td>
<td>0.85 ± 0.10</td>
<td>0.67 ± 0.05</td>
</tr>
<tr>
<td>VO$_x$/SiO$_2$</td>
<td>370-500</td>
<td>0.57 ± 0.01</td>
<td>0.20 ± 0.01</td>
<td>1.11 ± 0.08</td>
<td>1.06 ± 0.06</td>
</tr>
<tr>
<td>VO$_x$/MgO</td>
<td>375-430</td>
<td>0.75 ± 0.05</td>
<td>0.21 ± 0.01</td>
<td>1.62 ± 0.09</td>
<td>0.90 ± 0.01</td>
</tr>
<tr>
<td>VO$_x$/α-Al$_2$O$_3$</td>
<td>400-500</td>
<td>1.4 ± 0.1</td>
<td>0.50 ± 0.1</td>
<td>2.8 ± 0.3</td>
<td>1.13 ± 0.09</td>
</tr>
</tbody>
</table>

### 4.1.2.2. Defect Formation

The onset temperature of oxygen point defect formation is quite similar for all the catalysts and is in the range of 350 to 400 °C. When V$_2$O$_5$ is supported on MgO and TiO$_2$ (Anatase) the
slope of conductivity changes nonlinearly on heating above 475 and 450 °C, respectively. The catalysts with α-Al₂O₃, SiO₂ and m-ZrO₂ exhibit linear temperature dependency in the full temperature range. XRD on aged samples shows for the supports MgO and TiO₂ (Anatase) a transition to mixed compounds while for α-Al₂O₃, SiO₂ and m-ZrO₂ no transition is observed. Magnesia forms together with V₂O₅ several spinel phases like shown in Figure 4-19 and in thermal investigations done in [84]. Said and El-Wahab [85] found a decrease of conductivity on spinel formation and a migration energy of 0.24 eV which both is in agreement with results of this work on VOₓ/MgO. In order to investigate the influence of the phase transition on the defect formation enthalpy, conductivity experiments were done below the transition temperature (300 to 425 °C) (see appendix: Figure 7-1). These experiments gave an oxygen defect formation enthalpy of ΔHᵉ = 1.7 ± 0.1 eV. This value is very close to the enthalpy determined with a temperature scan above the transition region (1.62 ± 0.09 eV) and it is concluded that the influence is negligible. It was shown in [65,86] that V₂O₅ facilitates the transition of Anatase to Rutile via incorporation of vanadium into the TiO₂ lattice. The transition temperature was found to be 525 °C and therefore above the temperature of 450 °C obtained from the Arrhenius plot in Figure 4-22. But it is possible, that minute amounts of Rutile are formed already at 450 °C and alter the electrical properties of the catalyst. These small amounts would not have been detected by XRD or DTA applied in [86]. Further indication for this mechanism is the presence of Rutile after prolonged heating of the sample at 500 °C (Figure 4-23). Different defect formation enthalpies are found depending on the support giving following ranking: VOₓ/TiO₂ < VOₓ/m-ZrO₂ < VOₓ/SiO₂ < V₂O₅ < VOₓ/MgO < VOₓ/α-Al₂O₃. This is displayed in Figure 4-26 together with reference data.
Results and Discussion - Transport Properties

Figure 4-26: Comparison of defect formation enthalpies $\Delta H_f$ with literature data. Red [43], green [13], blue [16]. These are the results for the catalysts with high loading in oxygen with a heating rate of 0.5 K/min.

As discussed in the previous chapter (4.1.1.3), there are experimental [43] (1.3 eV) and calculated [13] (1.17 eV) results for pure V$_2$O$_5$ that are in good agreement with the experiments in this work (1.3 ± 0.1 eV). Furthermore, Todorova calculated for $\alpha$-Al$_2$O$_3$ supported VO$_x$ a defect formation enthalpy of 2.8 eV [16] which is also consistent with the result of 2.8 ± 0.3 eV. Calculations for VO$_x$ on SiO$_2$ yield a defect formation enthalpy of 2.9 eV [13] which is in contradiction with the value of 1.11 ± 0.08 eV derived from the conductivity experiments. Different aspects may influence the result of the experiments and calculations, like the presence of impurities at the grain boundaries, phase transitions, percolation aspects or the chosen conditions and models for the calculations. The impact of percolation properties of a 2-phase mixture M$_x$O$_y$/VO$_x$ will be discussed in Chapter 4.1.3 together with the influence of the interface support and active compound on the defect formation.
4.1.3. Concentration Dependent Conductivity of Supported Catalysts

In order to determine the kinetic path of the charge carriers and therefore the region that is characterized, the concentration dependent properties of VO$_x$/m-ZrO$_2$ and VO$_x$/SiO$_2$ catalysts are investigated. Furthermore, this gives the possibility to probe whether catalysts of low loading are suitable for this method.

In Figure 4-27 Arrhenius plots for VO$_x$/SiO$_2$ at different concentrations are depicted. On heating and cooling they show different apparent activation energies $\Delta E^*$ and migration energies $\Delta E_m$, respectively, like discussed in Chapter 4.1.1.1 and 4.1.2.

This behaviour is categorized into 3 regions:

Region (I): At high concentration activation energies close to pure vanadium pentoxide and the highest conductivity is found. But on heating above 480 °C a transition to higher activation energy is already observed.

Region (II): Here a smaller hysteresis is present and activation energies of approximately 1 eV are found.

Region (III): Without vanadium pentoxide no hysteresis appears and the activation energy is lower than in region (II). These features will be discussed in this chapter.
Results and Discussion - Transport Properties

Figure 4-28 and Figure 4-29 (page 55) show the total conductivity of VO$_x$/SiO$_2$ and VO$_x$/m-ZrO$_2$ as a function of V$_2$O$_5$ loading at 400, 450 and 500 °C. It is apparent that the conductivity behaviour for both catalysts can be divided into 3 regions:

Region (I): It shows a comparably high conductivity with $6.4 \times 10^{-4}$ Scm$^{-1}$ at 500 °C for pure vanadium pentoxide. With lower concentration a slight decrease of the conductivity is evident showing nearly a linear concentration dependency. A sudden drop at a mass fraction of 25 % (VO$_x$/SiO$_2$) and 20 % (VO$_x$/m-ZrO$_2$) is visible.

Region (II): In this region the VO$_x$/SiO$_2$ catalyst starts to plateau below $w = 20 \%$ at $1 \times 10^{-7}$ Scm$^{-1}$. VO$_x$/m-ZrO$_2$ shows similar behaviour and the conductivity appears to level out at $4.9 \times 10^{-7}$ Scm$^{-1}$ at 7.2 m% V$_2$O$_5$ but jumps with the mass fraction lowered to 3.6 % to $7.1 \times 10^{-7}$ Scm$^{-1}$.

Region (III): For both catalysts the conductivity drops without vanadium pentoxide to very low conductivity. For VO$_x$/SiO$_2$ the conductivity descends below $w = 7 \%$ down to $2.5 \times 10^{-8}$ Scm$^{-1}$. The zirconia supported catalysts shows a conductivity one order of magnitude higher: $2.9 \times 10^{-8}$ Scm$^{-1}$. 
Figure 4-28: Concentration dependent conductivity of VO$_x$/SiO$_2$ catalyst at different temperature in O$_2$.

Figure 4-29: Concentration dependent conductivity of VO$_x$/m-ZrO$_2$ catalyst at different temperature in O$_2$. 
The catalysts consist of a 2 phase mixture: $V_2O_5$ and the support $SiO_2$ or $m-ZrO_2$. Figure 4-30 shows the element distribution of vanadium (red) and silicon (yellow) at cross sections of $VO_x/SiO_2$ pellets used for conductivity experiments. This picture illustrates the percolation of $SiO_2$ and $V_2O_5$. At $w = 43\%$ a network of connected $V_2O_5$ areas is visible. With lower concentration these areas are getting smaller until at $w = 25\%$ most of the junctions vanish. Then at $w = 7\%$ the EDX mapping shows a homogeneous distribution of Si and V. These observations are consistent with the change of electrical properties in the same concentration range.

The conductivity of $VO_x/SiO_2$ and $VO_x/m-ZrO_2$ in Figure 4-28 and Figure 4-29 shows at high concentration in region (l) a conductivity close to that of pure $V_2O_5$. Furthermore a nearly linear concentration dependency is evident down to approximately $w = 30\%$. $V_2O_5$ is an n-type semiconductor and the supports are isolators with conductivities several orders of magnitude lower. Therefore at high concentration $V_2O_5$ forms a kinetic path for electrons. If its amount is reduced, the conducting cross section decreases. Due to the proportionality of the conductivity $\sigma$ to the cross section $A$

$$\sigma = I/(RA)$$

Figure 4-30: EDX mapping of $VO_x/SiO_2$ cross sections. The element distribution of Si and V is shown for catalysts with different loadings. 14 kV, 5000x magnification.

