Study of the surface structure of V2O5/-Al2O3 catalysts by LEIS

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1991

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Study of the surface structure of $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts by LEIS

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Master thesis
Eindhoven University of Technology
Department of Physics
Solid State Division
Surface and Interface Physics Group

Coached by dr. G.C. van Leerdam, and prof. dr. H.H. Brongersma
ABSTRACT

Within the scope of the catalytic research of the Schuit Institute of Catalysis at the Eindhoven University of Technology, the surface structure of V₂O₅/γ-Al₂O₃ catalysts has been investigated by low energy ion scattering (LEIS). LEIS is a unique surface analysis technique because its information depth is limited to the topmost atomic layer.

Supported vanadium oxides are widely used as oxidation catalysts. This investigation is performed in cooperation with the Delft University of Technology. The scientists from Delft are interested in the use of Pd/V₂O₅/γ-Al₂O₃ catalysts in the heterogeneous Wacker oxidation.

The LEIS experiments on the V₂O₅/γ-Al₂O₃ catalysts have been used to study the surface structure of these catalysts as a function of V₂O₅ loading. At low loadings (< 7 wt%) the vanadium species are found to be optimally dispersed over the support, while at medium loadings (< 11 wt%) multilayered structures are formed. In this thesis a three-dimensional model is presented for the surface structure of V₂O₅/γ-Al₂O₃ catalysts.

SAMENVATTING

In het kader van het katalytisch onderzoek van het Schuit Katalyse Instituut aan de Technische Universiteit Eindhoven is de oppervlakte structuur van V₂O₅/γ-Al₂O₃ katalysatoren met behulp van lage ionen verstrooiling (LEIS) onderzocht. LEIS is een unieke oppervlakte analyse techniek omdat de informatie diepte beperkt blijft tot de bovenste atoomlaag.

Gedragen vanadium oxides worden veel gebruikt als oxidatie katalysator. Dit onderzoek is in samenwerking met de Technische Universiteit Delft gedaan. De wetenschappers uit Delft zijn geïnteresseerd in het gebruik van Pd/V₂O₅/γ-Al₂O₃ katalysatoren in de heterogene Wacker oxidatie.

Met de LEIS experimenten van V₂O₅/γ-Al₂O₃ katalysatoren is de oppervlakte structuur van deze katalysator als functie van V₂O₅ belading bestudeerd. Bij een lage belading (< 7 wt%) zijn de vanadium zuurstof verbindingen optimaal over het oppervlak gespreid, terwijl bij middelmatige belading (<11 wt%) een structuur opgebouwd uit meerdere lagen wordt gevormd. In dit verslag wordt een driedimensionaal model gepresenteerd voor de oppervlakte structuur van V₂O₅/γ-Al₂O₃ katalysatoren.
ACKNOWLEDGEMENTS

The last year I spend in the group of surface and interface physics of the department of the physics at the Eindhoven University of Technology, has been of great value to me. I would like to thank all the people in the group for making my stay a pleasant and fruitful one. I especially would like to thank my mentor Kees van Leerdam for his encouragement, help, and friendship. Furthermore I would like to thank Hidde Brongersma for giving me the opportunity to present the work at home and abroad, Gerard Wijers for the technical assistance, Onno van Kessel for his contribution to the experiments, and Anja Stobbe-Kreemers for the preparation of the catalysts and the valuable discussions. Finally I would like to thank all the members of the debating club "Charm" for their enthousiasm.

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1 INTRODUCTION

1.1 Surface science

Surface science has developed enormously in the last two decades. It has proven to give unique and valuable information of the behaviour of solids at their surfaces. The knowledge is applied in various fields of industrial and academic interest, such as micro electronics, and heterogeneous catalysis.

During this period a whole range of surface analysis techniques has been developed. A selected list can be found in Table 1. Although a lot of these techniques are common in surface science, no single surface analysis tool has emerged. No technique has been found, which can give all the information on the structure and electrical properties of the surface. Every technique can give its part of this information. It is therefore essential to combine different techniques in order to develop a reliable model of a surface structure.

The surface analysis technique discussed in this thesis is Low-Energy Ion Scattering (LEIS) spectroscopy. LEIS is based on its unique capability of probing the topmost layer only. The basic principles of the technique are explained in Chapter 2. In Chapter 3 the ion scattering apparatus NODUS is discussed.

**Table 1** A selected list of surface analysis techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Auger electron spectroscopy</td>
<td>AES</td>
</tr>
<tr>
<td>Ultraviolet photoelectron spectroscopy</td>
<td>UPS</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>XPS</td>
</tr>
<tr>
<td>Electron diffraction</td>
<td></td>
</tr>
<tr>
<td>Low energy electron diffraction</td>
<td>LEED</td>
</tr>
<tr>
<td>Electron microscopy</td>
<td></td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>STEM</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>Tunneling microscopy</td>
<td></td>
</tr>
<tr>
<td>Scanning tunneling microscopy</td>
<td>STM</td>
</tr>
<tr>
<td>Photon spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Infrared spectroscopy</td>
<td>IR</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>NMR</td>
</tr>
<tr>
<td>X-ray absorption</td>
<td>EXAFS, XANES</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>XRD</td>
</tr>
<tr>
<td>Ion scattering</td>
<td></td>
</tr>
<tr>
<td>Secondary ion mass spectrometry</td>
<td>SIMS</td>
</tr>
<tr>
<td>Low-energy ion scattering spectroscopy</td>
<td>LEIS, ISS</td>
</tr>
<tr>
<td>Chemisorption techniques</td>
<td></td>
</tr>
<tr>
<td>Temperature-programmed desorption</td>
<td>TPD</td>
</tr>
</tbody>
</table>
1.2 Catalysis

A catalyst can be described as a substance which increases the rate of a chemical reaction without being consumed [1]. This can cause an increase of the production rate or soften extreme conditions under which the reaction takes place. Another advantage of the use of catalyst is the selective enhancement of a desired reaction, which decreases the amount of unwanted by-products. The importance of catalysis is reflected in the fact that about 90% of all processes in chemical and petro chemical industry is induced by catalysts. The total consumption of catalysts in 1989 has reached the 5 billion US $.

A good example where catalysts have changed the world is catalytic oil cracking. In the cracking process oil is distilled into naphtha, diesel, and gas oil. Without catalysts, so called thermal cracking, a pressure of 20-100 bar and temperatures between 770 and 970 K are necessary. Catalytic cracking reduces this to 1 bar and 600-700 K respectively. An additional advantage is a better product distribution which makes a better fuel. Considering that nowadays 700 million tons of petrol are consumed by cars only worldwide every year, it is easy to imagine that even the slightest improvement of the catalytic performance can result in a gigantic profit in industry.

In heterogeneous catalysis the catalyst is a solid while the reactants and products are in the gas or fluid phase, this in contrast to homogeneous catalysis where catalyst and reactants have the same, in most cases liquid, phase. Because a solid catalyst is not as accessible to the reactants as in the homogenous case, catalyst with a high surface area per gram (specific surface) are preferred. If for a active compound no stable structure is known which has a high specific surface area, this compound can be deposited on a compound which does have a high specific surface like alumina and silica. These systems are called supported catalysts. The use of a support on only changes the specific surface area, but the interaction with the support can affect the structure of the active compound, which can enhance the performance and/or the selectivity of the catalyst.

