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Spinel- and perovskite-type oxides: a low-energy ion scattering study

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Award date:
1994

Link to publication
SPINEL- AND PEROVSKITE-TYPE OXIDES:
A Low-Energy Ion Scattering Study

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June 1994
Acknowledgements

The last nine months of my studies, which I spent in the Surface and Interface Physics Group at the faculty of physics at the Eindhoven University of Technology, have been very pleasant and instructive to me. I owe special thanks to Jean-Paul Jacobs, my supervisor, for his continuous aid and coaching during the project. Also Hidde Brongersma deserves a word of gratitude, not only for giving me the opportunity to work in his group with stimulating people, but also for the possibility to do a project in the group of Robert Baudoing-Savois in Grenoble in 1992.

Concerning the preparation of the ferrites I would like to thank M.R. Anantharaman and Hans Dalderop, who was always willing to assist me with decomposition and XRD experiments. Thanks go to M. Valenzuela and his group for the catalytic activity measurements they performed. Leo van IJzendoorn deserves special thanks for the work he did on the ferrites using PIXE, and Adelheid Elemans for the AAS measurements. I also thank Harm van de Heijden en Rob van Kempen for doing the Mössbauer experiments.

The cooperation with Sylvia Meijers and Tjaarda Pruys van der Hoeven from the group of prof. Ponec (Gorlaeus Laboratories, Leiden) in the study of aluminates has been a nice and fruitful one.

Furthermore I would like to thank the people who supported me with some perovskite samples: Prof. Blasse and Dr Meyerink from the University of Utrecht, Ir Sywert Brongersma from the Free University of Amsterdam, Prof. Meyer from the Kernforschungszentrum in Karlsruhe, Germany, and finally Dr Ydo from the Gorlaeus laboratories in Leiden.

I would further like to thank all my fellow graduate students, for offering me an enjoyable stay, especially Jeroen Helwegen with whom I shared the NODUS. I am grateful to vacuum expert Gerard Weijers and system manager Wijnand Dijkstra for their technical support.

I realize that the pleasant and colourful times I spent the past six years with climbing, canoeing, volleyball etc. on the one hand and profound discussions about physics or other subjects on the other hand, are primarily due to the members of the debating club SPECTRA. Thanks guys!

Finally I want to thank my parents. They always supported and encouraged me during my study in Eindhoven and I therefore dedicate this report to them.
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Summary

For two series of spinel-type oxides (AB₂O₄) activity measurements were combined with quantitative surface analysis by Low-Energy Ion Scattering (LEIS). Since LEIS only probes the outermost atomic layer, the catalytic performance can in this way be related to the surface composition. The research concerns the inverse ferrites ZnₓMg₁₋ₓFe₂O₄ (0 < x < 1) and the normal aluminates Co₁₋ₓAl₂ₓO₄ (0 < x < 2). The results on the ceramic ferrites show that for inverse spinels octahedrally coordinated B-cations are present on the surface, whereas tetrahedral A-sites are almost invisible. The catalytic activity measurements of butene to butadiene did not show the expected behaviour, since it was not possible to synthesize magnesium containing ferrites having high surface areas. The study of the normal spinel Co₁₋ₓAl₂ₓO₄ is in agreement with the model where only octahedrally coordinated B-sites are exposed on the surface. Results on both ferrites and aluminates can be explained by a preferential exposure of the (111)B or (110)D plane. Alternatively, it is possible that tetrahedral sites are present just underneath the surface due to segregation of octahedral sites. The aluminates show 10% inversion at maximum. Furthermore, it was found that in the mechanism for selective reduction of nitrobenzene to nitrosobenzene, ensemble size effects play an important role: at least four cobalt cations are necessary to provide a surface site which is active in the selective reduction. First LEIS results on perovskite-type oxides (ABO₃) show a preferential exposure of one cation as was seen for the spinels. It was observed that the twelvefold coordinated A-sites are favoured at the surface, while only a small amount of the octahedrally coordinated B-site could be detected by LEIS.
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Spinel- and perovskite-type oxides: A LEIS study
CHAPTER 1

Introduction

1.1 Surface science

Processes that occur at surfaces of solids are of great importance in fields ranging from semiconductor technology to heterogeneous catalysis. Basic research in solid state science is increasingly confronted with problems connected with surface effects, since all solids have boundaries. The knowledge of surface properties is, however, still inferior to that of bulk phases due to the additional experimental and theoretical complications associated with the absence of the third dimension. One can visualize a surface, formed as the result of a cleavage along a crystallographic plane of the bulk material. The surface atoms will then exhibit more or less unsaturated valencies with a strong tendency for lowering the free energy. This can be achieved by forming chemical bonds with particles arriving from the gas in which the solid is placed. In order to maintain the original state long enough to conduct experiments, it is therefore of great importance that the pressure of the gas above the surface is kept low enough, which usually requires ultra high vacuum conditions. A large variety of experimental techniques has been developed over the last three decades, since UHV became available. They are based on the interaction of surface atoms with photons, electrons, neutrals, or, as in this work, with ions. A vacuum of at least $10^{-4}$ mbar is necessary for ions, because otherwise their main free path in the gas phase would be too small. Still, at that pressure, the surface will be quickly contaminated by the gas atmosphere. Usually a pressure of at least $10^{-9}$ mbar will be necessary to provide enough time for performing experiments without the surface being totally covered by sticking gas particles. This prevents the application of surface analysis methods under realistic conditions (1 atmosphere or higher), like is frequently encountered in heterogeneous catalysis. However, in literature examples can be found where a low pressure surface analysis is extended to high pressure conditions [1]. Also in this thesis, a correlation between catalytic activity measurements in reaction conditions and a Low-Energy Ion Scattering (LEIS) surface study will be presented. Only one surface analysis technique can never supply all relevant parameters. More than one technique usually have to be combined for presenting a complete picture of the analysed object. For the necessary characterization of bulk structure and stoichiometry, Proton Induced X-ray Emission (PIXE), Atomic Absorption Spectrometry (AAS), X-Ray powder Diffraction (XRD) and Mössbauer Spectroscopy have been used in addition to the surface analysis by LEIS.

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1.2 Oxides

The use of oxides in physical and chemical applications is widespread. The application of oxidic materials as catalysts in several oxidation and reduction reactions has become extensive. Corrosion protection is often ensured by a small oxidic layer. In the fast developing field of electrochemistry, oxides are used in fuel cells because of the ease at which oxygen can be exchanged.

A large group of oxidic compounds exhibits the spinel or perovskite structure. They are most widely applied and many properties concerning structure, stoichiometry, magnetic properties etc. have been extensively studied in recent years. However, most of the published work refers to characteristics of the bulk. In view of the importance of catalysis nowadays, it is almost surprising that little work has been done so far on the investigation of the surface of these oxides. Catalytic reactions do occur at the surface of the catalyst and therefore, knowledge obtained from the surface constituting elements can help understanding reaction mechanisms. It is known that specific elements or compounds can serve as a promoter, increasing the rate of the reaction, but even more often, the reason why is not perceived.

The aim of this project is to determine the surface elemental composition of spinel- and perovskite-type oxides and the possible relation to their catalytic activity. We investigated the catalytic properties of some polycrystalline materials which belong to the category of spinel ferrites (important as magnetic materials and in catalytic oxidation reactions) and aluminates (catalysts in selective reductions) and studied the surface composition of these materials by employing Low-Energy Ion Scattering Spectroscopy or in short LEIS. Evaluation or knowledge of catalytic properties together with surface structure data can establish the cation arrangement with respect to the bulk. Catalytically active and inactive cations are exchanged in the two possible interstitial positions of the spinel structure. It will be shown in this thesis that this is an elegant method for correlating LEIS and activity.

In chapter 2 of this thesis, the basic theory and experimental procedure of LEIS are described. Chapter 3 will give several techniques for preparing spinel structured ferrites and aluminates. Phase, structure and stoichiometry of all studied samples were thoroughly investigated. These characterization techniques are described in chapter 4. The results for the spinel ferrites and aluminates are presented in chapter 5. Finally, in chapter 6, the first results of a LEIS surface study of some perovskite-type materials are presented. Like the spinel structured oxides, it might be possible that perovskites also exhibit only certain sites at the surface.


CHAPTER 2

Low-Energy Ion Scattering

2.1 Introduction

Low-Energy Ion Scattering is a surface sensitive technique that can provide information about the structure and composition of the outermost atomic layer of a material, which can be a powder, a polycrystalline sample or a single crystal. This makes this method extremely valuable as a complementary technique in the surface analysis of multicomponent materials (next to XPS, AES and SIMS). It is, for example, a powerful tool in the characterization of catalysts, where the knowledge of surface composition is important for the understanding of the catalytic behaviour.

In a LEIS experiment mono-energetic gas ions are directed onto the surface. In principle, the physically relevant information is obtained by measuring the energy loss of the scattered ions. This energy loss is solely dependent on the mass of the atoms in the surface, so that the measured spectrum can be interpreted as a mass spectrum of the surface. A LEIS-experiment is done with inert noble gas ions with a relatively low energy (0.5 - 5 keV). In that case, the large surface sensitivity of the technique is provided by the large differential cross-section for ion scattering by surface atoms and by the high neutralization probability of the ions because of their large electron affinity. In this chapter the basic principles of LEIS will be described together with the experimental setup.

2.2 Basic principles

2.2.1 The binary collision model

In an ion scattering experiment, a beam of ions is directed onto the target surface. As a result of collisions with surface atoms, a fraction of these ions will be backscattered as neutrals, metastable particles and ions. In this experiment only the backscattered ions are detected. The interaction between the surface atoms and the incoming ions can be described, in a first approximation, using an elastic, binary
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collision model based on simple classical mechanics. This model is only valid when the following assumptions can be made:

- The de Broglie-wavelength of the ions should be much smaller than the interatomic distance at the surface. For a 3 keV $^4$He-ion the de Broglie wavelength is 2.6 mÅ, while the distance between two surface atoms is in the order of several ångstroms. Therefore, diffraction effects can be neglected.
- The collision between the incident ion and a surface atom can be described by an interatomic repulsive potential between the nuclei: a screened Coulomb potential is used. This means that the collision can be considered elastic.
- The influence of neighbouring atoms should be negligible, so that a collision can be considered binary. The distance of closest approach is about 0.1 Å and the interatomic distance several ångstroms, so this assumption holds.
- The interaction time of the collision should be much smaller than the vibration time of the surface atoms. The former time is about $10^{-16}$s, the latter about $10^{-13}$s. Therefore, during collisions the surface atoms can be considered at rest.

![Figure 2.1: Schematic view of the binary collision of the incident ion and the target atom](image)

In figure 2.1 the scattering of the ion is schematically shown. As the collision can be regarded as a simple binary collision a simple and straightforward formula can be deduced from the laws for conservation of energy and momentum. The incident ion with mass $m_{ion}$ and initial energy $E_i$ hits the surface and is scattered from a surface atom with mass $m_{atom}$ over an angle $\theta$. For the final energy $E_f$ of the ion after the
collision, the following expression holds, where \( r \) depicts the ratio between \( m_{\text{atom}} \) and \( m_{\text{ion}} \):

\[
E_f = \left( \frac{\cos \theta \pm \sqrt{r^2 - \sin^2 \theta}}{1 + r} \right)^2 \cdot E_i = K \cdot E_i.
\]  

(2.1)

\( K \) is called the kinematic factor. This equation gives a meaningful solution if \( r^2 > \sin^2 \theta \). When \( r > 1 \) only the plus-sign applies, whereas for \( r \leq 1 \) both signs give a physical solution. In the NODUS LEIS apparatus the scattering angle is fixed to 142°. This implies that only backscattered ions will contribute to the signal and therefore, atoms with a mass lower than the probing noble gas ions cannot be detected.

2.2.2 Interpretation of LEIS spectra

In LEIS experiments the energy distribution of the scattered ions at known \( E_i \), \( m_{\text{ion}} \) and \( \theta \) is measured. A LEIS spectrum arises when the measured signal is plotted against the energy of the backscattered ion. A typical spectrum is given in figure 2.2.

![LEIS spectrum of Co\(_2\)AlO\(_4\)](image)

Figure 2.2: LEIS spectrum of Co\(_2\)AlO\(_4\)

From the peak positions and equation (2.1) the mass of the surface atoms can be deducted. The peak height, or better, the peak area is a measure for the relative amount of a specific element at the surface. It should be noted that peak areas for
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different detected elements cannot be compared in a direct way due to the fact that
differential scattering cross-sections and neutralization probabilities are different. It
is nevertheless possible to obtain some quantitative details next to the directly visible
qualitative information by making use of calibration samples. This will be described
in the next paragraph.