The conductivity of $VO_x/SiO_2$ and $VO_x/m-ZrO_2$ in Figure 4-28 and Figure 4-29 shows at high concentration in region (l) a conductivity close to that of pure $V_2O_5$. Furthermore a nearly linear concentration dependency is evident down to approximately $w = 30\%$. $V_2O_5$ is an n-type semiconductor and the supports are isolators with conductivities several orders of magnitude lower. Therefore at high concentration $V_2O_5$ forms a kinetic path for electrons. If its amount is reduced, the conducting cross section decreases. Due to the proportionality of the conductivity $\sigma$ to the cross section $A$

$$\sigma = I/(RA)$$

4-7
the conductivity is lowered. Therefore in region (I) the properties of the V$_2$O$_5$ matrix phase dominate. This is visualized in Figure 4-31 (a).

![Figure 4-31: Conductivity percolation model. The arrows indicate the kinetic path for the charge carriers. At high loading (a) a better conducting V$_2$O$_5$ matrix (orange) is present. At low loading (b) the percolation path through V$_2$O$_5$ vanishes and a new kinetic path along the interface M$_x$O$_y$/VO$_x$ is formed (dark grey).](image)

The descent to a plateau in region (II) and the drop in region (III) cannot be explained by a simple mixture of 2 phases. In that case in region (III) the properties of the support would dominate and no further change like observed in region (III) would occur. A percolation model comprising an interface is suitable for explaining the experimental results and is depicted in Figure 4-31 (b). The junctions in the V$_2$O$_5$ matrix vanish at about $w = 30\%$ (see EDX mapping in Figure 4-30) and the conductivity drops to region (II) reflecting now the properties of the interface. The second percolation threshold in region (III) shows the transition to the isolator properties of the pure support. The sharp increase in conductivity for VO$_x$/m-ZrO$_2$ at $w = 7.2\%$ near the transition to region (III) may be caused by doping effects and hence promote electronic or ionic conduction. The temperature dependency in region (I) is less pronounced than in region (II) or (III) indicating a change in activation energy and transport mechanism.

4.1.3.1. Transport mechanism

In Figure 4-32 the total conductivity for VO$_x$/SiO$_2$ and VO$_x$/m-ZrO$_2$ at 500 °C is shown.
Results and Discussion - Transport Properties

Figure 4-32: Conductivity percolation behaviour for VOx/SiO2 and VOx/m-ZrO2 at 500 °C in O2.

Already at high concentration (region I) the support alters the electrical properties and VOx/m-ZrO2 exhibits a slightly higher conductivity. Below the drop in region (II) and (III) this difference is substantial and rises up to 1 order of magnitude.

Figure 4-33: Migration energy for VOx/SiO2 and VOx/m-ZrO2 at 500 °C in O2.
Results and Discussion - Transport Properties

Figure 4-33 depicts the V$_2$O$_5$ concentration dependent migration energy $\Delta E_m$ for both systems. Like the conductivity these are divided into 3 regions that correspond to the conductivity plots in Figure 4-32.

Region (I): At high V$_2$O$_5$ mass fractions both catalytic systems exhibit a low migration energy $\Delta E_m \approx 0.3$ eV that is comparable to pure V$_2$O$_5$. But when lowering the concentration below $w = 40\%$ the migration energy increases for VOx/SiO$_2$ to 0.34 ($w = 34.8\%$) and 0.38 eV ($w = 25.2\%$) while it remains at 0.24 ($w = 27.0\%$) and 0.29 eV ($w = 20.7\%$) for the VO$_x$/m-ZrO$_2$ catalyst.

Region (II): The migration energy of VO$_x$/SiO$_2$ starts to rise rapidly below $w = 25\%$ and peaks at $w = 13.7\%$ at $\Delta E_m = 1.03$ eV. As shown in the conductivity plots, VO$_x$/m-ZrO$_2$ exhibits a threshold lower than VO$_x$/SiO$_2$. The same behaviour is observed for the migration energy and the threshold is located at $w = 14.1\%$ V$_2$O$_5$. At this mass fraction $\Delta E_m$ jumps from 0.29 to 1.08 eV and rises further to $\Delta E_m \approx 1.14$ eV. The migration energy remains constant down to a concentration of $w = 3.6\%$.

Region (III): In this region the activation energy descends to lower values and the silica support shows an energy of 0.83 eV while pure m-ZrO$_2$ exhibits a value of 0.72 eV.

The change of migration energy correlates with the 3 regions observed in the concentration dependent conductivity. Above the percolation threshold in region (I) the migration energy is close to the value for pure V$_2$O$_5$. This behaviour is expected for a better conducting V$_2$O$_5$ matrix (see Figure 4-31 (a)). In region (II) the migration energies rise to 1.03 eV (VO$_x$/SiO$_2$) and 1.14 eV (VO$_x$/m-ZrO$_2$) and hence indicate a change of the transport mechanism from electronic to ionic. Because these migration energies are different from the pure oxides in region (III) (0.83 eV for SiO$_2$ and 0.72 eV for m-ZrO$_2$) this finding supports the percolation model comprising a transport path along the interface depicted in Figure 4-31 (b). The most likely majority charge carriers at the interface are oxygen ions. The lower activation energies in region (III) might be an indicator for another change of majority charge carriers from anionic to cationic. The higher conductivity of VO$_x$/m-ZrO$_2$ (Figure 4-32) in region (I) at high concentration may originate from several effects. The percolation threshold for VO$_x$/m-ZrO$_2$ is located at lower concentration than for the VO$_x$/SiO$_2$ catalyst. Thus at equal concentration in region (I), VO$_x$/m-ZrO$_2$ should exhibit the higher conducting cross section $A$ of the V$_2$O$_5$ matrix (see equation 4-7) and therefore a higher conductivity. The higher activation energy
of VO\textsubscript{x}/SiO\textsubscript{2} below w = 40 % may also be a reason for the lower conductivity of VO\textsubscript{x}/SiO\textsubscript{2}. At the plateau in region (II) and in region (III) the difference of about 1 order of magnitude may be explained by different charge carrier concentrations or mobilities. But the same difference in conductivity is found for the m-ZrO\textsubscript{2} and SiO\textsubscript{2} in region (III) and therefore the discussed effect in region (II) may also arise due to the intrinsic properties of the supports.

Figure 4-34 to Figure 4-39 show the impedance spectra for VO\textsubscript{x}/SiO\textsubscript{2} and VO\textsubscript{x}/m-ZrO\textsubscript{2}, respectively. In (a) the spectra for the different regions and in (b) the corresponding equivalent circuits are depicted. For VO\textsubscript{x}/SiO\textsubscript{2} in region (I) (Figure 4-34) the spectra form perfect semicircles and are therefore modelled using RC-circuits.

![Nyquist plot of VO\textsubscript{x}/SiO\textsubscript{2} at 500 °C in O\textsubscript{2} in region (I) and (b) the corresponding equivalent circuit: 1: resistor, 2: constant phase element.](image)

In region (II) the behaviour changes and in Figure 4-35 for VO\textsubscript{x}/SiO\textsubscript{2} below w = 25 % long stretched semicircles appear. At very low frequency (down to 7 mHz) a small spike is visible. For Figure 4-34 and Figure 4-35 the high frequency arc is attributed to the bulk conductivity. The stretched arc and spike at low frequencies in Figure 4-35 is attributed to an electrode reaction, polarization at the platinum contacts and diffusion of charge carriers through the porous platinum layer [67]. Therefore the Randles-like circuit depicted in Figure 4-35 (b) is used.
Results and Discussion - Transport Properties

Figure 4-35: (a) Nyquist plot of VO$_x$/SiO$_2$ at 500 °C in O$_2$ in region (II). (b) Corresponding equivalent circuit: 1: Charge transfer resistance, 2: Warburg diffusion element, 3: constant phase element for electrode polarization, 4: bulk resistance, 5: bulk capacitance (constant phase element).

The electrode reaction is described using the charge transfer resistance (1) and Warburg diffusion element (2). The polarization of charge carriers is represented by a constant phase element (3). The bulk resistance (4) is placed in series to the electrode and in parallel the bulk polarization (5). Best fit results gave the model with the bulk polarization parallel to bulk resistance as well as parallel to the electrode elements. The electrode reaction in the impedance plots is present in the entire region (II). But in region (III) with pure SiO$_2$ the Nyquist plot takes again the form of a perfect semicircle.

Figure 4-36: (a) Nyquist plot of VO$_x$/SiO$_2$ at 500 °C in O$_2$ in region (III). (b) Corresponding equivalent circuit: 1: resistor, 2: constant phase element.

Similar behaviour is observed for VO$_x$/m-ZrO$_2$ shown in Figure 4-37 to Figure 4-39. Above the threshold in region (I) perfect semicircles are present. At lower concentration in region (II) a
low frequency electrode arc starts to appear. But here in contrast to VO$_x$/SiO$_2$ without the electrode spike. Therefore, for modelling the circuit visualized in Figure 4-38 (b) is used.