Because the catalytic induced chemical processes take place at the surface of the catalyst, characterisation of this surface is of great interest. A lot of effort in the world is put into surface characterisation using the techniques discussed above. This thesis discusses the use of LEIS in catalyst characterisation concentrating on $\text{V}_2\text{O}_5$ supported by $\gamma$-alumina.

The support is described in detail in chapter 4, a model of the surface structure of the catalyst is presented in chapter 5. The results of this work and more detailed information of the latest developments and trends in heterogeneous catalysis can also be found in the proceedings of the ASI NATO summer school on "fundamental aspects of heterogeneous catalysis studied by particle beams" held in Alicante, Spain on 2-14 September 1990 (to be published).
2 LEIS, basic principles

2.1 Introduction

The ultra sensitivity of LEIS to the topmost atomic layer only, which no other technique can claim yet, makes this technique a powerful tool in studying the surface composition and structure of single crystals and alloys. The last decade the study of more complex materials like polymers and real catalysts has given an additional boost to the application and development of this technique. In this chapter the basic principles of LEIS are discussed. In the last paragraph the use of absolute signals rather than signal ratios is discussed.

2.2 Elastic low-energy ion scattering

2.2.1 The binary collision model

In LEIS surfaces are analyzed with inert gas ions, typically $^3$He⁺, $^4$He⁺, $^{20}$Ne⁺, $^{40}$Ar⁺, at any energy ranging from 0.1 to 10 keV. At these low energies an analytical expression between the energy of the scattered particle ($E_f$) and the mass of the probe ($m_{ion}$) and target atom ($m_{atom}$) can be derived when simple elastic binary collisions are involved. The use of classical laws of energy and momentum results in the following expression:

$$\frac{E_f}{E_i} = \left[ \frac{\cos \theta + \sqrt{(q^2 - \sin^2 \theta)}}{1 + q} \right]^2$$  \hspace{1cm} (2.1)

where

$$q = \frac{m_{atom}}{m_{ion}} > 1$$  \hspace{1cm} (2.2)

with $\theta$ the scattering angle and $E_i$ the energy of the probe before impact. The left hand side of the equation 2.1 is reflected to as the kinematic factor. A schematic representation of the process can be found in figure 2.1.

The validity of the classical model is based upon the following assumptions. The deBroglie wavelength of keV-ions is much smaller than interatomic distances. Consequently the scattering process can be described in a classical way and diffraction has not to be considered.

Furthermore the ion-atom scattering results from a screened Coulomb interaction between the nuclei. Therefore the collision can in first approximati-
on be considered to be elastic. Since the distance of closest approach will be very small compared to the interatomic distance the collision can be assumed to be binary. And finally because the interaction time of the ion with the target is a few orders shorter of magnitude than the vibration time the target can be assumed to be at rest.

![Schematic representation of the binary collision model.](image)

**fig. 2.1** Schematic representation of the binary collision model.

The final energies calculated in this way give fairly good agreement with those measured in practice. A typical example of a LEIS spectrum is shown in figure 2.2. Broadening of the peaks, which is not described in the classical binary collision model, can be assigned to several factors.

![Example of a typical LEIS-spectrum of a V<sub>19</sub>Mn<sub>30</sub>Co<sub>19</sub>Rh<sub>10</sub>Ir<sub>10</sub> sample contaminated with K.](image)

**fig. 2.2** Example of a typical LEIS-spectrum of a V<sub>19</sub>Mn<sub>30</sub>Co<sub>19</sub>Rh<sub>10</sub>Ir<sub>10</sub> sample contaminated with K.

There are practical limitations like spread of primary energy and scattered angle. The fact the surface atoms are not free but bound to a lattice
and it can be calculated that multiple collisions over a small scattering angle can in some cases cause less energy loss than one over a large scattering angle. Inelastic processes due to electronic excitation, and re-ionization affect the symmetry of the peak and should be considered when studying the spectrum more closely.

2.2.2. Scattered ion yield

LEIS is a unique technique in the sense that the large cross section (~1 Å²) and shadow cone radius (~1 Å) (see next section) guarantee that most ions never get past the surface layer. The ions that do, are neutralized. Due to the large ionization energies of inert gas atoms the number of ions surviving a collision, the ion fraction, is very low, in the order of 0.01-1%. The neutralized probes do not contribute to the signal intensity. Taking this into account the peak intensity of the spectrum is due to ions scattered of the topmost atomic layer only.

The intensity of ions backscattered from a particular atom (Y) is proportional to the density (Nₐ) of that atom at the surface and can be expressed as follows:

\[ Y = N_a C I_o \sigma P \]  

(2.3)

where \( \sigma \) is the differential cross section of the ion-atom interaction, \( C \) is a apparatus dependent factor, \( I_o \) is the primary ion current, \( P \) is the ion fraction of the scattered particles.

All the parameters are specified by the experimental setup except \( P \) and \( \sigma \). The differential cross section can be calculated using the Thomas-Fermi-Moliere potential. The ion fraction however is a uncertain quantity. Although a lot of research has been committed on the subject a full quantum mechanical description has not yet been found. The problem is circumvented by the use of calibration samples. But since calibration is necessary for each element on the surface samples containing more elements are more difficult. An alternative method (DISC), put forward by Ackermans et al. [2], suggest the use of the two helium isotopes to determine the quantitative surface composition analysis in situ.

2.2.3 The shadow cone

A basic element for structural analysis using LEIS is the shadow cone. Due to the repulsive Coulomb scattering between the ion and the target atom, the ion direction will be deflected. The distribution of scattered ions will form a characteristic shadow cone behind the surface atom. A shadow cone can be calculated from classical trajectories in a two body collision, and the envelope of trajectories can be presented as is shown in fig 2.3. At the edge of the cone the ion flux is enhanced, which can be used as a kind of focusing on a
second layer atom. If an atom lies in the shadow cone of the scatterer it will not be detected.

Since the shadow cone can be calculated fairly well the relative positions can be determined when the critical angle can be determined. The critical angle is defined as the angle where every atom focuses the ion on its neighbour. This concept is used in Impact Collision Ion Scattering Spectroscopy (ICISS) but can only be performed on well defined and well ordered surfaces like single crystals. An example is shown in figure 2.4.

*fig. 2.3 Examples of the shadow cone effect. Incident angle: a: 0° (perpendicular), b: 35°, c: 55°, d: 75°.*
The shadow cone is a handy tool in studying open structures like γ-Al₂O₃, which consists of micro crystallites. The size of these crystallites is about 10 nm. Shadow cone calculations can give you an indication if detection of a sub-surface atom is possible.