The mass resolution that can be obtained in a LEIS spectrum depends on the
scattering angle and the mass of the ion and primary energy used. Peak broadening
is caused by instrumental factors as well as by the scattering process itself. The
spreading in the primary energy and scattering angle finds its origin in the
construction properties of the apparatus, e.g. the finite widths of the apertures and
the finite angular acceptance of the analyser. Furthermore, the peak is broadened by
the vibration of target atoms. This vibrational energy is of the order kT (25 meV at
room temperature), which can usually be neglected compared with the energy of the
primary ions. This thermal broadening gets relatively more important at low primary
energies and at high temperatures. All these effects result in a symmetrical
broadening. Often a tail in the spectrum is seen, both on the low and on the high
energy side of the surface peak. This is an asymmetrical peak broadening and is
cased by inelastic scattering processes, such as electron excitation or reionization
(low energy side) or by multiple scattering of ions, where the total energy loss is less
than after a single collision process (high energy side). From the height of the low
energy tail one can get an idea of the composition in the second layer. Neutralized
ions can be reionized by atoms in this layer and contribute to the LEIS signal. Due to
the higher energy loss they are responsible for the low energy tail. Neutralization is
mainly responsible for the surface sensitivity of LEIS. The different neutralization
processes will be described hereafter.

The surface sensitivity of LEIS is guaranteed when noble gas ions are used. Due
to the relatively high differential cross-section (about $10^{-3}$ Å²/sr for 3 keV 4He ions)
and the fact that a large part of the ions will be neutralized in the first few layers of
substrate atoms, the majority of the primary ions that reach the detector as ions have
scattered from the outermost layer. There are several processes possible for
neutralization. In Auger neutralization the hole in the 1s subband of a He-ion is filled
by an electron from a higher energy level of a surface atom. The released energy
causes the emission of a second electron from the surface. In resonant neutralization
an electron can be exchanged without loss of energy if the energy level of an electron
from the surface atom equals the level of a hole in a subband of the ion. Which
process is the dominant one in LEIS experiments is still debatable [2]. The basic
mechanisms were firstly described by Hagstrum [3]. However, it is not in the scope
of this thesis to give a detailed description of all known neutralization processes and
we suffice with a schematic overview in figure 2.3.

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2.2.3 Quantification of the LEIS-signal

As mentioned above, the ion yield scattered from different surface atoms cannot be compared directly. Several factors contribute to the signal as is described in equation (2.2).

\[ S_A = c \cdot T \cdot I_{tc} \cdot P_A^* \cdot n_A \cdot \left( \frac{d\sigma}{d\Omega} \right)_A \cdot R. \]  

(2.2)

- **\( S_A \)** = LEIS signal
- **c** = instrumental factor (depending on analyser and detection efficiency)
- **T** = transmission function of the analyser (-\( E_i \))
- **\( I_{tc} \)** = target current
- **\( P_A^* \)** = ion fraction of ions scattered from atom A
- **\( n_A \)** = atomic density of element A on the surface
- **\( \frac{d\sigma}{d\Omega} \)** = differential cross-section
- **R** = factor to incorporate the influence of surface roughness

For each element in the sample one tries to find the surface concentration. \( S_A \), \( I_{tc} \) and \( E_i \) (from which the transmission T is deduced) are determined experimentally, whereas \( \frac{d\sigma}{d\Omega} \) can be calculated when the interaction potential is known. In LEIS usually an interaction potential is considered which is determined by the nuclei
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charges and the screening effect of the electron clouds. This screened coulomb potential has the general form

\[ V(r) = \frac{Z_1 Z_2 e^2}{4 \pi \varepsilon_0 a} \phi\left(\frac{r}{a}\right), \]  

(2.3)

where \( \phi \) is the Molière approximation of the Thomas-Fermi screening function and \( a \) the screening length [4,5]. The influence of roughness can be considered equal for different powders when scattering conditions are kept constant [6]. This leaves the ion fraction \( P_A^+ \), defined as the relative amount of ions that survive the scattering as an ion, as the only unknown factor in (2.2). The reason for this is that the exact behaviour of the ions in an ion-atom collision is still not well understood. However, a model has been proposed by Hagstrum [3] in the case of Auger neutralization. A strong dependence on the primary energy of the ions, the scattering angle and the ion-atom combination is assumed:

\[ P_A^+ = \exp \left[ -a \left( \frac{1}{v_i} + \frac{1}{v_f} \right) \right]. \]  

(2.4)

In this formula, \( a \) is a characteristic velocity, \( v_i \) the ion velocity before scattering and \( v_f \) the ion velocity after scattering. The fact that neutralization can occur at the incoming trajectory as well as at the outgoing trajectory is incorporated in this formula. From this formula it follows that the neutralization probability increases when the time spent by the ion in the interaction region of the surface atom is longer. Therefore, the ion fraction increases at higher primary energies of the ions. The characteristic velocity \( a \) depends on element specific properties such as the exact location of the energy levels in ion and atom.

Since a general theory for the ion fraction does not yet exist, the characteristic velocity has to be determined experimentally. Together with the influence of roughness, which is hard to determine, direct quantification following equation (2.2) is difficult.

A method that offers direct quantification is based on calibration against pure elements. The ratio of the signal of element A in the powder and the signal of the pure element A, measured under identical experimental conditions, gives directly the ratio of A atoms at the surface of powder and pure element.
Equation (2.2) is therefore written as
\[ S_A = \eta_A \cdot \theta_A \cdot R, \]  
(2.5)

where \( R \) is the influence of roughness, \( \eta_A \) the calibrated sensitivity for element A and \( \theta_A \) the surface coverage. The neutralization behaviour should be independent of the chemical environment, thus implying no different sensitivities due to matrix effects. By simple scaling of the sample and calibration signals, the surface coverage can be determined, provided that the influence of surface roughness is known. It was found by Jacobs et al. [7] by calculation that the ratio of \( R \) from a smooth and a rough spinel surface equals 0.6. In this view, the results in following chapters are presented in comparison to a polycrystalline and pure metal calibration sample, if available.

2.3 Experimental setup

2.3.1 The NODUS apparatus

The NODUS machine is one of the four machines in the group FOG (Eindhoven University of Technology) on which LEIS-measurements (= Low-Energy Ion Scattering) are done. NODUS stands for NOnt Destructive Ultra Sensitive. The basic design of this machine was built at Philips Research Laboratories, Eindhoven, in the early seventies and was firstly described by Brongersma et al. [8]. Despite of the recent realization of two very sensitive LEIS machines (EARISS in 1986, ERISS in 1993), the NODUS is still known to be a very reliable working apparatus for surface analysis. The configuration as it is used nowadays is drawn in figure 2.4. A mono-energetic ion beam is produced in the ion source (1). The ions are mass selected (2), deflected (3) and focused (4) onto the target, which is perpendicularly to the ion beam placed on a carousel (7), in which twelve samples holders can be placed. In that way it is possible to analyse several samples under the same measuring conditions. Only ions scattered over 142° are detected. They are collected and energy analysed in a cylindrical mirror analyser (CMA, 6). A detailed procedure for operating the NODUS is given by Rosink and Helwegen [9].

2.3.2 Cleanness of the sample: the UHV system

LEIS is a technique that is sensitive only to the outermost layer. It is therefore obvious that contamination of this surface layer should be avoided. During the preparation of the sample as well as during experiments the achievement and
Figure 2.4: Schematic representation of the LEIS apparatus NODUS: (1) ion source, (2) mass filter, (3) deflection plates, (4) einzel lenses, (5) aperture, (6) CMA, (7) carousel, (8) turbo molecular pump, (9) ion getter pump, (10,11) valve, (12) gas inlet needle valve
maintaining of a clean surface is thus of high importance. Contamination of the samples before measurement is avoided as much as possible by cleaning the preparative tools with demineralized water and ethanol. Under measuring conditions the cleanness of the sample is at best guaranteed in Ultra High Vacuum (UHV). In the NODUS, UHV is obtained by a differential pumping system which consists of a small turbo molecular pump (30 l/s) near the ion source, a turbo molecular pump (145 l/s) just before the aperture (n° 5 in figure 2.4) and finally an ion getter system with a titanium sublimation pump, which is cooled with liquid nitrogen. The background pressure that can be obtained is about $5 \cdot 10^{-10}$ mbar. When the ion beam is operated, the base pressure increases up to $2 \cdot 10^{-8}$ mbar. This raise is primarily due to the inert gas ions and does not influence the measurements.

2.3.3 Ion source and beam

The ion source, a Leybold IQE 12/38, is schematically shown in figure 2.5. It consists of a ring-shaped tungsten filament cathode, an anode cage, an electron repeller and an ion extractor. Electrons emitted from the cathode are accelerated towards the anode cage, where they can be captured. However, it is more likely that they miss the anode and pass through the cage. They will subsequently be accelerated back to the cage by the repulsive electron shield. The electron can pass the cage area several times before it is finally captured by the anode cage. When gas is introduced in the source, the atoms will be ionized by collisions with the accelerated electrons. Once ionized, the gas particles will be pulled out of the cage by the ion extractor electrode. The extracted ions can now be accelerated to the desired energy. A massfilter, consisting of an adjustable electric and magnetic field, perpendicular to one another, selects the desired ion mass, after which the beam is directed onto the target via an aperture, a set of deflection plates and electrostatic lenses. An einzel lens just in front of the sample can be used to focus the beam from a diameter of 5 mm down to 0.5 mm. A typical beam current in this study was 60 nA, whereas the spot size was usually about 20 mm$^2$. This means an ion dose of $1.9 \cdot 10^{12}$ s$^{-1}$ cm$^{-2}$.

2.3.4 The cylindrical mirror analyser

LEIS is based on an analysis of the energy distribution of ions scattered from a surface. In the cylindrical mirror analyser, the scattered ions are focused electrostatically in such a way that only those ions with energies within a certain small range pass through the analyser and arrive at the detector. Focusing is achieved by applying a potential to create a cylindrical electric field between the two

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coaxial electrodes. The outer cylinder is held at a positive potential with respect to the inner cylinder. The analyser allows ions with energy $E$ and energy spread $\Delta E$ to pass through the final slit to the detector; the energy resolution $\Delta E/E$ is constant and in our case about 10%. The most attractive feature of the cylindrical mirror analyser is its high sensitivity due to the acceptance of a full 360° solid angle of particles. In the
NODUS only ions scattered over an angle of 142° are selected. The CMA is schematically shown in figure 2.6. The detection system is based upon the gain provided by electron multipliers (8 channeltrons). These channeltrons have a conelike opening and a continuous tube of high resistivity, semiconducting glass with a high secondary emission coefficient. A large electric field is applied along the tube, and incident ions create an avalanche of secondary electrons. The detector efficiency is not clear due to the fact that it is not possible to operate the channeltrons in saturation mode. This is one of the reasons that a straightforward quantification of the LEIS-signal according to equation (2.2) is not possible.

2.3.5 Sample charging

An insulating material will be charged when the ion beam is directed onto its surface. Due to the successive deceleration and acceleration of the ions during collisions with surface atoms the overall energy loss will be less and the LEIS spectrum is shifted to higher energies. This effect is shown in figure 2.7. A compensation for this charging is necessary, since the existence of certain elements on the surface is determined from LEIS final energies.

![Graph showing influence of charging on the LEIS spectrum of Co₁₅Al₁₅O₄](image)

**Figure 2.7: Influence of charging on the LEIS-spectrum of Co₁₅Al₁₅O₄**
An expression for the charging is given in equation (2.6).

\[ E_f' = (E_i - \Delta E) \cdot K + \Delta E. \]  

(2.6)

In here, \( E_f' \) represents the measured energy, \( E_i \) the primary energy, \( K \) the kinematic factor and \( \Delta E \) the energy shift due to charging. Scattering from surface atoms causes an (elastic) energy loss so that the influence of deceleration before scattering and acceleration after scattering do not cancel out. In the NODUS the compensation is ensured by ring-shaped filament emitting low-energetic thermal electrons which are deflected towards the target surface (see figure 2.6).