![Nyquist plot of ZrV$_x$ at 500 °C in O$_2$ in region (I). (b) Corresponding equivalent circuit: 1: resistor, 2: constant phase element.](image1)

**Figure 4-37:** (a) Nyquist plot of ZrV$_x$ at 500 °C in O$_2$ in region (I). (b) Corresponding equivalent circuit: 1: resistor, 2: constant phase element.

It consists of the bulk response (bulk resistance (1) and bulk capacitance (2)) and of the electrode reaction (charge transfer resistance) (3) and electrode polarization (constant phase element) (4). Then in region (III) the electrode arc disappears and is replaced by a depressed arc that is best modelled using 2 RC-circuits in series (Figure 4-39 (b)).

![Nyquist plot of ZrV$_x$ at 500 °C in O$_2$ in region (II). (b) Corresponding equivalent circuit: 1: Charge transfer resistance, 2: constant phase element for electrode polarization, 3: bulk resistance, 4: bulk capacitance (constant phase element).](image2)

**Figure 4-38:** (a) Nyquist plot of ZrV$_x$ at 500 °C in O$_2$ in region (II). (b) Corresponding equivalent circuit: 1: Charge transfer resistance, 2: constant phase element for electrode polarization, 3: bulk resistance, 4: bulk capacitance (constant phase element).
The appearance of the impedance plots changes in correlation with the 3 regions in the conductivity plots and indicates changes in the transport mechanism. The absence of an electrode polarization in region (I), for both the VO$_x$/SiO$_2$ and VO$_x$/m-ZrO$_2$ catalyst, gives evidence for electronic conduction at high concentration through a V$_2$O$_5$ matrix, because platinum contacts reversible for electrons are used. The polarization apparent in Figure 4-35 and Figure 4-38 for compositions in region (II) is an indicator for ionic charge carriers blocked at the metal electrodes. In region (III) the polarization vanishes and shows again the change of transport mechanism. Again, this behaviour is in agreement with the proposed interface percolation model in Figure 4-31. A similar conductivity percolation of a mixed conductor is discussed in [87].

4.1.3.2. Defect Formation at the Interface Region

The interface exhibits properties other than the pure phases. Therefore the defect formation enthalpies were determined according to the approach in Chapter 4.1.1.3. Figure 4-40 and Figure 4-41 depict defect formation enthalpies $\Delta H_f$ as a function of V$_2$O$_5$ concentration together with the total conductivity. Figure 4-40 shows the results for VO$_x$/SiO$_2$. Region (I) exhibits a high defect formation enthalpy close to the value $\Delta H_f = 1.3$ eV of pure V$_2$O$_5$. Then in region (II) at $w = 13.7$ % it drops to about 0.5 eV.
Results and Discussion - Transport Properties

A similar behaviour is observed for VOₓ/m-ZrO₂ in Figure 4-41. Region (I) shows a constant defect formation enthalpy of 1.3 eV and is lowered in region (II) at 14 and w = 11% to approximately 0.7 eV. Then at w = 3.6% a moderate decrease to 0.54 eV is observed.

The results are in agreement with observations in previous chapters. At high concentration the defect formation enthalpy is close to pure V₂O₅ because the matrix phase is characterized. In the interface region (II) the enthalpy changes and is lowered. It is expected,
that the defect formation enthalpy plateaus in region (II). The results indicate such behaviour, but more data points are necessary especially for VO$_x$/SiO$_2$.

4.1.3.3. Redox Behaviour and VO$_x$-Species

It was shown that the transport properties change at the interface of vanadium pentoxide and the support. In this chapter the redox properties of these catalysts are discussed.

![Graph showing TGA results](image)

**Figure 4-42:** TGA in diluted reaction gas (90% N$_2$/8% Propane/2% O$_2$) at 2 K/min for VO$_x$/SiO$_2$.

The mass loss shows a shift to higher reduction temperature (T1) at lower loading.

Figure 4-42 depicts the vanadium pentoxide concentration dependent change of mass loss in reaction gas. In Figure 4-43 the corresponding 1st derivatives are shown. In Figure 4-42 the onset of reduction is labelled as T1 and a shift to higher temperature is evident for lower loading.
The derivative depicted in Figure 4-44 shows a very complex temperature dependency. Because the ODP is a redox reaction, several processes are superimposed and as a result the interpretation is difficult. Furthermore, the catalyst in the thermo balance was exposed to the atmosphere in a crucible. Therefore no gas flow through the sample was achieved and equilibration was hindered. Hence, the temperature dependency of the mass loss may originate in diffusion limitation and adsorption / desorption of gaseous species.
Results and Discussion - Transport Properties

Figure 4-44: TGA of SiV56 in reaction gas. The first derivative (blue) indicates that several processes are overlapping. The second derivative (red) gives the inflection points of the mass loss with the strongest change which are used as reference points for the calculation of the stoichiometry.

Due to the complex reaction the onset point of reduction is deduced from the 2nd derivative of the mass loss as shown in Figure 4-44. The stoichiometry can be calculated using the mass loss. For this purpose two reference points are necessary and because all curves show the same shape (see Figure 4-42) the region T1 to T2 is chosen. It is assumed that the same processes are occurring in this temperature range. Furthermore, it is assumed that during reduction exclusively oxygen from vanadium pentoxide is taken and that it is present in the highest oxidation state 5+ at T1. Figure 4-45 depicts the change of T1 and stoichiometry as a function of vanadium pentoxide concentration.

At high concentration in region (I) the reduction already starts at 450 °C but the onset point shifts in region (II) to 480 °C. Vanadium pentoxide is present in the lowest stoichiometry at high loading. SiV56 has a composition of V$_2$O$_{3.25}$. When lowering the concentration the oxide releases smaller amounts of oxygen and the composition shifts in region (II) to V$_2$O$_{3.59}$ at $w = 13.74\%$ vanadium pentoxide but drops at $w = 7.2\%$ to V$_2$O$_{3.11}$. These results are summarized in Table 4-4.
Results and Discussion - Transport Properties

Figure 4-45: Change of the redox properties of VO\textsubscript{x}/SiO\textsubscript{2} with concentration of V\textsubscript{2}O\textsubscript{5} by TGA in reaction atmosphere.

Table 4-4: TGA results of VO\textsubscript{x}/SiO\textsubscript{2} catalysts. T1 is the reduction onset temperature and V\textsubscript{2}O\textsubscript{5} gives the stoichiometry of the VO\textsubscript{x} phase. T2 is the reference temperature for the calculation of the stoichiometry. \(\Delta m\) is the mass loss in the range T1 – T2.

<table>
<thead>
<tr>
<th>w(V\textsubscript{2}O\textsubscript{5}) (%)</th>
<th>T1 (°C)</th>
<th>T2 (°C)</th>
<th>(\Delta m) (%)</th>
<th>V\textsubscript{2}O\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.46</td>
<td>457</td>
<td>508</td>
<td>7.34151</td>
<td>3.25</td>
</tr>
<tr>
<td>43.07</td>
<td>452</td>
<td>510</td>
<td>5.68344</td>
<td>3.31</td>
</tr>
<tr>
<td>34.81</td>
<td>464</td>
<td>506</td>
<td>4.20714</td>
<td>3.37</td>
</tr>
<tr>
<td>25.16</td>
<td>478</td>
<td>512</td>
<td>2.80869</td>
<td>3.51</td>
</tr>
<tr>
<td>13.74</td>
<td>484</td>
<td>507</td>
<td>1.27486</td>
<td>3.59</td>
</tr>
<tr>
<td>7.20</td>
<td>480</td>
<td>504</td>
<td>0.82784</td>
<td>3.11</td>
</tr>
</tbody>
</table>

The change of the redox properties correlates with the transition from 3 dimensional crystalline V\textsubscript{2}O\textsubscript{5} species in region (I) to 2 dimensional polymeric species in region (II). TPR experiments show different reduction behaviour of bulk V\textsubscript{2}O\textsubscript{5} and polymeric VO\textsubscript{x} species. Hydrogen TPR experiments usually exhibit a reduction peak of bulk like structures at higher temperature than 2-dimensional structures [88]. However, the conditions of the experiments are different. The experiments in reaction gas involve reduction and reoxidation processes and therefore not only the reducibility influences the onset of mass loss. The change of
oxidation state in Figure 4-45 of the catalysts may be connected to its reoxidation capability. In Chapter 4.1.3.1 it was shown that a transition from electronic to ionic transport occurs from region (I) to (II). Therefore oxygen ions may readily migrate through the interface region and enhance the reoxidation kinetics. Hence, the final oxidation state in region (II) may be higher. The inverse trend observed for the lowest concentration may arise due to experimental error but needs further investigation. Other compounds like hydroxides or carbonates may also decompose and increase the observed weight loss. This would be a very small amount and thus negligible at high vanadium pentoxide concentrations - but significant at the lowest. Because all the mass loss is attributed to vanadia the calculation would yield a lower oxidation state.