![Diagram](image.png)

**Fig 2.4** Schematic representation of the ICISS experiment. (a) The incident angle \( \alpha \) is varied. (b) At \( \alpha = \alpha_c \) the atoms lie on the edge of the shadow cone of their neighbours. (c) The enhanced intensity measured at a larger \( \alpha \) is due to focusing. [3]

### 2.3 Catalyst characterisation

#### 2.3.1 Introduction

LEIS is not a common technique in catalyst characterization, but it has proved to give valuable and unique information about the surface of catalysts [4]. Most applications are found in the study of supported metal and metal oxide catalysts. These systems have supports like Al₂O₃, SiO₂, and TiO₂, which have high specific surfaces (> 100 m²), on which a metal e.g. Pt, Pd, Rh, or a metal oxide e.g. MoO₃, WO₃, V₂O₅, is deposited. These catalyst are highly porous compounds. The surface of these powders are very rough because the random orientation of the crystallites. Therefore ICISS studies on these catalysts are impossible. In most applications a series of targets is analyzed under fixed conditions. The targets may differ in composition or in pretreatment.

If the scattering conditions are fixed then it follows from equation 2.3 that the change in signal intensity for each element is directly proportional to the change in surface concentration of that element. The requirement under
fixed scattering conditions, however, demands a great expertise. A few of the problems which should be mastered are the following. Instabilities of the ion beam must be kept to an absolute minimum. A storage facility for a series of samples is required. An in situ pretreatment of the samples is needed to reduce the surface contamination. The powdered metal oxides are insulating. This will cause charging of the sample when the ion beam is directed onto it. Eliminating this charging for these rough surfaces requires a specially designed neutralization system which is described in more detail in chapter 3. Most of the problems described can be circumvented by the use of signal ratios.

2.3.2 Absolute signals or signal ratios?

Why should you use absolute signal intensities when the use of signal ratios decreases the effect of experimental problems? Ratios will trouble the interpretation of the results. A nice example of the problems with the interpretation, when signal ratios rather than absolute signals are used, is MoO$_3$ supported on γ-Al$_2$O$_3$.

MoO$_3$/γ-Al$_2$O$_3$ is a catalyst where the catalytic active molybdena oxide species is optimally dispersed on the alumina support. Based on this property the catalyst is classified as a monolayer catalyst. This monolayer dispersion makes these catalysts especially interesting to LEIS studies, since LEIS probes the topmost layer only. MoO$_3$/γ-Al$_2$O$_3$ catalysts are used in the petrochemical industry to remove sulfur and nitrogen from petroleum feed stocks and coal products. This makes these hydrosulfurization (HDS) catalysts even more interesting for research.

![Graph](image)

**fig 2.5. Mo/Al LEIS (ISS) signal ratio as a function of MoO$_3$ content.**

The LEIS studies as presented by Zing et al. [5], see fig. 2.5, show at low coverage the Mo/Al signal ratio to increase much less with the Mo loading than at higher coverage. This was attributed to a preferential Mo occupation of subsurface interstices, which are partly shielded from detection.
at low coverage, and the occupation of surface interstices at higher coverage.

If instead of signal ratios absolute signals are used, a completely different picture arises. Fig. 2.6 shows the result of van Leerdam et al. [6] at our laboratory. These results show a linear increase of the Mo signal as the coverage increases. This points to an optimal dispersion of the active phase on the support. The change in slope as seen by Zing et al. is not due to shielding of Mo but to shielding of Al at higher coverage as is clearly shown in fig 2.6.

Recent investigations [7] show that shielding effects in oxides are not the major factor to consider, as is presented in literature. When the primary energy is varied, not the shielding effect changes, but it is shown that the change in signal intensity is an intrinsic energy dependence of the signal intensity of the target atoms.

Regarding these results the use of absolute signals is to be preferred, although it demands highly stable ion scattering conditions.

\[ \text{fig. 2.6} \quad \text{The LEIS signal intensity (S) of Mo (squares) and Al (circles) as a function of MoO}_3 \text{ content.} \]
3 EXPERIMENTAL SETUP

3.1 Introduction

In this chapter the LEIS apparatus NODUS will be described and the special adaptations will be discussed which are necessary to study complex insulating samples like supported catalysts.

For scientific purpose the surface of the target must be well defined and therefore not contaminated during the measurements. In LEIS, which is only sensitive to the topmost layer, it is evident that contamination should be kept to a absolute minimum. This is why Ultra High Vacuum (UHV) conditions are required, which means pressures less than $10^{-7}$ Pa.

In many cases the surfaces are cleaned by exposure of high doses of the ion beam using a heavy inert gas atom like Ar, which peels off the first atomic layers of a contaminated surface. This process is called controlled sputtering. Heating can have the same effect and gives the surface opportunity to re-order. In the case of micro crystallites this method can't be used. Sputtering will not clean the surface but will destroy the crystallites. Therefore a light ion (He⁺) is used and the ion doses on the surface is maintained as low is possible. This keeps the sputtering damage, which is inherent to shooting ions on a surface, as small as possible.

3.2 The NODUS apparatus

The NODUS apparatus was first introduced by Brongersma et al [8], as an essential Non Destructive Ultra Sensitive technique for surface analysis. The configuration as it is used nowadays is shown in fig 3.1. Different sections of the apparatus will be treated separately

3.2.1 UHV

The differential pumping system used consists, as is shown in figure 3.1, of a turbo molecular pump, a ion getter pumping system, and a titanium sublimation pump, which is cooled with liquid nitrogen. This ensures that the background pressure increases only from $5\times10^4$ Pa to $1\times10^6$ Pa when the ion beam is used. This increase is mainly due to He, which will not affect the scattering conditions because the gas is inert.
fig 3.1 Schematic representation of the low energy ion scattering apparatus NODUS: 1. ion source, 2. mass filter, 3. deflection plates, 4. einzel lens, 5. aperture, 6. CMA, 7 carousel, 8. turbo molecular pump, 9. ion getter pump, 10. valve, 11. valve, 12. gas inlet needle valve.
3.2.2 The ion beam.

Mono-energetic ions are nowadays produced in a Leybold ion source and directed perpendicular onto the target via a series of electrostatic lenses, deflection plates, a mass filter, aperture as is shown in figure 3.1. The electrostatic lens, situated just in front of the target, makes it possible to vary the beam diameter from 0.5 to 5 mm.

The basic design of our ion source is shown in fig 3.2. It consists of a filament anode, a cathode cage and a repulsive electron shield. The electrons emitted from the filament will be accelerated towards the cage. The electrons can be captured at the cathode, but it is more likely that they pass the cage. Leaving the cage region the repulsive shield will invert the travelling direction of the electrons and the electrons will be accelerated back into the cage. In this way electrons can pass the cage region several times before being captured. When gas atoms are introduced into the cage region they will be ionized upon colliding with an accelerated electron. The generated positive ions are caught in the cage region by the electric field which accelerates the electrons. The ions are extracted from the cage with an extraction electrode. The extraction process is of importance to the spread in the primary energy and the beam intensity that can be extracted. If the extraction is decreased, this will decrease the spread in the primary energy. It will lead to a better point source behaviour of the ion source, but it will decrease the beam intensity. Finally, the ions are accelerated to the desired primary energy.