2.3.6 Pretreatment

A pretreatment chamber is connected to the main vessel, where it is possible to insert e.g. oxygen or hydrogen gas for pretreatment. An oven for heating samples is mounted as well. Usually pretreatment is necessary to remove contamination, which is typically carbon. Also most hydroxyl groups can be removed. Heating the samples to 200 °C in 20 mbar oxygen for about 20 minutes is sufficient for this purpose. A further removal of hydrogen is established when analysing the samples due to sputtering by the ion beam. The chamber is seperately from the main vessel pumped by a turbo molecular pump (145 l/s) in order to limit entering of contaminations in the main vessel, when using the chamber as a load lock for fast sample exchange.
CHAPTER 3

Sample preparation

3.1 Introduction

The objective of this study is to get a better insight in the surface structure of spinel- and perovskite-like systems. These materials are widely applied in catalysis and, since a catalysed chemical reaction occurs at the surface of the catalyst, an investigation of the surface characteristics, such as the exposed face and sites, is worthwhile. The influence of cation exchange in these sites on the catalytic properties and the surface composition of zinc aluminates and manganates has been subject to earlier research [10]. A large part of this study has been devoted to the preparation of spinel ferrites. In this chapter several methods will be presented for synthesizing zinc and magnesium containing ferrites. The preparation of cobalt containing aluminates, also analysed in this study, is discussed as well.

In surface science, it is a prerequisite to have a clean surface, that is to say without any contaminations, such as sodium or potassium. These will partly cover the surface atoms incorporated in the spinel or perovskite structure of the catalyst. A consequence is that analysing the proper surface is hindered. It is known that little amounts of an impurity in the bulk can cause a reconstruction of bulk or surface or induce segregation. The presence of contaminations can induce the formation of totally different phases as expected from reaction equations (e.g. MgO and $\alpha$-Fe$_2$O$_3$ instead of the proper spinel phased MgFe$_2$O$_4$ [11]). Also, the presence of impurities has a non-negligible effect on the general catalytic performance of the spinel system. Stobbe [12] reported that the addition of potassium to the magnesium-ferrite system has a promoting effect on the reaction rate and selectivity for the dehydrogenation of butene to butadiene. Ponec et al. [13] reported the same influence of sodium and potassium on the catalytic behaviour of aluminates. However, Vepřek et al. [14] showed a deactivation of a CuMn$_2$O$_4$ catalyst in the presence of potassium.

For the above mentioned reason salt contamination is avoided as much as possible. Therefore, all chemicals used are fresh and of high purity (pro analysi, Merck). Furthermore, emphasis was put on the preparation of single-phasic compounds for obtaining a good model system. Both low and high temperature preparation techniques were used. The advantage of a low synthesis temperature is that it

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Sample preparation

provides a large surface area (typical 10 m$^2$ per gram), which is interesting for catalysis, where a large activity per gram catalyst is required. However, the preparation of mono-phasic compounds proved to be very difficult. On the other hand, a high calcination temperature usually ensures good structure forming but has the disadvantage that contaminations are hardly unavoidable.

We used five preparation techniques in total: the ferrites (spinel structure) have been made by decomposing coprecipitated mixed oxalates at low temperature (1) and with a conventional ceramic method at high temperature (2). Both the aluminates (spinel) and a perovskite (BaZrO$_3$) were prepared with the so-called citrate process (3). The ferrites were also made from mixed hydroxides in liquid ethanol (4) and with ammonia (5). The following paragraphs will give a detailed description of the applied preparative techniques.

3.2 Preparation of ferrites

3.2.1 Decomposition of coprecipitated mixed oxalates

This method is based on the preparation of hydrated mixed oxalates and is a low temperature technique. In view of the goal of this project [15], a series of ferrites containing zinc and magnesium ions has been prepared: Zn$_x$Mg$_{1-x}$Fe$_2$O$_4$ ($0 < x < 1$). The zinc and magnesium cations are not catalytically active, but due to the tetrahedral site preference of zinc and the octahedral site preference of magnesium, it should be possible to relate a possible preferential exposure of a specific site at the surface to the activity of the catalyst. A detailed description of the spinel structure and the applications of this series is given in chapter 5. The mixed oxalates were prepared as fine yellow crystalline powders and served as precursors for the forming of spinel structured materials by decomposition (see also Reijne [6] and Anantharaman [16]).

The solubility of the metal oxalates in water is an important parameter in the synthesis of the spinels. It has therefore to be taken into account when weighing the proper amount of the basic ingredients. The solubilities of magnesium, zinc and ferrous oxalate were taken at 100 °C: 0.08 g/100ml (MgC$_2$O$_4$), 0.00079 g/100ml (ZnC$_2$O$_4$) and 0.026 g/100ml (FeC$_2$O$_4$) [17]. The basic chemicals, which have been used in the preparation, were FeCl$_2$·4H$_2$O (green), Zn(NO$_3$)$_2$·6H$_2$O (white) and Mg(NO$_3$)$_2$·6H$_2$O (white).

These substances were dissolved in 300 ml of demineralized water in the desired ratio to form a solution of 1 M total metal concentration. A treatment with a solution of oxalic acid, taken in excess, follows; the total amount of water used was 1300 ml.
Oxalic acid was dissolved into the metal-salt solution drop by drop, aided by constant stirring. The temperature of the solution was maintained at 60 °C until the precipitation was complete. The precipitate was washed several times with hot water and finally dried at 100 °C overnight. A schematic view of the preparation setup is shown in figure 3.1.

![Sample preparation](image)

**Figure 3.1: A schematic overview of the preparative experimental setup**

The decomposition scheme for the synthesis of the mixed oxalate to form a spinel phase is based on the following reaction scheme for the forming of magnetite, which was taken from Anantharaman et al. [16]:

\[
\begin{align*}
\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} & \rightarrow \text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O} \\
\text{FeC}_2\text{O}_4 & \rightarrow \text{FeO} + \text{CO} + \text{CO}_2 \\
4\text{FeO} & \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe} \\
3\text{Fe} + 4\text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2 \\
3\text{FeO} + \text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2
\end{align*}
\]

These reactions have to take place in an inert atmosphere of oxygen free nitrogen with the presence of moisture. Addition of water vapour increases the yield of spinel phase as was reported in literature [16]. Therefore, nitrogen was bubbled through water at 32 °C and flowed continuously over the dihydrated mixed oxalate for about 30 minutes and then isothermally decomposed at 600 °C for 10 hours, still under
Sample preparation

nitrogen flow conditions. A schematic view of the decomposition setup is shown in figure 3.2.

Figure 3.2: A schematic overview of the decomposition experimental setup. (1) thermostat, (2) stirrer, (3) heater, (4) contact thermometer, (5) gas bubbler, (6) heating coil, (7) sample holder assembly, (8) crucible containing sample, (9) furnace, (10) thermocouple

For the precipitation of $\gamma$-$\text{Fe}_2\text{O}_3$ the sample holder assembly was cooled in the same atmosphere to 250 °C, instead of removing the intermediate $\text{Fe}_3\text{O}_4$ from the furnace. Moist technical air was led over the precursor, the system being kept at isothermal conditions for 2 hours. This yielded fine crystallites of gamma ferric oxide. The reaction can be written as follows:

$$\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \text{ (controlled oxidation)}$$

3.2.2 Ceramic method

The zinc and magnesium ferrites were also prepared by employing a conventional solid state reaction method. Because of the only low specific surface that
can be obtained in this way, they were meant to serve as calibration samples in the surface study, next to the catalysts prepared as described in the previous paragraph.

Appropriate amounts of ZnO and MgO were mixed with the α-phase of iron oxide in an agate mortar and prefired at 500 °C. The final firing (sintering) was carried out at 1200 °C for about 24 hours. The α-phase of iron oxide was made as follows: ferrous oxalate dihydrate was decomposed in air at around 600 °C for about 3 hours. The resulting product was reddish brown α-Fe2O3. The decomposition of ferrous oxalate dihydrate in air is as follows:

\[
\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} \rightarrow \text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}
\]
\[
\text{FeC}_2\text{O}_4 \rightarrow \alpha-\text{Fe}_2\text{O}_3 + \text{CO} + \text{CO}_2 \text{ (oxygen atmosphere)}
\]

### 3.2.3 Coprecipitation of mixed hydroxides with ammonia

Zinc ferrite (ZnFe2O4) was prepared employing low temperature preparative techniques as described by Sato et al. [18]. A 0.1 M aqueous solution of zinc nitrate and a 0.2 M aqueous solution of iron(III) nitrate were prepared separately. 100 ml of each solution were mixed. While stirring this mixture 25% ammonia was added until the pH reached a value of approximately 9-11 at 50 °C. The precipitate was dried at 100 °C and calcined in air at 500 °C, which yielded zinc ferrite.

### 3.2.4 Cold ethanol method

Because of the difficulties encountered during the preparation of single-phasic ferrites by decomposing mixed oxalates a cold ethanol coprecipitation method developed by Yang et al. [19,20] has been applied as well. This technique was chosen because of the absence of the solubility problem.

Mg(NO3)2.6H2O, Zn(NO3)2.6H2O and Fe(NO3)3.9H2O in the desired ratio were dissolved in ethanol (p.a.) to form a solution of about 0.3 M total metal concentration. A beaker of ethanol (p.a.) was cooled to about -30 °C with dry ice and saturated with ammonia by continuous bubbling to allow rapid precipitation. The salt solution prepared in the first step was sprayed into the ammonia-saturated cold ethanol using the nozzle of a flower spray in order to form a very fine precipitate of mixed hydroxides. It is anticipated that due to spraying of very fine drops it is relatively easy for the hydroxides to be formed: small particles have a higher reactivity. The dry ice was expected to keep the temperature at -30 °C and vigorous agitation was provided throughout the process by means of a magnetic stirrer and with the aid of
Sample preparation

air bubbling. The precipitate was filtered and dried at 100 °C overnight and then ground into a fine powder. This powder was calcined first in vacuum at 500 °C for 2 hours, then in static air at 500 °C for 4 hours and finally in flowing technical air at 700 °C for 2 hours. A problem we encountered with this method is that we were unable to stabilize the precipitation temperature at -30 °C. In addition, the formed precipitate was that fine that only a small part of it remained after filtering. XRD did not show a mono-phasic spinel structure. All this led us to the conclusion that this process was not suitable for serving as the standard preparation method.

3.3 Aluminate preparation by the citrate process

The aluminates were prepared in Leiden by Meijers and coworkers [21] by the amorphous citrate precursor method. This technique ensures a very good mixing of reactants at the atomic level [22,23]. The decomposition is based on the following reaction scheme:

\[ \text{Co(NO}_3\text{)}_2 + \text{citric acid} \rightarrow \text{Co}_2(\text{citrate})_3 \Delta T \rightarrow \text{Co}_3\text{O}_4 \]

The basic materials for the preparation of the cobalt aluminates are the metal nitrates \( \text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) and \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \). These materials in the desired ratios were dissolved in demineralized water. 2.5 M citric acid, taken in the quantity corresponding to the formation of citrates of all cations, was added. The aqueous solution of all components was evaporated at 90 °C under reduced pressure obtained with a water pump. The glass-like, purple amorphous solid product was ground and heated in the stream of oxygen up to 130 °C, followed by a gradual increase of 25 °C per hour up to 550 °C at which temperature the sample was kept for 24 hours in air. The sample was then cooled down to room temperature in 4 hours. Final calcination of the black powder was performed at 800 °C for 24 hours.
CHAPTER 4

Characterization techniques

4.1 Introduction

It is essential in this surface analysis of oxidic materials that the bulk structure of all studied samples is known. If the bulk structure is not correct, the sample cannot be used. To investigate whether or not the material had the right phase, X-ray diffraction has been applied on both spinels and perovskites. Mössbauer spectroscopy is used to determine the Fe cation distribution in tetrahedral and octahedral sites. For bulk stoichiometric measurements Proton Induced X-ray Emission is employed. A few samples were checked with Atomic Absorption to confirm the PIXE results. The catalytic activity of ferrites and aluminates is tested as well. This was done on the coprecipitated ferrites in the oxidative dehydrogenation of butene to butadiene. The test reaction used for the aluminates was the selective reduction of nitrobenzene to nitrosobenzene. For the aluminates the specific surface areas have been determined. In this chapter description of these characterization techniques is given.