Thus a change of redox and transport properties discussed in this chapter may arise due to the transition of bulk structures to 2-dimensional VO\textsubscript{x} interface structures.

4.1.4. Amorphous Monolayer Catalysts

The catalysts investigated in this chapter consist of high surface area supports that comprise highly dispersed VO\textsubscript{x} species. It was verified by UV-vis and other methods that these compounds exhibit only 2 dimensional VO\textsubscript{x} structures and no bulk V\textsubscript{2}O\textsubscript{5} [89]. Following samples were characterized: VO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3}, VO\textsubscript{x}/m-ZrO\textsubscript{2} and VO\textsubscript{x}/TiO\textsubscript{2}.

4.1.4.1. Modelling of the Impedance Spectra

The conductivity of the catalysts was investigated in oxygen and nitrogen. The Nyquist plots exhibit atmosphere dependent differences that are discussed in this chapter.

Zirconia Supported Vanadium Oxide Catalysts

Figure 4-46 depicts the Nyquist plots of the m-ZrO\textsubscript{2} supported catalyst. The spectra show in oxygen (a) and nitrogen (b) substantial differences.
Results and Discussion - Transport Properties

Figure 4-46: Nyquist plots of VO$_x$/m-ZrO$_2$ catalysts at 500 °C in (a) oxygen and (b) nitrogen.

In oxygen the spectrum consists of a high and low frequency arc and shows at very low frequency (down to 7 mHz) a 45° slope. The high frequency arc exhibits a capacity of $4.39 \times 10^{-10}$ F and is thus attributed to the bulk relaxation (see Appendix: Table 7-1 on page 110). The low frequency arc shows with characteristic grain boundary behaviour (capacity of $8.23 \times 10^{-8}$ F) and the spike at the lowest frequency exhibits a capacity of $4.44 \times 10^{-7}$ F and shows additionally with the CPE exponent $m$ equal to 0.49 Warburg diffusion characteristics. Therefore this is the electrode reaction [67]. In nitrogen the low frequency spike vanishes and the resistance is lowered. The high frequency relaxation is not completely resolved but is with $4.59 \times 10^{-10}$ F the bulk relaxation. The well developed low frequency arc exhibits a grain boundary capacity of $7.17 \times 10^{-9}$ F.

γ-Alumina Supported Vanadium Oxide Catalysts

Figure 4-47 displays the Nyquist plots for the γ-alumina supported catalyst. In oxygen two semi circles are evident and at very low frequency the onset of a small spike. The relaxation at about 22 Hz exhibits a bulk capacity of $2.45 \times 10^{-10} \pm 1.54 \times 10^{-11}$ F. At 1 Hz the grain boundaries yield a characteristic value of $5.53 \times 10^{-9} \pm 1.48 \times 10^{-10}$ F (Appendix: Table 7-2 on page 110). The spike at low frequency is too small to be fitted accurately but is most likely the electrode reaction. In nitrogen the two relaxations overlap but still contributions of the bulk and grain boundary process are evident.
Results and Discussion - Transport Properties

Titania Supported Vanadium Oxide Catalysts

Like the other catalysts the titania supported compounds exhibit well resolved arcs in oxygen. At high frequency the bulk, then at 4 Hz the grain boundary, and at low frequency the electrode reaction is observed. They all show the expected capacities (3.09*10^{-10} and 4.89*10^{-8} F) (Appendix: Table 7-3 on page 111). In nitrogen the bulk semi circle remains but no grain boundary relaxation is found.

Influence of Partial Pressure

The electrical properties and impedance spectra may change due to the interaction of oxygen with the electrodes and grain surfaces. Due to adsorption of oxygen at the electrode a space charge layer may evolve that can increase the blocking effect of the metal. Similar effects are created by the grain boundary relaxations. Oxygen adsorbs at the surface layer binding electrons from the conduction band and thus creating a depletion layer. This space
charge zone at the grain boundary leads to a capacitive behaviour in the impedance spectra and is an oxygen pressure dependent barrier for negative charge carriers [90] (Figure 4-49).

![Diagram showing charge distribution and energy levels](image)

**Figure 4-49:** Bulk electrons are drawn to the surface layer due to adsorption of oxygen. Electrons deplete at the boundary and a space charge region (grey) compensates the local deviation from charge neutrality. This layer blocks negative charge carriers (higher potential barrier at p(O2)₁) and causes a grain boundary relaxation in the impedance plot. At lower oxygen partial pressure less oxygen is adsorbed and thus the potential barrier is accordingly lowered (p(O2)₂). Hence the grain boundary relaxation may vanish. [90]

### 4.1.4.2. Hysteresis Characteristics

The temperature dependent bulk conductivity exhibits different hysteresis characteristics that may not yield the defect formation enthalpy. For the discussion of the extent of the hysteresis, the factor Δh* is used. This is also calculated according to equation (4-6) but does not represent the defect formation enthalpy.

**Zirconia Supported Vanadium Oxide Catalysts**

Conductivity experiments as performed in Chapter 4.1.1 to 4.1.3 were done using the highly dispersed VOₓ catalysts. Figure 4-50 and Figure 4-51 depict the temperature dependency of the conductivity for VOₓ/m-ZrO₂ in oxygen and nitrogen.
Results and Discussion - Transport Properties

**Figure 4-50:** Arrhenius plots of monolayer catalyst VOₓ/m-ZrO₂ in O₂ and N₂ at 0.1 K/min. ΔE₁ is the activation energy on heating, ΔE₂ is the activation energy on cooling.

VOₓ/m-ZrO₂ in oxygen exhibits virtually no hysteresis on heating and cooling. The activation energies ΔE₁ = 0.97 eV and ΔE₂ = 0.93 eV are nearly equal and thus yield a small value of Δh* = 0.12 ± 0.06 eV. On lowering the oxygen partial pressure to pure N₂ the conductivity rises on heating from 7.2*10⁻⁶ to 2.0*10⁻⁶ Scm⁻¹ at 500 °C. On cooling the hysteresis behaviour of the conductivity appears. The activation energy on heating changes to ΔE₁ = 1.35 eV and on cooling to ΔE₂ = 1.07 eV. Δh* rises to 0.84 ± 0.06 eV.

Table 4-5: Activation energies of VOₓ/m-ZrO₂ on heating ΔE₁ and cooling ΔE₂ for oxygen and nitrogen. As a descriptor for the intensity of the hysteresis, the difference (Δh*) according to the calculation of the defect formation enthalpy is given: (ΔE₁-ΔE₂)*3.

<table>
<thead>
<tr>
<th>Gas</th>
<th>ΔE₁</th>
<th>ΔE₂</th>
<th>Δh*</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOₓ/m-ZrO₂</td>
<td>0.97 ± 0.01</td>
<td>0.93 ± 0.01</td>
<td>0.12 ± 0.06</td>
</tr>
<tr>
<td>VOₓ/m-ZrO₂</td>
<td>1.35 ± 0.01</td>
<td>1.07 ± 0.01</td>
<td>0.84 ± 0.06</td>
</tr>
</tbody>
</table>

γ-Alumina Supported Vanadium Oxide Catalysts

Figure 4-51 depicts the Arrhenius-plot of VOₓ/γ-Al₂O₃ in oxygen and nitrogen. It shows similar behaviour, but already in oxygen a small hysteresis with Δh* = 0.51 ± 0.06 eV is visible. Activation energies on heating and cooling are ΔE₁ = 1.25 and ΔE₂ = 1.08 eV,
respectively. In nitrogen at 500 °C the conductivity drops from $3.1 \times 10^{-7}$ in oxygen to $1.2 \times 10^{-9}$ Scm$^{-1}$ and the hysteresis is stronger. $\Delta E_1$ on heating rises to 1.37 eV and $\Delta E_2$ on cooling is lowered to 0.98 eV. Hence, $\Delta h^*$ has more than doubled to 1.2 ± 0.1 eV. The activation energies are summarized in Table 4-6.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta h^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_x$/γ-Al$_2$O$_3$ O$_2$</td>
<td>1.25 ± 0.01</td>
<td>1.08 ± 0.01</td>
<td>0.51 ± 0.06</td>
</tr>
<tr>
<td>VO$_x$/γ-Al$_2$O$_3$ N$_2$</td>
<td>1.37 ± 0.02</td>
<td>0.98 ± 0.02</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

Titania Supported Vanadium Oxide Catalysts

Figure 4-52 shows the Arrhenius plots for VO$_x$/TiO$_2$ in oxygen and nitrogen at a heating rate of 0.1 K/min.
Figure 4-52: Arrhenius plot for V0x/TiO2 monolayer catalyst in O2 and N2 at 0.1 K/min. \( \Delta E_1 \) is the activation energy on heating, \( \Delta E_2 \) is the activation energy on cooling.