The maximum target current of a $^4$He ion beam ranges from 50 nA at a primary energy of 500 eV to approximately 600 nA at 4000 eV.

![Diagram of ion source](image)

**fig. 3.2** Detail ion source (Leybold IQ 12/38): 1. electron repellent, 2. anode (cage), 3. cathode (ring), 4. ion extractor.
3.2.3 The analyzer

Several electrostatic energy analyzers are in use nowadays. The energy of the ions, which reach the analyzer after the collision, is analyzed by deflecting the ions, by means of an electrical field, through slits. Early systems were built with a hemispherical analyzer (HSA) as is shown in fig. 3.3. It selects only a small solid angle which limits its sensitivity, but it can be mounted easily in such a way that the scattering angle can be varied. The analyzer used in the NODUS apparatus is a cylindrical mirror analyzer (CMA), which selects a complete cone. Only ions scattered at an angle 142° are selected. The cylindrical symmetry of the analyzer is clearly shown in fig. 3.4a. The way the CMA is fitted in the experimental setup is shown in fig. 3.4b.

fig. 3.3  Schematic representation of a hemi-spherical analyzer

fig. 3.4  a. Schematic representation of a CMA, b. schematic representation of the CMA of the NODUS
The CMA deflects the ions through two slits. The energy spectrum is obtained by varying the electric field strength. This varies the pass energy, while leaving the resolution $\Delta E/E$ constant. The detector, as is shown in figure 3.2, consists of a series of channeltrons. An ion hitting the channeltron will give rise to secondary electrons. These electrons are accelerated into the channeltron, inducing a avalanche of electrons which are then detected.

The measuring process and the data acquisition is fully computer controlled. Data processing is performed on an Atari computer.

3.2.4 The neutralizing system

When studying insulating samples charging effects must be compensated. Therefore a ring-shaped electron "shower" was constructed which ensures flooding from all sides. The flow of low energy electrons ($\sim 10$ eV) is emitted from filaments, which are placed out of the line of sight of the target. This prevents contamination of the filaments by sputtered particles. Deflection plates are mounted to direct the electron onto the sample. This configuration, which is shown in fig 3.4b, compensates charging very effectively, even when studying surfaces of rough and porous insulating systems such as catalysts.

3.2.5 Sample handling

Samples are mounted on a target holder. The targets can be stored in a transfer system called the "vacuum suitcase", which is shown in fig 3.5. In this vessel the targets can be stored under UHV. It is also possible to close the vessel which enables exchanging of the targets with other UHV vessels. In the case of the NODUS the "suitcase" can be mounted on a pretreatment vessel. In this pretreatment chamber an oven for heating of the samples is included and there is the possibility to insert oxygen or hydrogen gas for pretreatment. The vessel can be pumped by a separate Leybold turbo

fig. 3.5  The "vacuum suitcase", vessel for transporting samples at UHV.
molecular pump in order to limit the contamination of the UHV experimental vessel when the targets are inserted on the carousel in the experimental chamber via a loadlock. On the carousel twelve target holders can be stored, which makes analysis of different targets under identical experimental conditions possible. There are ovens mounted on the carousel too for in situ heating of the samples.

3.3 Pretreatment of the catalysts

The catalysts studied in this thesis are highly porous insulating powders. The catalysts are pressed in tantalum disks and then mounted onto the target holders. A series of target holders is placed into the "suitcase" and attached onto the pretreatment vessel. The vessel and the "suitcase" are separated by a valve. Before entering the UHV chamber the samples are treated with 10\(^3\) Pa O\(_2\) for 15 minutes. This treatment removes contamination from the surface like carbon. The thermal treatment also removes hydroxyl groups present on the surface. The hydroxyl groups are furthermore removed by slight sputtering when the samples are analyzed. This will be discussed in more detail in chapter 4. Typical experimental conditions when studying series of catalysts, as in chapter 5, were a 4He ion probe, a primary energy of 3 keV for the ions, a beam current of 200 nA, and a beam diameter between 0.5 and 5 mm depending on the desired sputtering rate.
4 γ-ALUMINA

4.1 Introduction

Already for a long time aluminas are used extensively both as a support and an active catalyst. The first description of a alumina induced reaction was the alumina catalyzed dehydration of ethanol, discovered in 1797 by the Dutch chemists Bondt, Deiman, van Troostwyk, and Lauwenburg [9]. Nowadays alumina is mostly used as a catalyst support, examples of which can be found in chapters 2 and 5.

Although a lot of research has been done worldwide on alumina and alumina compounds no conclusive answer about the exact nature of its surface has been found yet. When modelling a supported catalyst the interaction with its support is very important. Therefore the surface structure of the carrier must be known in order to explain the behaviour of the catalyst, especially in the case of monolayer catalysts. The ultimate goal is to try to design an ideal catalyst where the interaction of the support and the active phase can be predicted.

In this chapter only one modification of alumina, γ-Al₂O₃, will be discussed in detail. The results will be used in chapter 5 to describe the deposition of vanadium oxide species on the surface.

4.2 Classification of aluminas

The structural chemistry of alumina is complicated because of the number of different phases, and the numerous preparation methods used [10]. Aluminas can be obtained starting off with different kinds of aluminium hydroxide e.g. aluminium trihydroxyde Al(OH)₃ with the modifications gibbsite, nordstrandite and bayerite, or aluminium-oxidehydroxide (AlO(OH)) which is known in the modifications diaspore and boehmite. Many of these modifications are found in bauxite, depending on the area where it is found. Gibbsite is for example mainly found in bauxite from North and South America and is an intermediate for the production of aluminium metal, boehmite in its gelatinous form is found in the bauxite from Europe. The different modifications can be produced synthetically too. These aluminium hydroxides are dehydrated to form active aluminas. The dehydration process will define which alumina is found. A few of the processes are shown in fig. 4.1.

These transition aluminas are classified based on the temperature at which the aluminas were obtained from the hydroxides. Under all conditions at very high temperatures α-alumina is formed. It has a corundum structure, the surface consists of the (0001) face. Both the unit cell of the ideal corundum structure and its surface are shown in fig 4.2.
Schematic representation of the different modifications of alumina and the way it is formed.

At high temperatures between 1070 and 1170 K θ- and κ-alumina are formed, which structures (described by Lippens and Steggerda [10]) are too complicated and distorted to show in this introduction. At low temperatures, lower than 900 K, γ- and η-alumina are formed. These structures have a lattice which is closely related to the spinel structure. In γ-alumina the oxygen lattice is fairly well structured. This modification and its structure will be discussed in more detail in the next section.

In practice a wide range of specific surface areas and pore sizes of dehydrated aluminas is available. Specific surface areas up to about 400 m²g⁻¹ are commercially available. The specific area of the γ-alumina we are interested in is 250 m²g⁻¹.