4.2 X-ray powder diffraction

A powerful and non-destructive tool to obtain information on the bulk structure of a sample is X-ray diffraction. The basis of this technique is the Bragg equation which describes the condition for constructive interference for X-rays scattering from atomic planes of a crystal. The condition for constructive interference is

$$2d \sin \theta = n \lambda, \quad (4.1)$$

where $\lambda$ is the wavelength of the incident radiation. All the synthesized samples (see chapter 3) have been analysed in order to determine the crystallographic structure and the lattice parameter. The X-ray diffractograms of these fine-ground powder samples were recorded on a Philips (PW 1050/25) X-ray diffractometer using Cu-K$\alpha$ radiation ($\lambda = 1.5418 \ \text{Å}$). Scanning is performed in the Debye-Scherrer configuration, i.e. with the so-called $\theta$ - $\theta$ scan mode. Here, X-rays are incident at an angle $\theta$ with respect to the powder plane. This angle is varied through rotation of the sample (the X-ray source is fixed in position) and the intensity of X-rays scattered through an angle $\theta$
is measured with a proportional detector. The motion of this detector is coupled to the sample rotation in such a way that the angle of incidence equals the angle of detection. It has to be noted that the used equipment only senses impurity phases exceeding concentrations in the order of 1% of the crystal volume [24]. The diffractograms obtained for the ferrites are analysed visually. The XRD data from the aluminates were measured in Leiden [21] and treated with GSAS, a program for single crystal and powder structural analysis [25]. Lattice parameters are calculated making use of a number of reflections. For cubic crystals with planar Miller indices \((h k l)\) and interplanar spacing \(d\), the lattice parameter \(a\) is given by

\[
a = d_{hkl} \cdot \sqrt{h^2 + k^2 + l^2}
\]

and can thus directly be calculated from XRD data. A linear increase or decrease of the lattice parameter as a function of cation substitution indicates that the cations enter the spinel stoichiometry correctly. All samples prepared are studied by XRD to ensure mono-phasic compounds.

### 4.3 Mössbauer Spectroscopy

The Mössbauer effect technique is an effective tool for the determination of the cation distributions in spinel ferrites. It offers the possibility for analysing the magnetic properties of the ferrites: \(\text{MgFe}_2\text{O}_4\) should be ferrimagnetic, whereas \(\text{ZnFe}_2\text{O}_4\) should be paramagnetic. It is known that \(\text{MgFe}_2\text{O}_4\) is an inverse spinel and \(\text{ZnFe}_2\text{O}_4\) normal. Therefore, the amount of Fe ions in octahedral sites is different. With Mössbauer it is also possible to determine the ratio of Fe in tetrahedral and octahedral sites. This is done by calculating the ratio of peak areas [26,27,28]. Both tetrahedrally and octahedrally coordinated iron give their own sextet in a Mössbauer spectrum.

The Mössbauer effect is based on nuclear resonance between energy levels of source and absorber without any recoil. Both emitting and absorbing nuclei have to be bound in a crystal lattice, so that the mass that appears in the expression for the recoil energy becomes the mass of the entire solid, rather than the mass of one atom. The interaction of nuclear electromagnetic moments with the fields of the environment, usually called hyperfine interactions, gives rise to three possible effects. At first an isomer shift of the resonance energy - an overall center shift in the Mössbauer spectrum - can be present. This effect is due to different chemical environments of source and absorber. The main contribution in the Mössbauer spectra of our ferrite samples comes from the internal magnetic field (existing in ferrimagnetic materials) interacting with the nuclear electromagnetic moments, which causes a
Zeeman splitting of the energy levels, even without an external field present. In general two different hyperfine magnetic fields exist, one due to the Fe$^{3+}$ tetrahedral ions and the other due to the Fe$^{3+}$ octahedral ions. At last, a possible electric field gradient causes a quadrupole splitting. For spinels this splitting should only be visible for the sixfold coordinated Fe-ions in the octahedral interstices. Fe-ions in tetrahedral interstices are fourfold coordinated and have cubic symmetry and thus experience no electric field gradient. It is possible to distinguish between these transitions by making use of the Doppler effect. The radiation emitted by the source can in this way be fine tuned to the energy level distance in the iron core.

At the Instituto Mexicano del Petroleo (IMP) in Mexico D.F., Mössbauer spectra of the catalysts (oxalate coprecipitated ferrites) were obtained by Valenzuela and coworkers on a conventional constant-acceleration spectrometer Austin-5600 with a krypton proportional detector. The $\gamma$-ray source was $^{57}$Co, incorporated in a rhodium matrix of 25 mCi. Laser velocity calibration was performed using an iron foil as reference. A standard least squares minimization routine was used to fit the spectra as a superposition of lorentzian lines.

Mössbauer measurement were also done on both ceramic and coprecipitated ferrites by Van de Heijden and Van Kempen in the group Cooperative Phenomena (TUE). A $^{57}$Co source is used. Its decay product $^{57}$Fe emits the applied 14.4 keV $\gamma$-ray radiation. The velocity range of the detector varies from -9 to +9 mm/s. Data is collected in a 1024 channel MCA. Calibration is performed on a Fe target, showing one sextet. All measurements were done at room temperature without external magnetic fields. The spectra were fitted as a superposition of lorentzian lines with the program MM/Sirius, which makes use of a standard least squares minimization routine.

4.4 Proton Induced X-ray Emission

It is very important to know the exact bulk composition of the spinels. In earlier work [29] the two limits of the ferrite series, described in chapter 3, have been studied. The work described in this thesis reports on a whole series, so that it is necessary that bulk ratios cover the series range entirely. PIXE, which stands for Proton Induced X-ray Emission, has shown to be an adequate analysis technique for this stoichiometry checking. Due to its very low detection limit, PIXE is pre-eminently suited for the detection of trace elements (in the order of parts per million, ppm). However, it is not possible to detect elements with an atomic number less than 11, due to the absorption of X-rays with a low energy by the entrance slit of the detector. Magnesium, which has atomic number 12, can for this reason cause problems when
Characterization techniques

one tries to detect it. It will be shown in chapter 5 that we did not encounter any problems whatsoever.

The PIXE measurements were done at the cyclotron laboratory (TUE). 3 MeV protons are bombarded onto a sample. These protons can remove one of the core electrons (K- or L-shell). Electrons from a higher shell can fill up the so induced hole \((t = 10^{-17}\text{s})\). The released energy can be used by the atom for the creation of a free (Auger-)electron or an X-ray photon. So by measuring the energy of the electron (Auger Electron Spectroscopy) or the energy of the photon (PIXE), the excited element can be determined. The amount of a specific element can be determined because each element emits a range of X-rays with characteristic energy: the number of detected X-ray quanta (counts) in a peak of a PIXE spectrum is a measure for the amount of this trace element. However, the sole determination of peak areas belonging to a different \(\gamma\)-ray decay can never lead directly to absolute quantification. Firstly, it is important that the background radiation, originating from bremsstrahlung, is subtracted correctly. The branching ratio, fluorescence probability, ionization cross-section, detector efficiency, transmission coefficient of the absorbers, stopping power and solid angle of the detector all have to be known in order to do a quantitative determination [30].

Since we are only interested in the determination of the ratios of the elements iron, magnesium and zinc, a full quantitative approach was not necessary. The measurements were performed by Leo van IJzendoorn on both ceramic and coprecipitated ferrites. Calculations were done with the PIXE-quantification program PANEUT [31,32].

4.5 Atomic Absorption Spectrometry

Like PIXE, AAS can be used to analyse samples in order to determine small concentrations of metal elements [33]. The technique was performed as an extra check on one coprecipitated (oxalate) and two ceramic samples, because the first PIXE results presented some interpretation problems. A small portion of the material is dissolved in hydrochloric acid. This solution is led via a capillary in a flame of 2500 °C, where the solvent is evaporated and an atomic cloud of the constituting elements remains. The flame is placed before a metal vapour lamp, which emits light characteristic for that metal. The light is guided through the flame via a monochromator and if in the sample the same metal is present, the light will be absorbed. By measuring the decrease in light intensity the amount of metal present can be determined. Materials with known constituents can be analysed in this way by changing the lamps.

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4.6 Catalytic activity of coprecipitated ferrites

Catalytic activity of the coprecipitated ferrites (from oxalate precursors) is tested at the Instituto Mexicano del Petroleo in Mexico City. The oxidative dehydrogenation of butene to butadiene was carried out in a conventional continuous flow system at atmospheric pressure. A mixture of 5 mole % of 1-butene (Matheson C.P.), 5 mole % of oxygen (Linde, 99.6% purity) and 90 mole % of helium (Linde, 99.6% purity) was fed to the reactor. The total flow rate was 60 cm$^3$/min and 0.2 g of catalysts was used for each test reactor. The reaction temperature was 420 °C. The reaction products were analysed using an on-line gas chromatograph. Details of the reaction system and analysis are given by Armendáriz et al. [34].

4.7 Catalytic activity of the aluminates

At Gorlaeus Laboratories in Leiden, the catalytic activity of the aluminates was tested by Meijers and coworkers [21]. The test reaction used is the selective reduction of nitrobenzene to nitrosobenzene. The flow measurements were carried out in an open continuous flow system with a fixed bed reactor as is shown in figure 4.1.

![Diagram of flow system with fixed bed reactor](image)

**Figure 4.1**: Flow system with fixed bed reactor: (BTS) oxygen removal from flow, (MS) molecular sieves, (NB) vessel with nitrobenzene under saturation at RT, (T) temperature read out, (R) fixed bed reactor, (K) sample loop, (HC) temperature control
Characterization techniques

Helium was used as carrier gas and the reaction temperature was 300 ºC. Detection of the reaction products was done using gaschromatic analysis (Chrompack 438A with a packed Tenax column and flame ionisation detector).

4.8 Specific surface area: BET

Determination of the specific surface areas of the aluminates was also performed in Leiden by Meijers et al. [21], where a Quantachrome flow apparatus is used. A mixture of helium and nitrogen (He:N$_2$ = 2:1) is led over the catalyst. In this way the catalyst surface is cleaned by a tenfold nitrogen adsorption and desorption process. The nitrogen is adsorbed at -196 ºC and desorbed at room temperature. The specific surface area is determined from the volume necessary to fill a monolayer, which is detected with a thermal conductivity detector. After each measurement a calibration is performed by injecting a known amount of N$_2$ in the column. The surface is calculated with the BET (Brunauer, Emmet and Teller) equation [6].
Spinel-type oxides

5.1 Introduction

Materials with a spinel structure have many applications nowadays. Spinel-type ferrites are used in the electronics industry for their magnetic properties in passive devices like transformer materials or recording tapes. Another example, which elucidates the variety of applications for these structures, is their appearance in coatings: on NiCr-alloys a spinel structured oxygen layer is formed which serves as a protection against corrosion. A third application can be found in the field of heterogeneous catalysis. Spinel-structured ferrites and zinc aluminates are increasingly being used for the production of olefines from hydrocarbons and for the oxidative dehydrogenation of butene to butadiene [19,34,35,36,37]. Cobalt containing aluminates, as well as manganates, find their way as catalysts in the selective reduction of nitrobenzene to nitrosobenzene [38]. The vacancy ordered spinel γ-Al₂O₃ is used as a support for numerous catalysts.

Much research has already been done on spinels. The presence of active sites, the occurrence of vacancies and the preferential exposure of certain crystallographic planes with respect to the catalytic properties of these compounds have been subject to research. Much work has been devoted to establish the cation distribution in spinels. However, most of the research done is based on bulk properties or related to single crystal studies. Neither of them truly perform an investigation on industrial catalysts which are used in the form of polycrystalline materials. A study of the relation between surface structure and composition and the catalytic activity is new. Only recently attention has been paid to this field of research [10].

It is known that the arrangement of atoms or composition of the surface is different from that of the bulk. Jacobs et al. [10] and Rosink et al. [29] have presented results on ferrites, aluminates and manganates, studied with Low-Energy Ion Scattering. They found that only octahedral sites are exposed on the surface. The question arises whether or not this behaviour holds for a series of inverse ferrites and normal aluminates, when cations in both tetrahedral and octahedral sites are exchanged. Is the substitution linear and what is the effect on catalytic activity? In this
work we present the results on these polycrystalline powders and a comparison is
made between different preparation methods.

This study was done to elucidate the arrangement of cations in the first atomic
layer and to correlate this surface composition with the catalytic properties. Because
ferrites are important magnetic materials, vast literature exists on the role of cation
arrangement in explaining magnetic properties. Vice versa, knowledge of the magnetic
properties of these ferrites combined with structure data can establish the spinel
cation arrangement with respect to the bulk. A suitable analysis technique for this
purpose is e.g. Mössbauer spectroscopy. A structural analysis can be made because
of the ease with which various cations in the two interstitial positions, namely
octahedral and tetrahedral sites, can be exchanged. By substituting the active cation
(Fe, Co) by a not-catalytically active cation (Zn, Mg, Al) in the different sites, the
occupation of the tetrahedral and octahedral sites in the surface and their relation to
the catalytic properties is investigated.