In oxygen a low temperature region (400 – 460 °C) on heating and cooling is visible. On heating an activation energy of \( \Delta E'_1 = 0.77 \) eV and on cooling \( \Delta E'_2 = 0.75 \) eV is found. Above 460 °C a transition to higher activation energy is found (0.95 eV) exhibiting no hysteresis behaviour. In nitrogen the low temperature region vanishes and the activation energy shifts to \( \Delta E_1 = 1.33 \) eV on heating and \( \Delta E_2 = 1.31 \) eV cooling. This yields virtually no hysteresis with \( \Delta h^* = 0.1 \pm 0.1 \) eV. The conductivity at 500 °C exhibits a low partial pressure dependency and rises from \( 5.7 \times 10^{-7} \) to \( 6.4 \times 10^{-7} \) Scm\(^{-1}\) in nitrogen atmosphere.

In order to investigate the influence of reaction kinetics experiments were done at a higher cooling rate. In Figure 4-53 the conductivity in nitrogen with a heating rate of 0.1 K/min and cooling rate of 1 K/min is displayed. For comparison it is shown together with the experiment in nitrogen described in Figure 4-52.
Results and Discussion - Transport Properties

Figure 4-53: Arrhenius plot for VOₓ/TiO₂ monolayer catalyst in N₂ at 0.1 K/min and N₂ at 0.1 K/min on heating and 1 K/min on cooling. Δ₄₁ is the activation energy on heating, Δ₄₂ is the activation energy on cooling.

With a faster cooling rate the activation energy on heating stays constant but on cooling is lowered and a hysteresis appears. In order to investigate this behaviour, the sample was cycled 3 times (Table 4-7). In the 1ˢᵗ cycle Δ₄₁ = 1.28 eV on heating and Δ₄₂ = 1.13 eV on cooling is found. This hysteresis is characterized by Δh* = 0.5 ± 0.1 eV. For the 2ⁿᵈ cycle Δ₄₁ = 1.34 eV and Δ₄₂ = 1.10 eV is determined and Δh* = 0.7 ± 0.1 eV. In the 3ʳᵈ cycle the hysteresis disappears and the activation energies are lowered to Δ₄₁ = 1.23 eV and Δ₄₂ = 1.21 eV and thus shows with Δh* = 0.1 ± 0.1 eV no hysteresis.
Table 4-7: Activation energies for VOₓ/TiO₂ on heating (Δ𝐸₁) and cooling (Δ𝐸₂) for oxygen and nitrogen and for different heating rates (in Kmin⁻¹) and cycles. As a descriptor for the intensity of the hysteresis, the difference (Δh*) according to the calculation of the defect formation enthalpy is given: (Δ𝐸₁−Δ𝐸₂)*3.

<table>
<thead>
<tr>
<th>No.</th>
<th>Gas</th>
<th>Heating rate</th>
<th>Cooling rate</th>
<th>Cycle</th>
<th>Δ𝐸₁</th>
<th>Δ𝐸₂</th>
<th>Δh*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O₂</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>0.95 ± 0.01</td>
<td>0.95 ± 0.01</td>
<td>0.00 ± 0.06</td>
</tr>
<tr>
<td>2</td>
<td>N₂</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>1.33 ± 0.01</td>
<td>1.31 ± 0.02</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>N₂</td>
<td>0.1</td>
<td>1.0</td>
<td>1</td>
<td>1.28 ± 0.02</td>
<td>1.13 ± 0.02</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>N₂</td>
<td>0.1</td>
<td>1.0</td>
<td>2</td>
<td>1.34 ± 0.02</td>
<td>1.10 ± 0.02</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>5</td>
<td>N₂</td>
<td>0.1</td>
<td>1.0</td>
<td>3</td>
<td>1.23 ± 0.02</td>
<td>1.21 ± 0.02</td>
<td>0.1 ± 0.1</td>
</tr>
</tbody>
</table>

4.1.4.3. Defect formation

All the amorphous monolayer catalysts exhibit hysteresis characteristics that deviate from the behaviour of the crystalline samples. They need lower oxygen pressure for the development of a hysteresis and in the case of VOₓ/TiO₂, additionally, a faster cooling rate is necessary.

In [60,61,62,63,64] redox properties of vanadia-based mixed oxides and supported catalysts were investigated using coulometric titration. It was found that the bulk oxides exhibit lower oxygen partial pressures for the onset of defect formation than pure vanadium pentoxide (Table 4-8):

Table 4-8: Oxygen partial pressure pO₂ (bar) for the onset of reduction in mixed vanadium bulk oxides determined by coulometric titration [61].

<table>
<thead>
<tr>
<th>Mixed Oxide</th>
<th>CeVO₄</th>
<th>Mg₃(VO₄)₂</th>
<th>AlVO₄</th>
<th>V₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>pO₂</td>
<td>10⁻²²</td>
<td>10⁻¹⁵</td>
<td>10⁻⁷</td>
<td>10⁻⁸</td>
</tr>
</tbody>
</table>

This is in agreement with the partial pressure dependent hysteresis characteristics and with the increase of the activation energy on heating in nitrogen.

γ-Alumina Supported Vanadium Oxide Catalysts

VOₓ/γ-Al₂O₃ (Figure 4-51) exhibits in O₂ a less pronounced hysteresis than in N₂. This indicates that vacancy formation on heating in oxygen is impeded. This in agreement with literature data for AlVO₄ bulk oxide (Table 4-8) that shows compared to V₂O₅ a lower oxygen
pressure for onset of reduction. Therefore in nitrogen defects readily are formed and no reoxidation on cooling is possible. The calculated defect formation enthalpy is $\Delta H_f = 1.2 \pm 0.1 \text{ eV}$.

**Zirconia Supported Vanadium Oxide Catalysts**

This characteristic is also observed for VO$_x$/m-ZrO$_2$ - but even more distinct. In oxygen no lattice oxygen is released and thus no hysteresis of the conductivity is observed. Hence, even lower oxygen pressure is necessary. Therefore the activation energy on heating and cooling of $\Delta E_m = \Delta E_1' = 0.97 \text{ eV}$ and $\Delta E_m = \Delta E_2' = 0.93 \text{ eV}$ is ascribed to the migration of ionic charge carriers. In nitrogen the activation energy on heating rises and the hysteresis appears. The migration energy in nitrogen is close to that in oxygen with $\Delta E_m = \Delta E_2 = 1.07 \text{ eV}$ and therefore evidences the assumption above. Using the apparent activation energy of $\Delta E^* = \Delta E_1 = 1.35 \text{ eV}$ a defect formation enthalpy of $\Delta H_f = 0.84 \pm 0.06 \text{ eV}$ is calculated. This is very close to the values determined in Chapter 4.1.2 on polycrystalline samples of high loading (0.9 $\pm$ 0.1 eV) and in Chapter 4.1.3.2 at the interface region (0.7 $\pm$ 0.1 eV).

**Titania Supported Vanadium Oxide Catalysts**

Similar results are found for VO$_x$/TiO$_2$. In oxygen above 460 °C a migration energy for ions of $\Delta E_m = \Delta E_1 = 0.95 \text{ eV}$ is found and no defects are formed. In nitrogen the activation energy rises to $\Delta E^* = \Delta E_1 = 1.33 \text{ eV}$ (see Table 4-7) on heating and indicates an additional contribution due to defect formation. These findings are again in agreement with the lowered oxygen partial pressure – compared to V$_2$O$_5$ – for the onset of defect formation as found in [61] (Table 4-8). But on cooling this activation energy prevails ($\Delta E^* = \Delta E_1 = 1.31 \text{ eV}$) and additionally no hysteresis is found. This might be due to reoxidation of vanadium pentoxide by the titania support as indicated by EPR experiments [91]. But the migration energy can be obtained by rapid cooling and thus freezing the defects as done in Figure 4-53. The hypothesis of reoxidation by titania is supported by the hysteresis characteristics in the cycling experiments. The second cycle still shows a hysteresis but in the third run the oxygen supply is depleted and no further defects are formed. Therefore the defect formation enthalpy is calculated using the average values of all apparent and migration energies which yields a value of $\Delta H_f = 0.44 \pm 0.1 \text{ eV}$.

The defect formation enthalpies are summarized in Table 4-9.
Table 4-9: Defect formation enthalpies and activation energies for the supported monolayer catalysts. All values are in eV.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ΔE*</th>
<th>ΔE_m</th>
<th>ΔH_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO_x/TiO_2</td>
<td>1.32 ± 0.02</td>
<td>1.17 ± 0.02</td>
<td>0.45 ± 0.1</td>
</tr>
<tr>
<td>VO_x/m-ZrO_2</td>
<td>1.35 ± 0.01</td>
<td>1.07 ± 0.01</td>
<td>0.84 ± 0.06</td>
</tr>
<tr>
<td>VO_x/γ-Al_2O_3</td>
<td>1.37 ± 0.02</td>
<td>0.98 ± 0.02</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

4.1.4.4. Transport Mechanism

As found in the percolation experiments the amorphous monolayer catalysts show ionic and electronic partial conductivities.