The structure of α-alumina: a. the corundum structure, b. idealized model of the (0001) face of α-Al₂O₃ [27].
4.3 The structure of $\gamma$-Al$_2$O$_3$

4.3.1 Introduction

Before discussing the structure of the $\gamma$-alumina a few basics of closest-packed spheres should be known, which are explained in fig. 4.3. In all closest-packed arrangements three types of interstitial holes exist. The most simple one is the triangle hole, the hole in a triangle of three touching spheres. Then there is the tetrahedral hole which can be seen as a triangular pyramid hole surrounded by four touching spheres. The last is the octahedral hole which is formed by six touching spheres. Its form consists of eight triangles as is shown in the fig 4.3. As a measure of the size of a hole the maximum size of a sphere which can be fitted in the hole can be taken. Taken this measure, the triangle hole is about one-third, and the tetrahedral hole is about one-half of the size of an octahedral hole.

![Diagram of interstitial holes](image)

*fig. 4.3* Interstitial holes between closest-packed layers: (a) tetrahedral (x) and octahedral (●) holes; (b) and (c) plan and elevation views of tetrahedral and octahedral holes respectively.
4.3.2 The spinel structure

The support, γ-alumina has been studied extensively [10,11]. Lippens concluded that γ-alumina posses a defected spinel structure. The spinel structure has an elementary cell containing 32 oxygen ions in almost perfect cubic closest-packing. In an ideal spinel structure eight of the 64 tetrahedral interstices are filled by divalent metal ions and sixteen of the 32 octahedral interstices are filled with trivalent metal ions. In γ-Al₂O₃ the octahedral lattice is completely filled while one-third of the tetrahedral lattice is vacant. The vacancies are randomly distributed over the tetrahedral holes. This causes the spinel structure of the alumina to be slightly distorted. The unit cell and the layer sequence of the (100) face of a open ideal spinel structure is shown in fig 4.4.

Open spinel structure, A: tetrahedral interstices, B: octahedral interstices, O: oxygen lattice [27].
Usually, only the low-index planes (111), (110), and (100) are considered when discussing the surface structure of the γ-alumina. Although one-third of the tetrahedral sites is vacant, in the figures all positions are indicated as in an ideal spinel structure. A terminating layer which consists of O- or OH-groups is omitted and only ideal surfaces of the spinel structure are discussed in this section.

In the spinel structure there are two types of layers containing a different aluminium distribution. In figures 4.5-4.7 the structure of the different planes is shown. The figures are obtained using the computer simulation program LATUSE/SARCH, which is discussed in more detail in appendix A. Splitting the spinel lattice parallel to the (111)-plane the different layers are designated A- and B- layers, according to Knözinger and Ratnasamy [11]. Similar the cleavage planes for the (110) and (111) planes are denoted by C and D, E and F, respectively.

**fig. 4.5.a** (111)-face of alumina spinel lattice, A-layer.

**fig. 4.5.b** (111)-face of alumina spinel lattice, B-layer.
fig. 4.6.a (110)-face of alumina spinel lattice, C-layer.

fig. 4.6.b (110)-face of alumina spinel lattice, D-layer.

fig. 4.7.a (100)-face of alumina spinel lattice, E-layer.
fig. 4.7.b (100)-face of alumina spinel lattice, F-layer.

In the hexagonal oxygen packed (111)-faces the A- and B-layer have the same number of interstices, i.e. 9 on twelve oxygen atom. The B-layer consists of octahedral positions only. The A-layer is more complicated. It consists of 3 octahedral and 6 tetrahedral positions, 3 are situated closer to the surface than the other as is shown in figure 4.5. In the C-layer of the (110) plane, 12 interstices can be assigned, 6 are aligned in tetrahedral and the other 6 in octahedral interstices between rows of oxygen atoms. The D-layer has only 6 octahedral interstitial holes between the rows of the oxygen atoms. Finally the (100) face, which is represented by a square lattice of oxygen atoms with 6 octahedral sites in plane. In the E-, F-layer respectively 3 tetrahedral positions are located slightly under or above the oxygen plane. In the defect spinel structure of γ-Al₂O₃ only two-third of the tetrahedral sites are occupied, which results in the distribution as is shown in table 2.

**TABLE 2** Site occupation of Al in the different surface layers of γ-Al₂O₃

<table>
<thead>
<tr>
<th>crystal face</th>
<th>layer</th>
<th>tetrahedral Al</th>
<th>octahedral Al</th>
<th>total Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>A</td>
<td>4</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>110</td>
<td>C</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td></td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>100</td>
<td>E</td>
<td>2</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>
4.3.3 The surface structure of $\gamma$-alumina

In general only the ideal low index planes are considered when discussing the surface structure of the $\gamma$-alumina. Peri [12] has proposed a model where the (100) plane forms exclusively the surface to explain his results. Lippens concluded in the case of $\gamma$-$\text{Al}_2\text{O}_3$, the (110) and the (100) are preferentially exposed. It is known that it is possible to build crystallites which exposes only one face. The favoured terminating of a specific surface is also known. Take for example a GaAs (001) surface which can have a Ga or As terminated surface. By offering As or Ga respectively the termination can be changed. In growth process the preferential exposure is much more likely than when a crystal is cleaved. When cleaving an even distribution between the two possible surfaces is expected.

Based on the low index planes of $\gamma$-alumina Knözinger et al. [11] allow for the existence of five different of OH-groups, the properties of which are predominantly determined by their coordination and net electrical charge. From IR spectroscopic results it is concluded that all the proposed OH-groups are present. This leads to the conclusion that all the low index planes, namely the (100)-(110)-(111)-planes, are exposed. The exposure of all these crystal planes and site configurations is assigned to low ordering in transition aluminas and the small size of the microcrystallites ($\approx$10nm). Furthermore it is stated that the relative intensities of the surface OH-bonds vary for the different samples and may depend on the detailed preparation. It is however not possible to confirm these results with experiments on single crystals, because no large single crystal of $\gamma$-alumina has been grown yet.

**fig. 4.8** LEIS-spectra of the surfaces of $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ (primary ion $^4\text{He}^+$; primary energy of 3 keV)
Recent LEIS [13] results at our laboratory point to the preferential exposure of a specific surface plane, the (110) D-surface. In the LEIS study γ- and α-alumina are contrasted. From this is concluded that the Al signal intensity of the γ-Al₂O₃ is only 75 ± 5% of that of α-Al₂O₃. The normalised LEIS spectrum are shown in fig. 4.9. The γ-alumina spectrum is slightly shifted in order to make the difference more clear. This difference can only be explained in terms of the preferential exposure of the D-layer surface. The D-surface is characteristic because of its relative low Al contents and the fact that only octahedrally coordinated Al is exposed. Pretreatment at high temperatures could give a reordering to the (111) plane, which is the most stable. To give a definite answer to the question of the surface structure more research is necessary. Calculation of the stability of the different surfaces has to be considered.