5.2 Spinel structure

The oxidic spinels comprise a large class of ternary compounds of which the
structure resembles the crystal structure of the naturally occurring mineral spinel
MgAl₂O₄ [39]. The spinel structure has a cubic symmetry, consisting of a
face-centered cubic lattice of close-packed oxygen anions with the cations placed in
interstitial positions (spacegroup Fd3m).

![Figure 5.1: Unit cell of the spinel structure](image)

Spinel- and perovskite-type oxides: A LEIS study
The unit cell is rather large and contains 8 formula units $AB_2O_4$. Two types of interstitial positions are possible, one formed by four anions at the vertices of a tetrahedron and the other formed by six anions at the vertices of an octahedron. These sites are commonly referred to as tetrahedral or A sites and octahedral or B sites. A unit cell, which contains eight molecules, has 64 A-sites and 32 B-sites. Of these, 8 A-sites and 16 B-sites are occupied. The positions of the metal cations are fixed by the symmetry of the structure but the 32 anion positions are variable and are specified by the parameter $u$, also known as the oxygen parameter, indicating the height above the base plane in the unit cell relative to the lattice parameter ($u \cdot a$). A perfect cubic close-packing of the anions corresponds to $u = 0.375$. In figure 5.1 the unit cell of a spinel is given.

In simple spinels the valencies for the A and B cations may be either (2+,3+), (4+,2+) or (6+,1+), respectively. All samples within this work belong to the first group. The general formula can be written as $A_{1-\alpha}B_\alpha[A_\alpha B_{2-\alpha}]O_4$ where $0 \leq \alpha \leq 1$ and the square brackets indicate B sites. In this formula $\alpha$ can be seen as a measure for the degree of inversion. A perfectly normal spinel is one in which the single A cation of the formula unit occupies the tetrahedral site and the two B cations occupy the octahedral site ($\alpha=0$). The situation in which half of the B cations is placed in the A sites and all of the A cations in the B sites is called the inverse spinel ($\alpha=1$). In fact every configuration between $\alpha=0$ and $\alpha=1$ can be established. Where $\alpha=\frac{1}{2}$ the cation arrangement is described as random. All ferrites except Zn and Cd ferrite are inverse, while all the aluminates are known to be normal [40,41,42].

The actual configuration adopted by a given spinel depends on a variety of factors. The A sites are smaller than the B sites; thus, smaller ions which usually have a higher charge, tend to occupy the A sites. However, when the $u$ parameter increases and the two sites become approximately equal in size, this effect becomes less important. Also, the occupancy of the octahedral sites by the cation with the higher valency is electrostatically more favourable. In general, a balance will be found between the lattice parameter $a$ and the oxygen parameter $u$.

The question that now arises is what valency and coordination are responsible for the catalytic activity and selectivity. Numerous studies have been performed, theoretical [43,44] as well as experimental [45,46], and the major conclusion of all of them is that the tetrahedral sites are either inactive in accelerating the reaction or improving the yield of wanted products or just do not occur at the surface.

The absence of influence from tetrahedrally coordinated cations on the rate of the reaction can have two different reasons in our view. Tetrahedral sites are either not active which can be due to stronger metal-oxygen bonds or they are not present
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at the surface. It might be argued with respect to the latter explanation that cations in octahedral sites have segregated to the surface due to a lower surface energy, thus preventing that cations in tetrahedral sites take part in the reaction. Furthermore, it is evident that cations in the tetrahedral sites are more unsaturated electrically if one oxygen anion is missing at the surface, so that tetrahedral sites do not show up at the surface. A third possibility is that only planes with octahedral sites are exposed at the surface. When considering the low-index planes, 6 different layers can be distinguished. Following the notation of Knözinger and Ratnasamy [47], these are (111)A, (111)B, (110)C, (110)D, (100)E and (100)F as shown in figure 5.2. The B and D layer show only octahedral sites.

Figure 5.2: The low index planes of the normal spinel structured MgAl₂O₄, notation as in ref. [47]. The open spheres represent the oxygen anions, the solid spheres the octahedrally coordinated cations and the dotted spheres the tetrahedrally coordinated cations.
It will be shown in this chapter that LEIS can identify which atoms and, indirectly, which sites and planes are present at the surface and therefore determine the observed catalytic behaviour.

5.3 Ferrites

5.3.1 Introduction

The results on spinel ferrites (MgFe$_2$O$_4$ and ZnFe$_2$O$_4$) of Reijne [6] - a LEIS surface analysis correlated with catalytic activity - showed that only octahedral sites are exposed at the spinel surface. The presence of the Fe$^{3+}$ cation at the surface and the observed activity were found to be related. These promising results made it interesting to make a series of samples in which the Fe$^{3+}$ cations in tetrahedral and octahedral sites are gradually exchanged. It was anticipated that a direct relation should exist between the catalytic activity and the amount of Fe$^{3+}$ ions at the surface and thus in octahedral sites. Therefore, much work has been devoted to the preparation of a ferrite series (Zn$_x$Mg$_{1-x}$Fe$_2$O$_4$), what is described in chapter 3 of this thesis. By the gradual substitution, the Fe$^{3+}$ cations will be replaced by Zn$^{2+}$ in tetrahedral sites and by Mg$^{2+}$ in octahedral sites. Since catalytic activity measurements were planned, a start was made with a coprecipitation preparation technique, which ensures a high specific surface area. The different solubilities of the metal oxalates and the not exactly known reaction and decomposition temperature make this technique difficult to perform. Several preparation cycles of the ferrites were necessary to obtain X-ray diffractograms indicating the single spinel phase. In search for an easier and more reliable technique two other preparation ways have been applied: coprecipitation of mixed hydroxides with ammonia, which is more commonly applied in literature, and a cold ethanol method, where solubilities are not important. Experimental factors gave even more difficulties with the latter two techniques, and an emphasis was put on the coprecipitation of mixed oxalates followed by decomposition. The most reliable preparation technique is the ceramic one. This technique, however, gives a low surface area, and is therefore not interesting for catalysis. The ceramic ferrites are well-suited for structural analysis and are therefore studied next to the coprecipitated ones.

5.3.2 Characterization of the bulk structure

Before a structural surface analysis of the prepared spinel ferrites is justifiable, phase and bulk stoichiometry have to be tested. Therefore several techniques as described in chapter 4 have been applied. Eventually we were able to make ferrites
Spinel-type oxides

demonstrating X-ray diffractograms, which showed sharp peaks and a low background. They indicated that all samples have the cubic spinel phase with no evidence of impurities or separate phases. A typical XRD pattern is shown in figure 5.3.

![XRD spectrum of coprecipitated Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$](image)

**Figure 5.3: XRD spectrum of coprecipitated Zn$_{0.2}$Mg$_{0.8}$Fe$_2$O$_4$**

![Lattice parameter of the ferrites, determined by XRD](image)

**Figure 5.4: Lattice parameter of the ferrites, determined by XRD**

From the observed $d$ spacings the lattice parameter $a$ was calculated. The Vegard plot of $a$ against $x$ (in Zn$_{1-x}$Mg$_x$Fe$_2$O$_4$) shows an almost linear behaviour as is illustrated in figure 5.4. This indicates the formation of solid spinel phase materials, both for the ceramic and for the coprecipitated ferrites. Both ends of the series (MgFe$_2$O$_4$ and ZnFe$_2$O$_4$) show a lattice constant in good agreement with literature data [MgFe$_2$O$_4$: 8.375 Å, ZnFe$_2$O$_4$: 8.4411 Å, from ref. 48], although the lattice constants...
of the coprecipitated samples have a tendency to higher values. It increases with zinc concentration, which is to be expected from consideration of ionic radii [17]. By substituting the Mg\(^{2+}\) cations (0.66 Å) with the Zn\(^{2+}\) cations (0.72 Å) the spinel lattice is enlarged and changes from inverse to normal. It was concluded that single phasic compounds were prepared.

After it was confirmed that all prepared ferrites exhibited a single phasic spinel structure, the bulk stoichiometry was checked with PIXE and AAS (see chapter 4). First PIXE results showed that the coprecipitated series was depleted in magnesium by a factor 10. Since there were some doubts about the accuracy of the measurements, a few samples were double-checked with atomic absorption. These measurements confirmed all the results obtained from PIXE. The stoichiometry data for the two ferrite series are presented in table 5.1 and 5.2. From the synthesis mixture a certain ratio between the elements is expected. Following this model, ratios of the different elements can be calculated as is shown in the tables.

### Table 5.1: Bulk stoichiometry ratios of ceramic ferrites from PIXE and AAS (T=TUE, M=IMP)

| Ferrites (ceramic) | Zn/Fe | Mg/Fe | | 
| --- | --- | --- | --- | --- | --- | --- | 
| | model | PIXE, T | AAS, T | AAS, M | model | PIXE, T | AAS, T | AAS, M | 
| MgFe\(_2\)O\(_4\) | - | - | - | - | 0.5 | 0.61 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.1 | 0.10 | 0.094 | | 0.4 | 0.42 | 0.42 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.2 | 0.21 | | | 0.3 | 0.31 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.3 | 0.32 | | | 0.2 | 0.22 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.4 | 0.42 | 0.40 | | 0.1 | 0.05 | 0.13 | 
| ZnFe\(_2\)O\(_4\) | 0.5 | | | | - | - | - | 

### Table 5.2: Bulk stoichiometry ratios of coprec. ferrites from PIXE and AAS (T=TUE, M=IMP)

| Ferrites (coprec.) | Zn/Fe | Mg/Fe | | 
| --- | --- | --- | --- | --- | --- | --- | --- | --- | 
| | model | PIXE, T | AAS, T | AAS, M | model | PIXE, T | AAS, T | AAS, M | 
| MgFe\(_2\)O\(_4\) | - | - | - | - | 0.5 | 0.062 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.1 | 0.13 | 0.13 | 0.26 | 0.4 | 0.050 | 0.067 | 0.058 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.2 | 0.22 | | | 0.3 | 0.031 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.3 | 0.33 | | | 0.2 | 0.016 | 
| Zn\(_{0.5}\)Mg\(_{0.5}\)Fe\(_2\)O\(_4\) | 0.4 | 0.40 | 0.46 | | 0.1 | 0.009 | 0.011 | 
| ZnFe\(_2\)O\(_4\) | 0.5 | 0.60 | | | - | - | - |
As can be seen from the tables the bulk composition of the ceramic ferrites was about as expected from the synthesis mixture. For the depletion of magnesium in the coprecipitated samples one can think of a number of explanations. As was mentioned in chapter 3 the preparation of ferrites by a coprecipitation technique is rather difficult. Firstly, it is possible that magnesium oxalate has a larger solubility than was found in literature, which is not likely. An alternative explanation is that the precipitation temperature, which was currently set to 60 °C, is too low for the synthesis of magnesium oxalate and the magnesium ions are washed out during filtering. The most probable reason, however, is that magnesium forms a charged complex due to excess oxalic acid so that it stays in solution as was suggested by Zhang et al. [49]. A final parameter that can play a role is the decomposition temperature for the spinel phase forming. It might have been too low what seems to be confirmed by AAS measurements on coprecipitated Zn_{0.2}Mg_{0.8}Fe_{2}O_{4} where traces of carbon were found, indicating an incomplete conversion. The fact that XRD indicates a mono-phasic spinel structure can be explained by the simultaneous forming of Fe_{3}O_{4} and ZnFe_{2}O_{4} during the decomposition. The slight deviation of the lattice parameter from literature to higher values confirms this. These results show that no coprecipitated ferrite series (Zn_{0.2}Mg_{0.8}Fe_{2}O_{4}) was formed. Therefore, the catalytic activity measurements (oxidative dehydrogenation (OHD) of butene to butadiene) at the Instituto Mexicano del Petroleo based on the promising XRD data did not show the expected strong correlation, where ZnFe_{2}O_{4} and MgFe_{2}O_{4} favour the forming of butadiene and the combustion reaction, respectively. This is illustrated in figure 5.5.

![Conversion and selectivity of the coprecipitated ferrites in the ODH of butene](image)

**Figure 5.5**: Conversion and selectivity of the coprecipitated ferrites in the ODH of butene

At the IMP also Mössbauer spectra were taken for the coprecipitated series. The results are given in table 5.3. The idea is that magnesium enters the octahedral sites...
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and zinc enters the tetrahedral sites. A good agreement with this model for the iron cation distribution was found. This is rather puzzling since from PIXE, it was concluded that only the ceramic samples had been synthesized correctly. It was therefore decided to investigate all ferrites with Mössbauer spectroscopy in Eindhoven (TUE).