Electronic conduction

The observed changes on lowering the oxygen partial pressure indicate different partial electronic contributions. VO_x/m-ZrO_2 exhibits an increase in conductivity in N_2 atmosphere. This shows clearly n-type semiconducting properties at low pO_2. With a drop of conductivity in N_2 substantial p-type contribution is found for VO_x/γ-Al_2O_3 most likely dominating at high partial pressure. VO_x/TiO_2 exhibits only a small change but n-type conductivity. These findings are supported by the reoxidation experiments in the following chapter that clearly show the discussed electronic contributions.

Ionic conduction

Migration energies of about 1 eV are found as shown in the percolation experiments in previous chapters (Chapter 4.1.3, page 57) indicating similar ionic transport at the interface. Further evidence is given by the electrode reaction in the impedance plots. VO_x/TiO_2 shows in O_2 a low temperature region with a lowered migration energy ΔE_m = 0.77 eV. Thus a transition from cationic to anionic conduction may occur at 460 °C in O_2.

4.1.4.5. Reoxidation Behaviour

In order to investigate the reoxidation behaviour conductivity relaxation experiments were done. The oxygen partial pressure was rapidly changed from 10^{-4} to 1 bar and the impedance spectra were recorded. On raising the partial pressure a decrease or increase of the conductivity is observe. The data is fitted using the exponential function:

\[ \sigma = \sigma_0 + A \cdot \exp(\gamma t) \]
\[ \sigma \text{ is the conductivity at time } t, \sigma_0 \text{ is the conductivity at } t = 0 \text{ s, } A \text{ is the pre-exponential factor and } r \text{ the rate constant.} \]

**Zirconia Supported Vanadium Oxide Catalysts**

Figure 4-54 depicts the conductivity relaxation behaviour of VO\(_x\)/m-ZrO\(_2\):

![Figure 4-54](image)

**Figure 4-54: Conductivity relaxation experiments of VO\(_x\)/m-ZrO\(_2\) from 1.04*10\(^{-4}\) to 1 bar O\(_2\).** The data is fitted using an exponential function.

The calculated rate constant for VO\(_x\)/m-ZrO\(_2\) is \[ r = -3.20*10^{-4} \text{ s}^{-1}. \]

**γ-Alumina Supported Vanadium Oxide Catalysts**

The conductivity relaxation experiment (Figure 4-55) shows, that an increase of the oxygen partial pressure yields a higher conductivity. The fit gave a reoxidation rate of \[ -2.48*10^{-4} \text{ s}^{-1}. \]

![Figure 4-55](image)

**Figure 4-55: Conductivity relaxation experiments of VO\(_x\)/γ-Al\(_2\)O\(_3\) from 1.04*10\(^{-4}\) to 1 bar O\(_2\).** The data is fitted using an exponential function.
VO<sub>x</sub>/TiO<sub>2</sub>

On increasing the oxygen partial pressure the conductivity shows n-type behaviour and drops. The rate for equilibration is found to be \(-1.04 \times 10^{-3}\) s\(^{-1}\).

![Conductivity relaxation experiments of VO<sub>x</sub>/TiO<sub>2</sub> from 1.04 \times 10^{-4} to 1 bar O<sub>2</sub>. The data is fitted using an exponential function.](image)

The calculated rate constants for the reoxidation process are shown in Table 4-10.

<table>
<thead>
<tr>
<th>sample</th>
<th>r</th>
<th>error</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO&lt;sub&gt;x&lt;/sub&gt;/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-1.04 \times 10^{-3}</td>
<td>6.01 \times 10^{-5}</td>
<td>0.97751</td>
</tr>
<tr>
<td>VO&lt;sub&gt;x&lt;/sub&gt;/m-ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-3.20 \times 10^{-4}</td>
<td>1.30 \times 10^{-5}</td>
<td>0.98377</td>
</tr>
<tr>
<td>VO&lt;sub&gt;x&lt;/sub&gt;/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-2.48 \times 10^{-4}</td>
<td>4.39 \times 10^{-5}</td>
<td>0.81627</td>
</tr>
</tbody>
</table>

The conductivity relaxation experiments have shown different reoxidation kinetics for the catalysts. Following sequence is found:

\[
r(\text{VO}_x/\text{TiO}_2) > r(\text{VO}_x/\text{m-ZrO}_2) > r(\text{VO}_x/\gamma-\text{Al}_2\text{O}_3)
\]

Furthermore, VO<sub>x</sub>/TiO<sub>2</sub> exhibits a rate that is nearly 1 order of magnitude higher than for the other compounds (Table 4-10). Due to the closed porous structure of the pellets the rate will probably be controlled by two mechanisms: oxygen diffusion in the solid and oxygen surface exchange within the pore volume. However, this rate shows, that the samples with the
fastest rate constant exhibit also the highest rate constant for the ODH [89] stressing the importance of the exchange reaction and defect formation.
4.2. Origin of Enhanced Transport Properties

In the previous chapters I have shown, that the supporting metal oxides change the conduction mechanism of vanadium pentoxide from electronic to ionic and that the defect formation properties are influenced. The enhancement of ionic conductivity in a 2 phase mixture can have several origins. The most obvious reason is a reaction of both compounds creating a better ion conducting phase. But also in the absence of a global phase transition strong interactions can lead to modified transport properties [92]:

1. The phase transition may restrict to the interface,
2. or due to 2-phase-interactions, like interfacial stress, higher-dimensional defects are formed (surfaces, dislocations, grain-boundaries, etc.) and hence yield a kinetic path with enhanced mobility.
3. Space charges may arise below the interface
4. and homogeneous bulk doping may occur.

A mechanism comprising option 1. or 2. creates entirely new kinetic paths and therefore the migration enthalpies are independent of the bulk value. Consequently 3. and 4. show migration enthalpies close to the original data.

4.2.1. Micro-Structural Investigation

Figure 7-2 and Figure 7-3 in the Appendix show the XRD pattern for the percolation samples. Only vanadium pentoxide and the support oxides are present and thus proof that no global phase transition is observed.

Neutron diffraction on supported catalysts comprising a mole fraction of 10 % V₂O₅ gave evidence for highly non-linear thermal expansion behaviour (Figure 4-57).
Figure 4-57: Temperature dependency of b-axis of 10 mol% V$_2$O$_5$ on different supports in oxygen. The red line indicates the theoretical lattice parameter of the b-axis. The expansion behaviour can roughly be divided into 3 domains: I. increase of strain, II. relaxation and III. stagnation.

The lattice parameters of vanadium pentoxide and support show that the interface support/VO$_x$ results into lattice strains at 30 °C (Figure 4-58) and an increase with rising temperature is expected. On all supports, except for γ-Al$_2$O$_3$, vanadium pentoxide exhibits an expansion of the b-axis and compression in a-c direction. The active compound is strained in various degrees giving following ranking: TiO$_2$ > m-ZrO$_2$ > γ-Al$_2$O$_3$ > α-Al$_2$O$_3$. The supports show mainly compressed lattice parameters, except γ-Al$_2$O$_3$, which extends to small degrees in a-b direction. On heating the catalysts (Figure 4-57) the lattice shows anomalies in thermal expansion. The length of the vanadium pentoxide b-axis changes non-linearly and for all supports this behaviour can be divided into three regions. Region (I) extends up to 300 – 400 °C and is characterized by an increase or stagnation in b-axis lattice parameter. Region (II) shows at 300 – 400 °C a sudden drop followed by a nearly constant value in region (III).
On calcination at 500 °C an interface VOₓ/support is formed due to an esterification reaction of the basic hydroxyl groups at the metal oxide surface [2]. At this temperature the system is stress free. The presence of an interface is supported by high resolution TEM images that show wetting of vanadium pentoxide on silica (Figure 4-60). The compounds exhibit different thermal expansion coefficients compared to V₂O₅ [93] which additionally expands strongly anisotropic. Therefore on cooling, support and active compound shrink to different extents. But due to the interface a strain hindrance is present and thermal stress results (Figure 4-59).
Figure 4-59: Evolution of strain in supported catalysts. On calcinations an interface is formed (1). Vanadium pentoxide and support exhibit a thermal misfit and on cooling (2) the active compound is strained.

Very large stress may develop even exceeding the yield stress of vanadium pentoxide and thus creating a defect rich nano-crystalline mosaic structure (Figure 4-60). When heating the powder samples (Figure 4-57) stress affects the thermal expansion due the interface structure.
Results and Discussion - Origin of Enhanced Transport Properties

Figure 4-60: TEM micrograph of VOₓ/SiO₂. The image shows the contact of vanadium pentoxide grain to the support. On calcinations wetting of vanadia is observed (arrow shows good wetting angle). Very small grains are present with a thickness of ca. 20 nm that exhibit a mosaic structure with ~5 nm grains in various orientations. Grains of this size exhibit a very high surface to volume ratio and show thus the enhanced diffusion properties of the surface.