In this calculation the OH-groups should be incorporated too. As is discussed in the last section the different planes, which can form the surface of the γ-alumina, can be terminated by a layer of OH-groups. During thermal treatment over a temperature range of 400-1400 K, γ-Al₂O₃ loses water, because neighbouring hydroxyl groups condense. A maximum of 90 % for γ-Alumina is estimated [28]. This conclusion agrees with the observation that conversion from γ-Al₂O₃ to α-Al₂O₃ requires a minimum critical temperature rather than a prolonged treatment. leads us to believe that the treatment of the γ-alumina in oxygen at 400-500 K, discussed in section 3.3, doesn’t change the surface structure of the alumina significantly. When analyzing the alumina with LEIS at room temperature initially a rapid increase of the Al and O signal in time is found, after which they develop much more gradually. This is assigned to slight sputtering of hydrogen. With higher pretreatment temperatures the initial Al and O signal intensities are higher, but the final values are the same.
5 THE SURFACE STRUCTURE OF $V_2O_5/\gamma$-Al$_2$O$_3$ CATALYSTS [14]

5.1 Introduction

Supported vanadium oxides are widely used as oxidation catalysts and have therefore, been studied extensively by various experimental techniques. In this paper only the interaction between $\gamma$-alumina and $V_2O_5$ will be considered. According to Murakami et al. [15,16], who used benzaldehyde-ammonia titration, NO-NH$_3$ rectangular pulse methods, X-ray diffraction, IR, ESR, and UV-reflectance spectrometry, V-species are optimally dispersed on the support at low loadings (< 4 wt%). At medium loadings (< 35 wt%) lamellae are formed and at even higher loadings the support is completely covered. The model is shown schematically in fig. 5.1.

Haber et al. [17] concluded from chemical analysis and reduction-oxidation studies that monolayer coverage is reached at a loading of 20 wt%. The formation of dimeric V-O species is inherent to the $\gamma$-alumina surface and is not forced by too high concentration. A dimeric structure is proposed on the (111) surface of the support, as is shown in fig 5.2. This figure only shows that it is possible to place the dimer on the surface. This is confirmed by Nag and Massoth [18] by means of XPS and gravimetric reduction studies.
shows that it is possible to place the dimer on the surface. This is confirmed by Nag and Massoth [18] by means of XPS and gravimetric reduction studies.

fig. 5.2  $V_2O_5$ polyhedra on the (111) plane of $\gamma$-Al$_2$O$_3$ [17].

Laser Raman spectroscopic experiments by Roozeboom et al. [19,20] showed that three different species may be present on the catalyst: vanadate tetrahedra, two-dimensional polymeric octahedral clusters and at higher loadings $V_2O_5$ crystallites. Solid state $^{51}$V NMR structural studies on the catalyst [21] show a predominance of a tetrahedral oxygen coordination of V atoms at low loadings. At higher loadings (up to monolayer coverage) a strong increase of octahedrally coordinated V-species is found. Average interatomic distances

fig. 5.3  (a) RED of vanadium pentoxide/alumina. The RED of pure alumina has been subtracted. (b) RED of vanadium pentoxide calculated from single crystal data [22].
of the vanadium oxide supported on γ-alumina (9.8 wt%) have been given by Bergeret et al [22] using RED (radial electron distribution). These results indicate that the structure of the supported vanadium oxide is different from bulk vanadium pentoxide (fig. 5.3) In this chapter the different models are compared and contrasted with the results of our LEIS experiments.

The research was performed in cooperation with Anja Stobbe-Kreemers from Delft University of Technology, chemical engineering department. Besides the LEIS results, a model is proposed, and the preparation of the catalyst and the specific interest from Delft in the system is discussed.

5.2 Catalysts for the heterogeneous Wacker oxidation

5.2.1 The heterogeneous Wacker oxidation [23]

The catalytic oxidation of ethylene to acetaldehyde in a homogeneous aqueous solution with a palladium copper catalyst at mild conditions of 10^5 Pa and 293-333 K is known as the Wacker process. The catalyst consists of palladium chloride dissolved in hydro-chloric acid where CuCl₂ is added. A scheme of the reaction can be found in fig. 5.4. The Cu is needed to increase the reaction rate because the reaction of Pd with oxygen is slow. In its liquid, homogeneous form the Wacker process has a number of technological disadvantages. The combination of hydro-chloric acid and oxygen is very corrosive, which destroys the reactor, piping and pumps. Furthermore undesired byproducts are generated.

\[
\begin{align*}
H_2C=CH_2 + H_2O & \xrightarrow{\text{Pd(II)}} \xrightarrow{\text{Cu(I)}} \xrightarrow{O_2} \xrightarrow{\text{Pd(0)}} \xrightarrow{\text{Cu(II)}} \xrightarrow{H_2O} H_3C-CHO
\end{align*}
\]

*fig. 5.4*  The oxidation of ethylene to acetaldehyde by palladium chloride/copper chloride

These disadvantages can be largely circumvented if a solid instead of a liquid catalyst is used. Research resulted in substitution of the homogeneous PdCl₂/CuCl₂ catalyst by a heterogeneous catalyst based upon palladium-doped vanadium pentoxide supported by γ-Al₂O₃. Good activities and high selectivities have been found. To get a better understanding of this catalyst the V₂O₅/γ-Al₂O₃ system is studied by LEIS in this thesis.
5.2.2 *The preparation of the V\textsubscript{2}O\textsubscript{5}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts*

To give the reactants a good accessibility to an active catalyst, materials with a high specific surface are preferred. Because no such structure of vanadia oxides exists, the vanadium oxide is supported by \gamma-alumina. The \gamma-alumina used in this study, obtained from AKZO, has a specific surface area of 250 m\textsuperscript{2}g\textsuperscript{-1}.

The supported vanadia catalysts were prepared by continuous adsorption by leading a NH\textsubscript{4}VO\textsubscript{3} solution through a bed of \gamma-Al\textsubscript{2}O\textsubscript{3} at 343 K following the method described by Roozeboom et al [24]. The apparatus which is used for the preparation of the catalysts, is schematically shown in fig 5.5. The catalysts were then calcinated in air at 673 K for 4 hrs. A monolayer coverage was estimated to correspond to 15.3 wt% V\textsubscript{2}O\textsubscript{5} [23].

![Diagram](image)

**fig. 5.4** Apparatus used for catalyst preparation: 1. NH\textsubscript{4}VO\textsubscript{3} solution, 2. cooler (343 K), 3. \gamma-Al\textsubscript{2}O\textsubscript{3}, 4. pump, 5. pH electrode.