Table 5.3: Iron cation distribution from Mössbauer spectroscopy, IMP

<table>
<thead>
<tr>
<th>x</th>
<th>Cation distribution (model)</th>
<th>Fe_{th}/Fe_{tet} (model)</th>
<th>Fe_{th}/Fe_{tet} (Mössbauer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Fe^{3+}[Mg^{2+}Fe^{3+}]O_{4}</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.2</td>
<td>Zn_{0.2}^{2+}Fe_{0.8}^{3+}[Mg^{2+}Fe_{3}^{3+}]O_{4}</td>
<td>0.67</td>
<td>0.91</td>
</tr>
<tr>
<td>0.4</td>
<td>Zn_{0.4}^{2+}Fe_{0.6}^{3+}[Mg^{2+}Fe_{3}^{3+}]O_{4}</td>
<td>0.43</td>
<td>0.55</td>
</tr>
<tr>
<td>0.6</td>
<td>Zn_{0.6}^{2+}Fe_{0.4}^{3+}[Mg^{2+}Fe_{3}^{3+}]O_{4}</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>0.8</td>
<td>Zn_{0.8}^{2+}Fe_{0.2}^{3+}[Mg^{2+}Fe_{3}^{3+}]O_{4}</td>
<td>0.11</td>
<td>--</td>
</tr>
<tr>
<td>1.0</td>
<td>Zn^{2+}[Fe^{3+}Fe^{3+}]O_{4}</td>
<td>0.00</td>
<td>--</td>
</tr>
</tbody>
</table>

It was possible to reproduce the spectra from Mexico on the catalysts. Fitting of the spectra gave, however, consequently different values for the cation distribution and never the from model considerations expected ones. So far, it is not understood what parameters (isomer shift, quadrupole and Zeeman splitting) should play the most important role and mainly determine the fitting. In spite of the presence of octahedrally coordinated Fe^{3+} an almost zero quadrupole splitting has been found. This has been explained by Daniels and Rosencwaig [28] who attributed the absence of a quadrupole splitting in a Ni-Zn ferrite system to chemical disorder of the cations.

At the moment work still has to be done on the interpretation of spectra of the ceramic ferrites. Therefore, the following approach was used: from Mössbauer we want to obtain the ratio of Fe cations in tetrahedral and octahedral sites. A search in the parameter space was done, while varying the area ratio between the sextets originating from octahedrally and tetrahedrally coordinated iron. The Chi-square value from the fit was plotted against this ratio and resulted in a parabola. For ceramic Zn_{0.2}Mg_{0.8}Fe_{2}O_{4} the minimum of this curve, and thus the value for Fe_{oct}/Fe_{tet} is at around 2. From model considerations it should have been 1.5. Further research is being done to analyse the whole ceramic series with this fitting procedure, which looks promising. A likewise approach is described for a LEED analysis by Gauthier et al. [50].

5.3.3 LEIS results

All ferrites were calcined prior to analysis at 200 °C in 20 mbar oxygen for 20 minutes. Some typical LEIS spectra of the ceramic and coprecipitated ferrites are given
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in figure 5.6 and 5.7, respectively. As is shown in these plots, the oxygen signal remains constant in the whole series. This was expected because the structure is not changed during substitution of cations.

![Figure 5.6: LEIS spectrum of ceramic ferrites. 3 keV \(^{4}\)He\(^{+}\), 60 nA, 680 s](image)

The ceramic MgFe\(_2\)O\(_4\) shows a considerable amount of Mg which is in agreement with the results of Reijne [6]. After calibration against pure elements the amount of Mg appeared to be about the same as the amount of Fe. The zinc peak increases with increasing x. It is difficult to estimate correctly a quantitative amount due to the overlapping with the iron peak and the overall presence of contaminations, although it is possible using peak deconvolution [10]. The relative large amount of contaminations present at the surface is inherent to the ceramic preparation technique. The LEIS spectra from the coprecipitated ferrites agree with PIXE results and show no magnesium at the surface.

![Figure 5.7: LEIS spectrum of coprecipitated ferrites. 3 keV \(^{4}\)He\(^{+}\), 60 nA, 680s](image)
5.3.4 Discussion ferrites

The ferrite catalysts prepared from coprecipitation and decomposition of mixed oxalates, and ceramic ferrites prepared by a conventional solid state reaction were considered in this investigation. Both these coprecipitated and ceramic ferrites revealed a proper spinel phase and structure by X-ray diffraction. Samples prepared by other techniques were not reliable due to experimental problems, what was confirmed by their XRD spectra, which did not show the required single phase spinel. The lattice parameters calculated from the XRD data agree very well with the literature values [48] in the case of the ceramic samples. However, the parameters for the coprecipitated samples have a structural tendency to slightly higher values.

To check the bulk stoichiometry PIXE measurements on the samples were performed. Since magnesium is at the edge of the detection limit, some samples were checked using AAS. The ceramic samples showed the correct bulk structure as was expected for this straightforward preparation technique. However, the coprecipitated samples turned out to be not synthesized correctly. They showed a magnesium concentration that was a factor ten too low. In view of these stoichiometry data, the XRD results can be explained by the fact that during decomposition only Fe$_3$O$_4$ and ZnFe$_2$O$_4$ have been formed. Fe$_3$O$_4$ has about the same lattice constant as MgFe$_2$O$_4$, whereas that of ZnFe$_2$O$_4$ is higher due to the larger Zn-cation size. The overall lattice parameter as obtained from XRD will in this case be higher than expected.

The fact that the catalysts did not show the right bulk stoichiometry had a large impact on the investigation. Relying on the XRD results a series of catalysts was measured in the oxidative dehydrogenation of butene to butadiene at the Instituto Mexicano del Petroleo (IMP) in Mexico City. It is obvious that no clear correlation between the Mg/Zn content and the catalytic activity was found due to the magnesium depletion. At the IMP also Mössbauer measurements were performed and the results seem to confirm our XRD results. This leads to the conclusion that, since PIXE and AAS were considered reliable, the Mössbauer experiments were not performed correctly, which will be discussed below. LEIS did not show any magnesium and no zinc as expected from PIXE experiments (no Mg) and the surface model (no Zn). Furthermore it was found that the ferrites were very sensitive to the UHV and the ion beam and reduced very fast which largely hindered the measurements. At the moment the only reasonable explanation for the failure of the preparation method is a reaction which was not considered by Anantharaman et al. [16] but is suggested by Zhang et al. [49] for the preparation of a BiSrCaCuO superconductor compounds. They also applied an oxalate coprecipitation technique. It is argued that, in addition to the oxalate that stays in solution according to the solubility, the precipitated metal oxalates can redissolve, forming the complex
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Me(C₂O₄)₂. In this way the deposit of the ferrite mixed oxalate precursor is depleted in magnesium oxalate.

The picture for the ceramic materials looked more promising. XRD and PIXE showed that the right model system had been prepared. Therefore, the ceramic series could possibly provide the information about the surface structure of these inverse spinels. Catalytic measurements could not be done in this case because of the low specific surface. The LEIS results showed magnesium and practically no zinc indicating a preferential exposure of octahedral sites. However, also a large amount of contaminations of alkali atoms was detected, which could not be decreased. Therefore, from the LEIS surface analysis no reliable conclusions could be drawn concerning the amount of magnesium and zinc on the surface and the preferential exposure of octahedral sites. However, Mössbauer spectroscopy should be able to provide interesting spectra for the determination of cation distribution in the bulk of these inverse spinels and were therefore performed in Eindhoven. It was intended to check the Mössbauer results for the catalysts obtained in Mexico as well.

Mössbauer spectra were taken for both catalysts and ceramics. Fitting of the spectra proofed rather complicated. The spectra for the catalysts as were taken at IMP were reproduced. However, the fitting data gave a different cation distribution, not in agreement with XRD. The same holds for the ceramic ferrites. The impact which the gradual substitution of zinc cations for the magnesium cations would have on the spectra was only observed qualitatively. Iron in tetrahedral sites in MgFe₂O₄ (ferrimagnetic) is gradually replaced by zinc cations due to a decreasing internal magnetic field, which indicates the forming of a paramagnetic state (ZnFe₂O₄). This shows in the spectra by the vanishing of the tetrahedral and octahedral sextet with higher x values. In ZnFe₂O₄ only a quadrupole doublet is visible.

Referring to our findings, the work on ferrites done by Reijne [6] have to be placed in another perspective. Conclusions were drawn based on systems prepared in the same way we did, but no bulk characterization was performed. It might be possible that his results are attributed to systems that were wrongly synthesized. In view of the great difficulties both in the preparation as well as in the analysis of the ferrites it was decided not to pursue this subject but to continue on a cobalt-aluminate series which was prepared in Leiden in the group of prof. Ponec.
5.4 Aluminates

5.4.1 Introduction

Many products from the chemical industry are formed by catalytic oxidation reactions. Oxides are used as catalysts in these heterogeneous reactions, such as the oxidative dehydrogenation of butene to butadiene. In this case ferrites are known to be good catalysts. Research has been done in this work to find a correlation between the ferrite surface characteristics and the activity of these catalysts. In the previous paragraph this has been described. It was found that mainly octahedrally coordinated cations were present at the surface, but no clear relation could be found between surface composition and catalytic activity due to contaminations or unexpected cation depletion.

In addition to the selective oxidation reactions, oxides can also be used to catalyse selective reduction reactions. In this paragraph we present an investigation on catalysts that are used with such reactions, namely spinel structured cobalt aluminum oxides. They are good catalysts for the selective reduction of nitrobenzene to nitrosobenzene. Nitrosobenzene is an intermediate of numerous organic syntheses leading to widely used anti-oxidants. It was found by Jacobs et al. [10] that octahedral sites are exposed almost exclusively at the surface. They studied Mn$_3$O$_4$ and Co$_3$O$_4$ where the Mn and Co cations in different sites in the spinel structure are substituted by other cations which are not active in the reduction of nitrobenzene. However, attempts to find a correlation between octahedral Mn ion concentration and activity failed due to the impossibility of synthesizing the aluminates without the Al$_2$O$_3$ phase.

In this work the influence of the octahedral site occupation on the mechanism of the selective reduction has been subject to research. A series of cobalt aluminum oxides was made in Leiden [21] with the citrate coprecipitation process (chapter 3). The catalytically active Co$^{3+}$ cations in the octahedral sites were gradually replaced by inactive Al$^{3+}$ cations, resulting in the following single phasic spinel series: Co$_{1+x}$Al$_{2-x}$O$_4$ (x = 0.00, 0.50, 1.00, 1.24, 1.30, 1.44, 1.50, 2.00). If the reaction mechanism requires transition metal cations in the catalyst surface, the gradual replacement of octahedrally coordinated Al$^{3+}$ by Co$^{3+}$ is expected to result in a proportional increase in nitrosobenzene production. The hypothesis of the necessity of octahedral transition metal ions is investigated by the synthesis (citrate process), characterization (XRD, LEIS) and catalytic activity of the above described series.
5.4.2 Characterization of the bulk structure by XRD

In the light of the ferrite experiments, it is obvious that checking bulk phase and composition is of extreme importance. It is impossible to find a direct relation between catalytic activity of spinels and their surface composition, when stoichiometry or phase are not correct. Therefore, all aluminate samples were characterized using XRD. The analysis of the diffractograms showed that the oxides had a well defined and mono-phasic spinel structure. Less than 3% of the aluminum from the synthesis mixture was not incorporated in the resulting cobalt aluminum oxide. A typical aluminate diffractogram is shown in figure 5.8.

![XRD spectrum of Co$_2$AlO$_4$](image)

**Figure 5.8: XRD spectrum of Co$_2$AlO$_4$**

The lattice parameters calculated from the XRD data were in excellent agreement with literature data [CoAl$_2$O$_4$: 8.103 Å, Co$_2$AlO$_4$: 8.086 Å, Co$_3$O$_4$: 8.0837 Å, from ref. 48] and showed a practically linear decrease with increasing cobalt concentration (figure 5.9). From a quantitative XRD analysis it appeared that all aluminates showed little inversion of about 10%. For each sample the inversion parameter $\alpha$ as defined in paragraph 5.2 has been calculated, following the formula $(\text{Co}_{1-\alpha}\text{Al}_\alpha)_{\text{th}}[\text{Co}_{x+\alpha}\text{Al}_{2-x-\alpha}]_{\text{oh}}\text{O}_4$, where $\text{th}$ and $\text{oh}$ depict

![Lattice parameters of the aluminates](image)

**Figure 5.9: Lattice parameters of the aluminates, determined from XRD**
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tetrahedral and octahedral sites, respectively. Cation distribution, relative amount of cobalt in octahedral sites, inversion parameter and lattice parameter, all determined from XRD data, are given in table 5.4.