Thus depending on the support different behaviour is observed. Interestingly, the supports that give the best catalysts (TiO₂ and m-ZrO₂) exhibit the strongest expansion of the b-axis in region I. Region II coincides with the onset of defect formation determined by conductivity experiments and shows a relaxation of the b-axis what is in agreement with calculated lattice relaxations on reduction [94] and partial pressure dependent XRD experiments discussed on page 41. The experiments indicate the formation of new grain boundaries (mosaic structure [95]) on calcination and cooling due to a thermal misfit. Therefore the transport properties can change due to the new microstructure but mechanical stress can itself alter the defect formation properties as discussed for ceria in [96,97,98,99,100] as chemical strain effect.
4.2.2. The Chemical Strain Effect

In the literature a connection between externally applied stress and defect interaction is discussed [96,98,100]. It is called the “chemical strain effect” and describes the conversion of elastic energy into chemical energy of point defects. This relaxation process requires a finite time to equilibrate and thus if a solid is strained fast enough, only linear elastic behaviour is observed. Therefore, the strain causes an unrelaxed stress, \( \sigma_{el} \), with an elastic modulus \( E_{el} \):

\[
\sigma_{el} = E_{el} \cdot \varepsilon_{el}
\]

This results into an elastic energy, \( U_{el} \):

\[
U_{el} = E_{el} \cdot \frac{1}{2} (\varepsilon_{el})^2.
\]

The elastic energy is the driving force for a reversible defect interaction reaction that results into a change of volume, \( \beta \), and a change of defect concentration or other kind of defect interaction, \( \Delta C \). The strain caused by this interaction is the chemical strain \( \varepsilon_{ch} \):

\[
\varepsilon_{ch} = \beta \cdot \Delta C
\]

Hence, a material may be able to partially compensate the applied mechanical strain by a thermodynamic relaxation process. This gives a relaxed strain, \( \varepsilon_{rel} \):

\[
\varepsilon_{rel} = \varepsilon_{el} - \varepsilon_{ch}
\]

and with that a relaxed modulus \( E_{rel} \):

\[
\sigma_{rel} = E_{rel} \cdot \varepsilon_{rel}.
\]

Hence, the elastic energy in the relaxed state is given by:

\[
U_{el} = E_{rel} \cdot \frac{1}{2} (\varepsilon_{el} - \varepsilon_{ch})^2.
\]

Spontaneous release of mechanical stress yields therefore a sudden relaxation of elastic strain, but the chemical strain will decline over a period of time corresponding to the time constant of the defect reaction. The chemical strain is characterized by the stress-reduction factor, \( f \), which is the ratio between the relaxed and unrelaxed modulus [99]:

\[
f = \frac{E_{rel}}{E_{el}} < 1
\]

The chemical strain effect is often discussed for the defect complex association and dissociation reaction in gadolinium doped ceria [97,101,96,99,98]:

\[
Gd_{Ce}^* + V_o^{**} \leftrightarrow [Gd_{Ce}V_o]^{*}.
\]
The pairing of defects leads to a decreased volume with $\beta > 15 \text{ Å}$. Thus, extensive chemical relaxations are observed with stress-reduction factors of 0.07 [96]. Further interactions of point defects like:

- clustering
- and reduction/oxidation

are also discussed. The strain effect induced by reduction shows a volume change in the same order of magnitude as the defect association reaction. On reduction an oxygen vacancy and two electrons that are localized at two ceria sites are generated:

$$2\text{Ce}^{3+} + \text{O}^{2-} \xrightarrow{\text{reduction}} 2\text{Ce}^{4+} + \bigcup_{\text{O}}^* + 1/2 \text{O}_2.$$  

The oxygen vacancy exhibits a volume 16\% smaller than the oxygen ion [102] and the ionic radius of Ce$^{3+}$ compared to Ce$^{4+}$ is about 18\% larger. Therefore, the lattice parameter of micro-crystalline ceria increases linearly with increasing oxygen deficiency [101]. In [103] the influence on the volume change on reduction is investigated and it is found, that composition, crystal structure and doping change the resulting volume relaxation.

The chemical strain effect should also apply for other materials than doped ceria. These should exhibit large amounts of point defects ($> 10^{21} \text{ cm}^{-3}$), a substantial change in volume on interaction (a few Å³) and the rate constant for the reaction must be high enough to achieve equilibration within reasonable time [100,98]. Lubomirsky suggests in [99] that materials with a high tolerance for deviations from stoichiometry like $\text{V}_2\text{O}_{5-x}$ may exhibit chemical strain due to oxidation or reduction.

Temperature has an important influence on the chemical strain effect, because mobile point defects are necessary and activation of the interaction reaction e. g. association or dissociation. The strain effect will be most distinct at medium temperature, because at high temperature the defect equilibrium shifts to mostly dissociated species. At low temperature the point defects will be mostly present as associated complexes and the strain effect will be negligible. [100]

It was found that materials exhibiting a strong chemical strain effect also show anomalies in thermal expansion [100]. Experiments on Gd-doped ceria show 2 thermal expansion domains. The first domain with linear expansion at high oxygen partial pressure and the
second exhibiting abnormal expansion at low pressure. This is attributed to chemical strain due to formation of oxygen vacancies at low pressure. Doping with gadolinium lowers the transition temperature because the oxygen bond is weakened \([104]\). Further evidence is given by Kossoy et al. \([105]\). They found for Gd-doped ceria a hysteresis of lattice parameters on heating and cooling that is caused by large concentrations of interacting point defects. On heating the complexes dissociated and recombine at low temperature. But the association process exhibits very slow kinetics.

Vanadium pentoxide exhibits a high potential for the chemical strain effect. It is highly redox active, shows very large anisotropic expansion, and volume relaxation effects on defect formation.

\[
2V'_v + O'_o \leftrightarrow 2V'_v + \cup'_o + 1/2O_2
\]

Furthermore, the thermal expansion shows anomalies that indicate stress and strain influences (Figure 4-57) on the defect formation. Hence, interfacial stress might be the driving force for the enhanced oxygen release in the supported catalysts.
4.3. Impact on Catalysis

The conductivity experiments have shown a support effect on the defect formation enthalpy and moreover a change of electronic to ionic transport is observed. The impact of these effects on the catalytic reaction is discussed in this chapter.

The reaction in equation 4-20 shows the overall reaction for the ODH:

$$V^{4+}\cdot V^{4+}O + 1/2O_2(g) + C_3H_8(g) \rightarrow V^{4+}\cdot V^{4+}O + H_2O(g) + C_3H_6(g)$$  \hspace{1cm} 4-20

The educts are the reduced catalyst, oxygen and propane which react to water and propene. This is a multi step reaction and is discussed in the following. The catalyst for the ODH starts in the reduced state with 2 $V^{4+}$ and the gas phase species oxygen and propane. The first step is the oxidation of the $V^{4+}$-centres followed by adsorption of propane (equation 4-21).

$$V^{4+}\cdot V^{4+}O \xleftarrow{\frac{3}{2}O_2} V^{4+}\cdot V^{4+}O_2$$  \hspace{1cm} 4-21

This is followed by the rate limiting hydrogen abstraction and vanadia reduction via the transition states TS1 and TS2 (equation 4-22).

$$\xleftarrow{C_3H_8} V^{4+}\cdot V^{4+}(OH)_2 - C_3H_6$$  \hspace{1cm} 4-22

The energy for reaching TS1 is the propane activation energy $E_A$ but experimentally only the apparent activation energy $E_{A,app}$ is measured that includes the adsorption enthalpy $\Delta H_{ad}$. Finally, in the last two steps the products propene and water desorb (equation 4-23) and the next cycle starts again with the oxidation.

$$\xleftarrow{-H_2O,C_3H_6} V^{4+}\cdot V^{4+}O + H_2O + C_3H_6$$  \hspace{1cm} 4-23

The overall energy difference from beginning to the end of the cycle gives the reaction enthalpy $\Delta H_R$. The lower the reaction enthalpy the higher the reaction rate should be. Figure 4-61 depicts a reaction profile for the oxidative dehydrogenation from Beck et al. together with the elementary reaction steps [89].
A connection to the solid state properties is made by the first oxidation step in equation 4-21 which corresponds to the back reaction of the oxygen vacancy formation investigated in previous chapters:

$$2V^{4+}_o + O^{x}_o \xrightarrow{\text{reduction}} 2V^{5+} + O^{2-} + 1/2O_2.$$  

4.3.1. Supported Catalysts at High Loading – Correlation to Catalytic Reaction

In order to correlate the defect formation enthalpies with catalytic properties catalytic tests were done in separate experiments. The propane activation energy was derived from an Arrhenius plot of propane conversion \(X(\text{propane})\) and temperature. Figure 4-62 depicts this diagram together with the linear regression of the measured data.
Results and Discussion - Impact on Catalysis

Figure 4-62: Catalytic test results for the VO\textsubscript{x}/M\textsubscript{O\textsubscript{y}}. Calculation of the propane activation energy \( E_a \) from an Arrhenius plot of propane conversion X(propane) vs. temperature.