5.3 *LEIS experiments and three dimensional model*

5.3.1 *Introduction*

During the last decade low energy ion scattering (LEIS) has developed to a valuable technique for the analysis of the atomic composition and structure of solid surfaces (see chapter 1,2). LEIS is based on the unique capability of probing only the topmost atomic layer. Depth information may be obtained by sputter etching. The use of absolute LEIS intensities rather than signal ratios proved to be very useful and lead to quite a different model for the alumina supported molybdena catalysts (see section 2.3.2). Since both molybdena and vanadium are classified in the category of monolayer-type catalysts [17,25] it seems interesting to investigate the structure of V\textsubscript{2}O\textsubscript{5}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts.
5.3.2 Surface analysis equipment

Before presenting the results, the experimental conditions are recap­tured. The surface analysis was performed with the LEIS apparatus NODUS, which basic design has been outlined earlier in chapter 3. Mono-energetic ions are nowadays produced in a Leybold ion source and directed onto the target. A kind of CMA (cylindrical mirror analyzer) selects ions scattered at an angle of 142°. The energy spectrum of the selected ions is recorded. The differential pumping system ensures that the background pressure increases only from $5 \times 10^{-8}$ Pa to $1 \times 10^{-6}$ Pa when the ion beam is used. This increase is mainly due to He. The catalysts studied were pressed in tantalum disks and then mounted onto the target holders. Before entering the UHV chamber the samples were treated with $10^3$ Pa O₂ for 15 min. at 500 K in a reaction chamber. Then the reaction chamber was evacuated for 10 min. to limit contamination of the experimental UHV chamber when the samples are inserted via a loadlock onto the carousel. The carousel can hold twelve samples which ensures identical experimental conditions when analyzing a series of targets. Different series can be compared by means of a normalization sample. Typical experimental conditions were a "He" probe, a primary energy of 3 keV for the ions, a beam current of 200 nA, and a beam diameter between 0.5 and 5 mm depending on the desired sputtering rate. Surface charging effects were eliminated by flooding the surface with low-energy electrons from a ring shaped neutralizing system which ensures flooding from all sides.

5.3.3 Results and discussion

A series of $V_2O_5/\gamma-Al_2O_3$ catalysts with a $V_2O_5$ content ranging from 0 to 14 wt% has been analyzed. Figure 5.5 shows a typical LEIS spectrum which is used in the analysis of the alumina supported vanadia catalysts. The peak height is taken as a measure of the scattered intensity. Identical results were obtained if areas were used instead. The $V_2O_5$ loading dependence of the peak intensities is shown in figure 5.6.

The behaviour of the LEIS signal as function of vanadium pentoxide loading can be divided into three regimes. At low loadings ($<7$ wt%) a linear increase of the V signal is found together with a linear decrease of the Al signal. This linearity points to a monolayer dispersion of V species, which shields part of the aluminium from detection. In the regime from one half to three quarters of a monolayer (7-11 wt%) both the V and Al signals have a constant value. The plateau of the V signal indicates that extra V atoms are deposited on the surface in such a way that they cover already present V atoms. This means that a multilayered structure is formed. The growth of multilayered species, which doesn't cause any additional shielding of the aluminium atoms, is consistent with the Al signal plateau. An increase of the vanadium signal and simultaneously a decrease of the aluminium signal is observed when the loading is increased up to monolayer coverage. This can be accounted for by the deposition of V species on locations where they shield aluminium. The fact that the slope of the second linear increase of the V
signal is the same as in the first regime suggests not only a monolayer dispersion, but also a deposition of V species in such a way that they do not cover any already present V atoms. Note that there is no significant change in the O signal over the whole regime.

The insensitivity of the oxygen signal indicates a growth of V species on the γ-alumina surface which extends the oxygen lattice of the support. The structure of γ-Al₂O₃ is a defected spinel. The preferential exposure of one of the cleavage planes has been discussed before but no conclusive answer has been reached yet. Recent results at our laboratory point to the D-layer of the (110)-face as the predominant face of the γ-alumina. The D-layer, as shown is figure 5.7.a, distinguishes itself by the low aluminium content at the surface and the exposure of only octahedral interstices which are filled with aluminium atoms. In the following a model for the V₂O₅/γ-Al₂O₃ catalysts is proposed which assumes the D-layer to be the predominant surface structure of the support.

![Typical LEIS spectrum](image1)

**fig. 5.5.**
Typical LEIS spectrum of a 8.84 wt% V₂O₅/γ-Al₂O₃ catalyst (*He⁺, primary energy of 3000 eV)

**fig. 5.6.**
The peak intensities (S) of Al, O, V as a function of V₂O₅ content

Extension of the spinel structure starting from the D-layer will give the C-layer. This layer contains alternating rows of tetrahedral and octahedral interstices in the oxygen lattice. As stated in the introduction the vanadium is found tetrahedrally coordinated at low loadings which suggests a filling of only
tetrahedral interstices in the C-layer. This procedure will preserve the oxygen lattice of the spinel structure and gives rise to a monolayer dispersion of vanadium on the surface as is shown in figure 5.7.b. The shielding of aluminium atoms, as observed in the LEIS experiments, is clearly visible in the figure. In the C-layer the tetrahedral interstices would be completely filled at 4.6 V atoms per nm$^2$ which corresponds to 14.6 wt\% [23]. The end of the linear increase of the V signal however is reached at about 7 wt\%. This indicates that only half of the tetrahedral interstices are filled. This behaviour could be accounted for by the fact that only one OH-group is available per octahedrally coordinated aluminium atom in the D-layer of the $\gamma$-Al$_2$O$_3$ [11]. The formation of dimers as observed by Haber et al. [17] at low coverage is supported by this model.

\[\begin{array}{c}
\text{V atoms} \quad \text{Al atoms} \quad \text{O atoms top layer} \\
\text{O atoms layer underneath}
\end{array}\]

\textit{fig. 5.7} (a) D-layer of (110) plane, (b) expansion of the D-layer by V species, which occupy the tetrahedral sites of the complementary C-layer, (c) formation of a multilayered structure by deposition of octahedral V species on top of the tetrahedrally coordinated V atoms.

In the next regime (7-11 wt\%) the experiments show shielding of V atoms by additional V species without affecting the Al or O signal. The additional V atoms have an octahedral environment [20,21], which is consistent with the growth of a multilayered structure or lamellae as is shown in figure 5.7.c. The octahedral V species will shield the tetrahedrally coordinated V atoms from detection. From the size of the plateau in figure 5.6 it follows
that only half the amount of vanadium which could be accommodated in the tetrahedral interstices can be deposited in the octahedral sites. This growth process supports observations by Inomata et al. [15], who detect the coverage of inactive tetrahedrally coordinated sites by active octahedral sites. When the loading is increased they detect further coverage of the surface until full coverage is reached. At loadings greater than 11 wt% the increase of the V signal and the simultaneous decrease of the Al signal can be explained by the coverage of the empty rows between the lamellae. Following the C-layer, which has left octahedrally favoured interstices, the oxygen lattice is preserved and a further increase of octahedral species will be the result. The proposed structure gives good agreement with the V-V distances presented by Bergeret et al. [22]. The difference is no more than a few hundredths of a nanometre.

The three dimensional model as proposed is shown in fig. 5.8.

5.3.4. Conclusion

The present investigations show how powerful a tool LEIS can be because of its ability of selective probing of the topmost atomic layer only. When combining these results with the results presented in literature one is able to build a consistent model for the surface structure of the V₂O₅/γ-Al₂O₃ catalyst when assuming the D-layer to be the predominant face of the support crystallites. Further investigations, which will consider the stability and thermodynamics of the proposed structure, should give a conclusive answer whether it is really possible to pinpoint the location of the atoms on the catalyst.

fig. 5.8 Three-dimensional model of structure of the V₂O₅/γ-Al₂O₃ catalyst studied. (red: V, blue: O, white: Al)
6 CONCLUSION AND IDEAS FOR THE NEAR FUTURE

LEIS has been used to study the surface structure of V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ catalysts as a function of V$_2$O$_5$-loading. At low loadings (< 7 wt%) the vanadium species appears to be optimally dispersed over the support, while at medium loadings (< 11 wt%) multilayered structures are formed. Three-dimensional models for the surface structures based upon the preferential exposure of the (110) D-surface of the spinel structure of support, are proposed.