<table>
<thead>
<tr>
<th>x</th>
<th>cation distribution</th>
<th>relative amount of octahedral Co</th>
<th>inversion parameter α</th>
<th>lattice parameter a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(Co&lt;sub&gt;0.76&lt;/sub&gt;Al&lt;sub&gt;0.24&lt;/sub&gt;)[Co&lt;sub&gt;0.36&lt;/sub&gt;Al&lt;sub&gt;0.64&lt;/sub&gt;]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>13%</td>
<td>0.26</td>
<td>8.0966 Å</td>
</tr>
<tr>
<td>0.5</td>
<td>(Co&lt;sub&gt;1.00&lt;/sub&gt;)[Co&lt;sub&gt;0.50&lt;/sub&gt;Al&lt;sub&gt;0.50&lt;/sub&gt;]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>25%</td>
<td>0</td>
<td>8.0927 Å</td>
</tr>
<tr>
<td>1</td>
<td>(Co&lt;sub&gt;0.86&lt;/sub&gt;Al&lt;sub&gt;0.14&lt;/sub&gt;)[Co&lt;sub&gt;1.14&lt;/sub&gt;Al&lt;sub&gt;0.86&lt;/sub&gt;]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>57%</td>
<td>0.14</td>
<td>8.0903 Å</td>
</tr>
<tr>
<td>1.44</td>
<td>(Co&lt;sub&gt;0.94&lt;/sub&gt;Al&lt;sub&gt;0.06&lt;/sub&gt;)[Co&lt;sub&gt;1.06&lt;/sub&gt;Al&lt;sub&gt;0.94&lt;/sub&gt;]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>75%</td>
<td>0.06</td>
<td>8.0890 Å</td>
</tr>
<tr>
<td>1.5</td>
<td>(Co&lt;sub&gt;0.90&lt;/sub&gt;Al&lt;sub&gt;0.10&lt;/sub&gt;)[Co&lt;sub&gt;1.10&lt;/sub&gt;Al&lt;sub&gt;0.90&lt;/sub&gt;]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>80%</td>
<td>0.10</td>
<td>8.0866 Å</td>
</tr>
<tr>
<td>2</td>
<td>(Co)[Co, Co]O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>100%</td>
<td>0</td>
<td>8.0823 Å</td>
</tr>
</tbody>
</table>

### 5.4.3 Results

All samples were pretreated in 20 mbar oxygen at 200 °C for 20 minutes, before LEIS measurements. Some typical LEIS spectra of the aluminates are shown in figure 5.10. As can be seen in these spectra, the surface peak of oxygen is similar. This is in accordance with the idea that the spinel structure remains intact when cations are exchanged. The gradual substitution of cobalt by aluminum is reflected on the surface composition by an increase and decrease of their surface peaks, respectively.

---

**Figure 5.10:** Typical LEIS spectra of the aluminates (3keV <sup>4</sup>He<sup>+</sup>, 60 nA, 680s)
All samples showed practically no contamination except \( \text{Co}_2\text{O}_4 \). We were not able to produce a clean surface for this spinel despite several preparation runs. The contaminations had a drastic diminishing influence on the LEIS signal of the different elements.

**Table 5.5: Results of LEIS and activity measurement on aluminates**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>LEIS peak area ([10^3 \text{ cts}])</th>
<th>BET area ([\text{m}^2/\text{g}])</th>
<th>activity ([10^{10} \text{ mol s}^{-1} \text{ m}^{-2}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CoAl}_2\text{O}_4 )</td>
<td>5.9 16.4 8.34 33.1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{1.5}\text{Al}</em>{1.5}\text{O}_4 )</td>
<td>6.2 10.8 21.4 15.9</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}_2\text{AlO}_4 )</td>
<td>4.9 7.3 24.9 5.9</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{2.24}\text{Al}</em>{0.76}\text{O}_4 )</td>
<td>4.5 6.3 27.5 --</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{2.3}\text{Al}</em>{0.7}\text{O}_4 )</td>
<td>4.5 5.8 32.2 --</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{2.4}\text{Al}</em>{0.56}\text{O}_4 )</td>
<td>6.9 4.9 33.9 2.1</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}<em>{2.5}\text{Al}</em>{0.3}\text{O}_4 )</td>
<td>4.0 4.0 42.5 2.7</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4^* )</td>
<td>5.0 -- 37.6 1.3</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

* contaminated with Na, K

\( \Delta \% \text{ Co XRD} \quad \bullet \% \text{ Co LEIS} \quad \square \text{ rate} \)

**Figure 5.11: Catalytic activity and cobalt octahedral site occupation**

\( x \) in \( \text{Co}_{1+x}\text{Al}_{2-x}\text{O}_4 \)
In the table the results from the catalytic experiments are listed. Unlike the expected proportional increase in activity with increasing cobalt content in the bulk, the activity shows a steep raise at \( x = 1 \) (Co\(_2\)AlO\(_4\)). In figure 5.11 the catalytic activity in the selective reduction of nitrobenzene to nitrosobenzene is combined with the relative amount of cobalt in octahedral sites as was determined from XRD and LEIS measurements. Figure 5.12 gives the surface aluminum/cobalt ratio, determined after calibration to the pure metals. From a comparison with the bulk stoichiometry, it was found that the aluminum/cobalt ratio determined from LEIS signals showed a global increase. Therefore, in figure 5.11 the LEIS data are normalized to the XRD data, where Co\(_{2.5}\)Al\(_{0.5}\)O\(_4\) was taken as reference sample. This is done because this sample showed no surface contamination and the high cobalt content in octahedral sites ensured a large LEIS signal. A clear correlation between XRD and LEIS measurements was found in this way. It is therefore concluded that the surface of these aluminates contains only octahedral sites, which leaves the (111)B and (110)D layer as possible terminating planes of the spinel powders.

![Graph](image)

**Figure 5.12: Surface aluminum/cobalt ratio, from LEIS**

Furthermore, it was found that the surface spinel structure is destroyed due to the sputtering effect of the ion beam in LEIS experiments as is shown in figure 5.13 for Co\(_2\)AlO\(_4\). Therefore, only the first few measured spectra of each sample were considered in the analysis to be sure that the spinel structure was not yet damaged.
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Figure 5.13: Depth profile of $\text{Co}_2\text{Al}_2\text{O}_4$ (a dose of $10^{16}$ ions cm$^{-2}$ = 1 ML sputtered)

5.4.4 Discussion aluminates

It was found that the preparation of the aluminates from coprecipitation techniques following the methods used in the preparation of the ferrites showed problems as well. Therefore, in Leiden another method for the aluminate series has been applied, namely the coprecipitation from citrates. From a quantitative XRD analysis the phase of the aluminates was checked for each sample of the series ($\text{Co}_{1-x}\text{Al}_{2x}\text{O}_4$) and found to be single phasic spinel. An almost linear decrease of the lattice parameter as a function of $x$ showed that cobalt atoms entered the spinel structure during the gradual substitution for the aluminum cations. The aluminates showed inversion up to 10%. This is in contradiction with Romeijn [40] but in agreement with Schmocker et al. [51] and Dickson and Srivastava [52] who reported a small deviation from the perfect normal spinel structure in aluminates allowing the $\text{Al}^{3+}$ cations to enter the tetrahedral sites. So the octahedral site preference energy of aluminum [53] does not offer a mechanism strong enough to ensure normality of the spinel.

The LEIS results showed aluminum and cobalt contents at the surface in agreement with the model that mainly octahedral sites are on the surface. The aluminum/cobalt ratio on the surface (after calibration against polycrystalline metals), plotted for the whole series in figure 5.12, indicates a increase with respect to the ratio determined from bulk stoichiometry. For the $\text{CoAl}_2\text{O}_4$ spinel, the low cobalt
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concentration detected with LEIS is an indication for inversion as was already found with XRD. LEIS measurements of the whole series showed that the cobalt concentration at the surface tends to follow the octahedral site distribution as was determined for the bulk with XRD, confirming the idea that almost all aluminum is entering the octahedral sites and that the remaining sites are filled by the cobalt cations. This correlation is demonstrated above in figure 5.11. It is therefore concluded that only octahedral sites appear at the surface.

The catalytic activity measurements in the selective reduction of nitrobenzene to nitrosobenzene show an increase in rate as a function of cobalt concentration in octahedral sites as expected (see figure 5.11). However, this raise is not linear, but shows a steep increase for \( x > 1 \) (\( \text{Co}_2\text{AlO}_4 \)). This can be explained by a well-known phenomenon in catalysis on metals, namely the ensemble size effect. Here, several active surface metal atoms are needed for the reaction to occur. The reaction site is thus an ensemble of several atoms. One can picture the same thing for the cobalt-aluminates where an active site consists of an oxygen vacancy surrounded by a number of octahedrally coordinated cobalt cations. In the case of the (111)B and (110)D layer (see figure 5.2), a maximum of six cations are involved. The observed behaviour can be explained by an ensemble of at least 4 cobalt cations as is shown in figure 5.14.

\[
P_{>3\text{Co}} \quad \quad P_{>4\text{Co}} \quad \quad P_{>5\text{Co}} \quad \quad \text{rate}
\]

\[
\begin{array}{c|c|c|c|c|c|c|c}
[\text{Co}] \text{ in octahedral sites} & 0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\hline
P_{\text{cobalt}} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\hline
\text{rate} \times 10^{-10} \text{ mol m}^{-2} \text{s}^{-1} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\end{array}
\]

\textbf{Figure 5.14: Probability of a certain number of Co cations in octahedral sites}

The probability that at least four cobalt cations out of six places surround an active site was calculated from a binomial distribution and becomes important at a cobalt concentration in octahedral sites above 50%, thus for \( x \) values of 1 and higher. The
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sudden increase in activity occurs indeed from $\text{Co}_2\text{AlO}_4$ ($x = 1$). In this way the observations of Jacobs et al. [10] still hold when only comparing $\text{Co}_3\text{O}_4$ with $\text{CoAl}_2\text{O}_4$. In addition to their findings, it was found in this study that the ensemble effect definitely plays an important role in the reduction mechanism.

Furthermore, alkali metal contaminations were detected especially for the $\text{Co}_3\text{O}_4$ sample. Their role is not yet clear. For LEIS measurements they could cause a lower detected cobalt concentration than expected from clean and polycrystalline cobalt, but their influence will be only minor. It is known from literature that impurities such as sodium or potassium can serve as promoters in a catalytic reaction [12]. However, Vepřek et al. [14] reported a strong enrichment of potassium at the surface when $\text{CuMn}_2\text{O}_4$ was crystallized at high temperatures, which was found to be responsible for the loss of activity of the catalyst. In the study on the aluminates which we performed no clear correlation between contaminations and activity could be found.
6

Perovskite-type oxides

6.1 Introduction

Many kinds of mixed oxides exist in the perovskite family. Perovskite structured oxides have the general formula $\text{ABO}_3$. Within certain limitations of the ionic radii of the A- and B-cation and the oxygen anion and the principle of electroneutrality taken into account many variations in compounds exhibiting this structure can be found. This wide variety makes the perovskite family very useful in practical applications. They exhibit several interesting properties such as ferromagnetism, ferroelectricity, pyro- and piezoelectricity, large thermal conductivity, fluorescence and catalytic activity. High $T_c$ superconductors with the perovskite structure are currently of great interest (e.g. $\text{YBaCuO}$), although classic superconductivity can also be found among these type of oxides.

Like the spinel structured materials described in the previous chapter, also perovskites can be used to elucidate the relationship between surface composition and, e.g. catalytic activity, since the cations can be exchanged in a systematic way, keeping the perovskite structure unchanged. It was anticipated that also perovskites might expose only certain sites on the surface. Therefore, an investigation using Low-Energy Ion Scattering is envisioned to give a decisive answer concerning this idea.