Different propane activation energies are found for each catalyst and are summarized in Table 4-3 on page 50. VO\textsubscript{x}/m-ZrO\textsubscript{2} shows with 0.67 ± 0.05 eV the lowest activation energy followed by VO\textsubscript{x}/TiO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5} with 0.70 ± 0.02 and 0.73 ± 0.04 eV, respectively. VO\textsubscript{x}/MgO exhibits a value of 0.90 ± 0.01 eV for propane activation. The highest activation energies are found for the catalyst VO\textsubscript{x}/SiO\textsubscript{2} and VO\textsubscript{x}/α-Al\textsubscript{2}O\textsubscript{3} (1.06 ± 0.06 and 1.13 ± 0.09 eV).

In order to investigate the impact of defect formation on the catalytic reaction the Brönsted-Evans-Polanyi (BEP) relation was used, that correlates the activation energy and the most important thermodynamic property in the system. For different surface reactions on transition metal surfaces linear relations between e.g. activation energies and reaction energies are found [106]. The correlation plot for the apparent propane activation energy and the defect formation enthalpy is shown in Figure 4-63. It is evident, despite of the strong scatter, that the catalysts exhibiting a small defect formation enthalpy also show low propane activation energies and thus show BEP behaviour.
Results and Discussion - Impact on Catalysis

Figure 4-63: Brönsted-Evans-Polanyi relation of the apparent propane activation energy $E_a$ and defect formation enthalpy $\Delta H_f$.

The catalysts applied for the experiments comprise large amounts of vanadium pentoxide. This is an advantage for the conductivity experiments due to the lower resistivity of the samples. But with loadings above 30 m% there will be a vanadium pentoxide phase not in interaction with the support. This may influence the results of the conductivity experiments by changing the kinetic path from interface to bulk $V_2O_5$. Nevertheless, a support effect on the defect formation is found. The catalytic tests have also shown a support effect despite of the high loading. This can be explained by diffusion of gas molecules to the interface region that exhibits properties different from the pure vanadium pentoxide phase. But vanadium pentoxide is also in contact with the gas phase and contributes therefore to the reaction. Thus the determined propane activation energies do not reflect purely the interface properties.

4.3.2. Amorphous Monolayer Catalysts – Correlation to ODH

Figure 4-64 depicts the catalytic test results for the monolayer catalysts that were used to calculate the apparent propane activation energy $E_a$. 
Results and Discussion - Impact on Catalysis

Figure 4-64: Catalytic test results for the monolayer catalysts. Calculation of the propane activation energy $E_a$ from an Arrhenius plot of propane conversion $X$(propane) vs. temperature.

Table 4-11 shows the porpane activation energies of the monolayer catalysts together with the defect formation enthalpies determined in Chapter 4.1.3.3.

Table 4-11: Ethanol activation energies $\Delta E_a$ of the amorphous monolayer catalysts [89] and the defect formation enthalpies $\Delta H_f$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta E_a$ (kJmol$^{-1}$)</th>
<th>$\Delta H_f$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{VO}_x$/TiO$_2$</td>
<td>66 ± 5</td>
<td>43 ± 10</td>
</tr>
<tr>
<td>$\text{VO}_x$/m-ZrO$_2$</td>
<td>80 ± 5</td>
<td>81 ± 6</td>
</tr>
<tr>
<td>$\text{VO}_x$/γ-Al$_2$O$_3$</td>
<td>91 ± 5</td>
<td>116 ± 10</td>
</tr>
<tr>
<td>$\text{V}_2\text{O}_5$</td>
<td>77 ± 5</td>
<td>119 ± 10</td>
</tr>
</tbody>
</table>

Figure 4-65 depicts the BEP correlation diagram for the propane activation energy and the defect formation enthalpy and for the supported catalysts a very good linear correlation with $r = 0.999$ is found. The deviation of the pure vanadium pentoxide might originate from the different experimental conditions for the defect formation enthalpies. The pure oxide was thermally reduced in oxygen but the monolayer catalysts needed a lower oxygen partial pressure for defect formation and were thus measured in nitrogen. The defect formation
enthalpy can be a function of partial pressure and thus the value for the pure vanadium pentoxide might deviate.

Figure 4-65: BEP correlation plot $E_a$ and $\Delta H_f$. The supported catalysts give a very good correlation. The displacement of vanadium might originate in the different experimental conditions. The formation enthalpies of the monolayer catalysts were determined in nitrogen while the pure oxide was measured in oxygen.

The correlation shows that the reducibility of the oxygen site has a direct connection to the catalytic reaction and can therefore be used as a reactivity descriptor. This connection is further discussed in the following chapter.

4.3.3. Defect Formation and ODH Reaction Profile

The oxidation step corresponds to the defect formation enthalpy. Thus, the higher the formation enthalpy the deeper the minimum in the energy profile and the higher the propane activation energy. This is observed in the correlation plot Figure 4-65 and is shown in the reaction energy profiles shown in Figure 4-66.
Results and Discussion - Impact on Catalysis

Figure 4-66: Energy reaction profile for the ODP with the corresponding defect formation enthalpies. [89]

These results indicate that the oxygen defect formation enthalpy is a suitable reactivity descriptor as proposed by Sauer et al. [13].
5. Summary and Conclusion

A reduction of polycrystalline vanadium pentoxide powder samples was observed under high oxygen partial pressure starting at 380 °C. RBS analysis and UV-Vis spectroscopy provides evidence for a reduction from $V^{+5}$ to $V^{+4}$. It is possible to assign the reduction to the vanadyl oxygen site, as partial pressure dependent XRD experiments at 500 °C revealed a lattice relaxation on vacancy formation in c-direction, which is in agreement with calculations done by [13]. The enthalpy to form the defect site is $1.3\pm0.1$ eV. This value could be derived from the Arrhenius-plot using the activation energy on heating and cooling. Due to dissociation on heating and slow reoxidation on cooling, the energies for electron activation and vacancy formation could be separated.

The reducibility of the vanadyl oxygen site is a key feature for the catalytic activity and therefore the method was applied to metal oxide supported catalysts in order to investigate the “support effect” that enhances the catalytic performance. Making use of percolation effects in 2-phase mixtures, it was possible to show the importance of the interface between support and vanadium oxide that revealed a “support effect” on the transport properties. The conduction mechanism of vanadium pentoxide changes from electronic to ionic at the interface and the defect formation enthalpy is lowered. The presence of ionic and electronic transport is an important aspect, because for reduction and oxidation the catalyst needs to transport electrons. Moreover, it is assumed, that the reoxidation of the catalyst can occur at a different site than it was reduced [48] and via lattice diffusion oxygen is transported to the according site. This mechanism is supported by the presence of ionic conductivity.

In-situ neutron diffraction experiments gave evidence for a highly strained interface that is attributed to a thermal misfit between vanadium pentoxide and the supporting oxide. A highly disordered and defect rich micro-structure was found that itself can enhance the transport properties. Furthermore, the function of lattice strain as driving force for the formation of oxygen vacancies is discussed in connection to the chemical strain effect that can furthermore enhance the evolution of oxygen vacancies.

Well defined amorphous monolayer catalysts have been used for the correlation to catalytic properties. Compared to crystalline compounds the evolution of point defects starts at lower
Summary and Conclusion

Oxygen partial pressure, which is attributed to the presence of highly dispersed vanadium species. Correlation to the alkane activation energy for the ODH show that the defect formation enthalpy is a good reactivity descriptor and that the support influences the reducibility of the oxygen and hence the catalytic performance.

In order to gain further insight, future research should comprise modification of the catalyst’s transport properties and investigation of the influence on the catalytic performance. Together with detailed micro-structural analysis this will give more information about the origin of the support effect. It will be necessary to develop new well defined sample geometries like meso-porous structures and coatings. These will facilitate the gas equilibration process and may therefore enhance the speed and accuracy of the experiments. Furthermore, the interface properties are very important and the influence of strain on the defect formation properties is a promising task.
6. References


References


References


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References

7. Appendix

Figure 7-1: Conductivity of VOₓ/MgO. The experiment was conducted below the transition temperature to spinel phases in order to investigate the influence of phase transition on the defect formation enthalpy.

Table 7-1: Fit parameter of VOₓ/m-ZrO₂ in oxygen and nitrogen.

<table>
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<tr>
<th></th>
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<th>Error</th>
<th>Unit</th>
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</table>

Table 7-2: Fit parameter of VOₓ/γ-Al₂O₃ in oxygen and nitrogen.

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Table 7-3: Fit parameter of VOₓ/TiO₂ in oxygen and nitrogen.
Figure 7-2: XRD phase analysis of VO$_x$/SiO$_2$ catalysts. No global phase transition is observed.

Figure 7-3: XRD phase analysis of VO$_x$/ZrO$_2$ catalysts. No global phase transition is observed.
Figure 7-4: Calcination furnace. A setpoint temperature of 427 °C gives a temperature at the sample of 500 °C.