This investigation is another example where the use of absolute signals has provided much more information from LEIS experiments than can be obtained by the use of signal ratios. It is, however, essential to keep the ion scattering conditions constant and to compensate surface charging when performing absolute LEIS measurements.

Further investigations on the V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ catalyst will be carried out with the scientists from Delft University of Technology. Pore distributions investigations show a decrease of the pore sizes by about 0.3 nm. This supports the monolayer deposition. The preparation of the catalyst shows two regimes in the deposition of the vanadium oxide species. The first at low temperatures shows a fast increase until a equilibrium at 7 wt% is reached. Is the temperature increased then a slow deposition takes place until a new equilibrium is reached at about 14 wt %. These regimes correspond nicely with our results, but because a calcination step is performed afterwards the relevance is not yet clear. In the near future the performance of the catalyst as a function of loading in a simple oxidation process will be studied. The same regimes should be distinguished. Another suggestion is to study the micro crystallites with the use of high resolution electron microscopy to determine the preferential exposure of the alumina face. Nicely faced crystallites should be detected. At last force field cluster calculations are recommended to investigate the stability of the proposed structure and the role of OH-groups on the structure of the support.

As a result of this investigation a lot of other systems were put forward for LEIS studies, like the V$_2$O$_5$/TiO$_2$ catalyst. Unfortunately it has the disadvantage that, because of the small difference in mass of Ti and V, the peaks are not completely separated. Another monolayer catalyst Re$_2$O$_7$/$\gamma$-Al$_2$O$_3$ shows a characteristic change in catalytic activity. This could be uncovered by LEIS experiments. The preliminary results of the study of a monolithic catalyst are presented in appendix B. Another possibility would be to add an element on the support. One could study for example the real Wacker catalyst, Pd/V$_2$O$_5$/$\gamma$-Al$_2$O$_3$ or add Co or Ni to the MoO$_3$/$\gamma$-Al$_2$O$_3$ HDS catalyst, which is of real interest to industry.
REFERENCES

APPENDIX A THE SIMULATION PROGRAM LATUSE/SARCH

The program (version 2.0) consists of the different programs LATUSE and SARCH. LATUSE (written by K. Hermann, Berlin, Germany) and SARCH (written by M.A. Van Hove, Berkeley, California, USA) can interact and can both be used to visualize atomic structures. Both are IBM PC XT/AT compatible.

LATUSE (lattice use) can be used to determine and visualize lattice planes and surfaces of periodic lattices. For a specific lattice geometry the surface layers can be determined when the Miller indices are defined. Sections of the surface structure can be displayed starting with any layer. The structure can be visualized as dots or three-dimensional as balls which radii can be inserted. If the program is used with a EGA high resolution screen the colour of different atoms or layers can be defined separately. Simple manipulations like enlargement/reduction, rotation, and translation can be performed. Geometries of several standard lattices (sc, fcc, bcc, hcp, diamond, NaCl, CsCl, zincblende, graphite) are directly available, but there is an option to build a lattice from scratch too. The lattice vectors and the vectors to every atom in the unit cell can be inserted. The unit cell is then multiplied to obtain the lattice and the surface planes. The unit cell of the structure built, can be saved in a file. Examples of the structures generated by LATUSE can be found in chapter 4 where the faces of the spinel structure are displayed (fig 4.5-4.7).

fig. A.1 Example of the ball/stick mode of SARCH, a tetrahedrally surrounded Si atom in SiO₄.
SARCH, surface architecture in short, can not only be used to produce surfaces of periodic systems. It is possible to construct the surface structure atom by atom, and layer by layer. Interacting with LATUSE a face of periodic lattices can be constructed and displayed. This surface can then be manipulated by adding or deleting atoms. SARCH has an additional option to manipulate groups of atoms which can be used to multiply, or delete more than one atom. There is also an option where distances, in nm or in lattice vectors, between atoms can be determined. Besides displaying the structure like LATUSE, 2D (dots) or 3D (balls), there is an option which is called the ball and stick mode. In this mode the balls can be connected by sticks which represent bonds. The radius of the balls and sticks and the maximum and minimum length of the bond can be inserted. An example of this mode is shown in fig A.1. An example of a structure built atom by atom with SARCH is shown in full colour in fig 5.9.

The program has no possibilities to print or reproduce the displayed structure. Some possibilities are suggested but those where not available or involved photography. The solution was found in a memory resident version of PAINTBRUSH. This program can capture the screen and save it to disk. If then the normal active version of PAINTBRUSH is started this screen can be manipulated. Colours can be changed, lines, text, pictures can be added. The screen can also be sent to a printer. To produce full colour picture a inkjet printer is needed. The inkjet printer that was available was however not compatible with the program. The printer driver of that inkjet was not included in the program. This problem was solved by the use of the program PIZZAS. This program can also be used to capture a EGA colour screen, but further manipulation is not possible. With this program the screen generated with PAINTBRUSH could be reproduced on the inkjet printer.

The program has proved itself a powerful tool in producing presentations of surfaces. There is however room for improvement. The communication between LATUSE and SARCH has failed several times. It was not possible to load a surface of the spinel structure built by LATUSE into the SARCH program. Furthermore it proved very difficult and complicated to generate output of the structures. Another point is that when saving several structures in one file, the file can destruct itself and all its information is lost. And finally last I would like to mention the fact that in SARCH only the positions of the atoms can be saved. The colours, radii, nor rotations can be saved which makes fast generation of a structure impossible. When a new improved version of the program is available, one should consider to buy it.
APPENDIX B MONOLITHIC CATALYSTS

Another totally different system that has been studied is a monolithic catalyst. This catalyst is usually made from a ceramic and its basic form is a block of material through which pass macroscopic holes (1 to 20 mm). A few examples of monolithic structures are shown in fig B.2. On the monolith studied a layer of $\gamma$-Al$_2$O$_3$ is deposited. This configuration combines rapid gas flow with a strong structure and the high specific surface of the alumina. On the alumina Pd/Pt particles are deposited. The catalyst described can be used for the exhaust treating of cars. Spectra obtained from the studied structure is shown in fig B.1. Although difficult the active components can be detected. Further research will be performed to obtain quantitative results and show the effect of steaming on the catalyst.

![Graph showing LEIS experiments on monolithic catalysts.](image)

fig B.1 LEIS experiments on monolithic catalysts. The active phases are Pt and Pd. The figure shows the LEIS spectras of the samples M13 (untreated) and M19 (steam treated).
Examples of commercial available monolithic structures, (a) (upper) Corning W-1 supports, (b) (lower) DuPont Torvex supports.