Perovskites are known to have well-defined bulk structures. However, their surface compositions have been reported to differ significantly from the bulk in some cases, depending on the conditions in which they were prepared and the bulk composition [54]. The surface often tends to be poor in catalytically active B-site cations, and Tabata et al. [55] have correlated the CO-oxidation activity with the surface concentration of B-cations, whereas Shimizu reported that in the oxidation of Co over a series of $\text{LaBO}_3$ (B=3d transition element) the catalytic activity increased with a decrease in B-O bond strength [56]. It was found by Fierro using XPS [57] that surface segregation of the active B-element occurs upon $\text{H}_2$ reduction. A maximum in activity is found when the reduction temperature is increased. The perovskite oxides most frequently used in heterogeneous catalysis are those containing a lanthanide element in site A and a transition metal in site B [58].
6.2 Perovskite structure

The perovskites form a family of compounds having a crystal structure similar to that of the mineral perovskite CaTiO$_3$. The ideal perovskite structure has the cubic unit cell of figure 6.1 with space group Pm3m. The basis of the structure is formed by a framework of corner-shared octahedra BX$_6$ where X represents the anion and B the smaller cation placed in the center of the octahedron. The larger A cation occupies a cavity of the same size as the X anion, formed by eight octahedra. In this way a closed-packed stacking is obtained in which the A-cations and B-cations are twelve- and sixfold coordinated, respectively.

![Figure 6.1: Unit cell of the perovskite structure](image)

![Figure 6.2: The low index planes of the perovskite BaTiO$_3$.](image)

The notation corresponds to that of spinel planes as was suggested in ref. [47]. The open spheres represent the oxygen anions, the solid black spheres the smaller B-sites (Ti) and the dotted spheres the larger A-sites (Ba).
The structure is rarely cubic at room temperature and exhibits distortions to lower symmetry as a result of atomic displacements. The A- and B-cations will only fit into a perovskite lattice when the so-called tolerance factor $t$ as given in equation (6.1) meets the condition $0.75 < t < 1$. 
where $r_A$, $r_B$ and $r_O$ are the radii of the respective ions. Dependent on these values, the crystal will undergo a deformation. Instead of having the cubic symmetry, such as SrTiO$_3$ and BaZrO$_3$, some are tetragonal (BaTiO$_3$), orthorhombic (CaTiO$_3$, NdGaO$_3$) or rhombohedral (LaAlO$_3$) [59]. The condition mentioned above is not sufficient. The A- and B-cations must, in themselves be stable in twelvefold and sixfold coordinations. The lower limits for the cationic radii, that are the consequence of this latter condition, are $r_A > 0.90 \text{ Å}$ and $r_B > 0.51 \text{ Å}$ [60]. Cation valencies possible for oxides are (1+,5+), (2+,4+) and (3+,3+). When cleaving the perovskite structure, eight sublayers can be distinguished. These are plotted in figure 6.2.

6.3 Preliminary LEIS results

Several perovskite samples were studied. A LaAlO$_3$ and a LiBaF$_3$ powder were kindly supplied by Blasse and Meijerink from the University of Utrecht. LaAlO$_3$ (100) and NdGaO$_3$ (100) single crystals were obtained from prof. Meyer from the Kernforschungszentrum Karlsruhe, Germany. Brongersma (Free University, Amsterdam) supported us with a SrTiO$_3$ crystal and a YBaCuO high T$_c$ superconductor material. A Sm$_{0.8}$Sr$_{0.2}$CoO$_3$ fuel cell constituent was already present in the group, obtained from Kilner, Imperial College, London. Finally, a BaZrO$_3$ sample was prepared for this investigation by Ydo in Leiden, because it is one of the few perovskites exhibiting a stable cubic structure at room temperature.

LaAlO$_3$, LiBaF$_3$ and BaZrO$_3$ powders have been investigated with XRD. Only BaZrO$_3$ did not show the proper perovskite structure and was therefore excluded from further investigation. After confirmation of the proper phase, LEIS spectra were taken in order to establish the surface composition and to see if a preferential exposure of a certain site could be observed. A standard pretreatment of 20 mbar oxygen at 200 °C for 20 minutes was performed. The LEIS spectra for the LaAlO$_3$ and LiBaF$_3$ powders are given in figure 6.3 ($^3$He) and 6.4 ($^4$He), and 6.5 ($^3$He) respectively. For both samples very small amounts of the B-cations were found at the surface. It has to be noted that LiBaF$_3$ is the only inverse perovskite known. In this inverse structure the A-cation (Ba$^{2+}$) has the higher charge. The radii of the cations have to fulfill relation (6.1) and Li$^+$ would be to small to fit in the cavity formed by the eight octahedra. The fact that LEIS measurements did not show any lithium at all is also due to the very low sensitivity for this element. It can therefore not be concluded that
no lithium is on the surface. An additional study on e.g. BaTiO$_3$ could provide the information needed.

**Figure 6.3:** LEIS spectrum of LaAlO$_3$, 3 keV $^3$He$^+$ 80 nA, 840s

**Figure 6.4:** LEIS spectrum of LaAlO$_3$, 3 keV $^4$He$^+$ 80 nA, 840s
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Figure 6.5: LEIS spectrum of LiBaF$_3$, 3 keV $^3$He$^+$ 80 nA, 1105s

Figure 6.6: LEIS spectrum of Sm$_{0.8}$Sr$_{0.2}$CoO$_3$, 3 keV $^4$He$^+$ 80 nA, 680s
When the barium signal for this sample compared to the oxygen signal is equal to the barium to fluorine signal in LiBaF$_3$, it is clear that A-sites are preferentially exposed. LEIS measurements on Sm$_{0.8}$Sr$_{0.2}$CoO$_3$ (figure 6.6) confirmed the results obtained from the powders and showed only little amounts of the B-sited cobalt. This is not due to a low sensitivity, since LEIS measurements on pure metallic cobalt, used for calibration of the aluminates (chapter 5 of this thesis) showed high signals. The two possible layers that expose only the twelffold coordinated A-sites are the (111)A and (100)G plane. For the proposed layers the ratio between the A-sited cations and the anions (A:O) differ considerably in the sense that the (111)A plane exposes practically no oxygen. This should be reflected in the LEIS signals.

The study of a SrTiO$_3$ substrate was hampered by the fact that a thin layer of YBaCuO was deposited on the surface, as was only confirmed after the experiment. As the results show (figure 6.7), this layer was heavily contaminated by Na, S, Cl and K. A chemical etching procedure using HNO$_3$ will remove this layer and in this way clean the SrTiO$_3$ perovskites for analysis.

A LaAlO$_3$ (100) single crystal was used to reveal whether it is just the (100)G plane that is exposed at the surface of perovskite powders or a mixture of the (100)G and (111)A plane. In general, two types of the (100) planes can exist as is seen in figure 6.2. They alternate in composition between AO ( (100)G ) and BO$_2$ ( (100)H ). Since both lanthanum and aluminum have a valency 3+, neither of the two planes are charge neutral. On the AO surface, the large A cations have eight O ligands, compared with twelve in the bulk. On the BO$_2$ surface the smaller B cations are fivefold coordinated with O ions. From this consideration it is expected that the (100)G plane is favoured at the surface. LEIS should be able to give an indication. Before measurement, the single crystal was pretreated in 20 mbar oxygen at 500 °C.

![LEIS spectrum of SrTiO$_3$, 3 keV $^4$He$^+$ 80 nA, 680s](image)
for 1 hour after which a depth profile was measured. In figure 6.8 three successive LEIS spectra are given. The overall signal increases in time, probable due to sputtering of contaminations, such as carbon and hydrogen. The depth profile is shown in figure 6.9. The lanthanum signal increased largely in time compared to the signals of the other elements, which remained approximately constant. However, the signals are largely influenced by alkali contamination on the surface. The difficulty with a single crystal is that the impurities cannot be easily removed since a small amount in the bulk can provide a very large reservoir for the alkali contamination. It is known that strong segregation of alkali metals takes place in oxides. A procedure to clean the single crystal would be to heat the crystal in flowing oxygen at 1200 °C for more than 12 hours. In this way, the alkali oxides are evaporated from the surface and removed with the flowing oxygen. The same procedure is envisioned for the NdGaO$_3$ (100) single crystal, which has not yet been subject to analysis.

![LEIS spectra of LaAlO$_3$ (100), 3 keV $^4$He$^+$ 80 nA; 1275s, 5200s, 11475s](image)

**Figure 6.8: LEIS spectra of LaAlO$_3$ (100), 3 keV $^4$He$^+$ 80 nA; 1275s, 5200s, 11475s**

The present results on the perovskites look promising and show a preferential surface exposure of the A-sited cations. However, further research is necessary to confirm the idea that only the (100)G layer is exposed. This layer is expected to be favoured because electric neutrality is more guaranteed.
6.4 Discussion and recommendations for further research

The results on the spinel surfaces showed that only octahedrally coordinated cations are exposed at the surface. For another important group of oxides, the perovskites, a similar effect was expected due to the stable and well-defined perovskite structure, which would result in small crystallites in powders.

A number of perovskites was studied. The powders LaAlO$_3$ and LiBaF$_3$ prepared by Blasse and Meijerink (University of Utrecht) proved to be clean and showed the correct perovskite phase as was evidenced from XRD measurements. With LEIS it was observed that these powders showed a site preference at the surface of the twofold coordinated A-sites. This was also confirmed for a Sm$_{0.8}$Sr$_{0.2}$CoO$_3$ fuel cell material (Imperial College London). The two planes that satisfy the condition of no A-site exposure are the (111)A and (100)G layer.

The LaAlO$_3$ (100) single crystal was used to give a decisive answer which plane is exposed. However, it was found that the surface was largely contaminated by alkali atoms. These can be removed by heating at very high temperatures in flowing oxygen. Also a NdGaO$_3$ (100) single crystal will then be used.
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A final remark concerns the SrTiO$_3$ and YBCO samples. These were contaminated and an etching procedure with HNO$_3$ is needed to clean the surfaces. This will remove impurities but also the thin YBCO layer that was deposited on the SrTiO$_3$ substrate. New samples, where the cleanliness should be better guaranteed, will be provided.

The present results on the perovskites, although preliminary, look promising and support further research. Eventually, calculations can give an interesting picture of preferential site exposure, but since no experimental data was available, it was not yet considered worthwhile by theoretical physicists. It is hoped that the LEIS experiments can provide enough discussion to arouse the interest in this very important but also very complex field of surface science: the surface of oxides.
CHAPTER 7

Conclusions

By combining activity measurements with quantitative surface analysis by LEIS, which only probes the outermost atomic layer, the catalytic performance can be related to the surface composition. The results on the ceramic ferrites show that for inverse spinels octahedrally coordinated cations are present on the surface, whereas tetrahedral sites are almost invisible. A relation to catalytic activity could not be established because of the difficulties in preparing coprecipitated ferrites (catalysts). It was not possible to prepare a well defined series. The study of the normal spinel Co$_{1+x}$Al$_{2-x}$O$_4$ is in agreement with the model where only octahedral coordinated sites are exposed on the surface. LEIS signals, solely originating from the surface, show cobalt contents in agreement with XRD findings for octahedral cobalt in the bulk. Furthermore, it was found that in the mechanism for selective reduction, ensemble size effects play an important role: at least four cobalt cations are necessary to provide a surface site where reactants can attach sufficiently. Na and K impurities hamper the interpretation, but no direct correlation is found between the presence of contaminants and catalytic activity.

The present results support the idea that mainly octahedral coordinated cations are exposed on the surface and that therefore these sites determine the catalytic activity. The two low-index planes that could satisfy this condition are the (111)B and the (110)D plane. It is believed that chemically induced segregation does not have a large influence on the presence of only octahedral sites at the surface. It is more likely that these sites are favoured because electric neutrality at the surface is more guaranteed. The stronger binding of cation-anion bonds in tetrahedral sites will also favour octahedral sites at the surface.

From the first perovskite measurements a preferential exposure of one cation was observed as was seen for the spinels. It is concluded that only twelvefold coordinated A sites are exposed at the surface. It is anticipated that the only plane that is exposed is the (100)G layer, but further research on the LaAlO$_3$ (100) single crystal, which is currently at our disposal, should confirm this. So far, this has not been possible due to alkali contamination.
Conclusions

It would be interesting to perform calculations in order to predict the preferential site exposure for both spinels and perovskites. However, since no experimental data was available, calculations on these systems were not yet considered worthwhile by theoretical physicists. It is hoped that the LEIS experiments can provide enough discussion to arouse the interest in this very important but also very complex field of surface science: the surface of oxides.
CHAPTER 8

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