Production of $^{15}$O$_2$ for PEP analysis of ammonia oxidation on Pt sponge

Kieft, I.E.

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Production of $[^{15}\text{O}]\text{O}_2$ for PEP analysis of ammonia oxidation on Pt sponge

Ingrid Kieft
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Supervisors: dr. ir. A.M. de Jong
ir. D.P. Sobczyk

Graduate professor: prof. dr. M.J.A. de Voigt
Abstract

Ammonia oxidation is an important process in the reduction of the amount of ammonia wasted into nature. Platinum can be used as a catalyst for the reaction to nitrogen and water. The exact reaction mechanism that takes place at the surface of the Pt is not yet fully understood. PEP experiments are done to gain more insight in this reaction process. The production method for $[^{15}\text{O}]\text{O}_2$ is investigated for use in PEP experiments.

A nitrogen gas target is irradiated with 7.1 MeV deuterons for the production of $[^{15}\text{O}]\text{O}_2$. A sodalime adsorber and activated carbon trap purify the flow. An H-mordenite trap is tested for the adsorption of $[^{15}\text{O}]\text{N}_2\text{O}$ from the flow. The labelled oxygen is separated from the nitrogen flow with a Mol. Sieve 13X GC column. A second method for labelled oxygen production is bombarding an oxygen/helium target with protons. An explorative study of this second production process is performed because the new cyclotron facility is incapable of accelerating deuterons.

Besides labelled oxygen also labelled ammonia is used for the analysis of the ammonia oxidation on Pt sponge. At temperatures below 400 K the catalyst shows a deactivation in a few minutes. PEP experiments indicate that the deactivation is mainly caused by nitrogen containing species. Temperature programmed desorption spectra indicate that the reactions of NH and NH$_2$ with OH are the rate limiting steps. Experiments prove that preadsorption of oxygen at the Pt sponge results in a faster deactivation, possibly by a non reactive form of oxygen on the platinum. Selectivity of the catalyst to N$_2$O production increases after initial deactivation. This suggests that N$_2$O is formed at higher surface coverages.
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Chapter 1

Introduction

An important topic in research nowadays is environmental pollution. To keep our environment clean, one of the problems to work on is the exhaust of ammonia. Ammonia is a waste product in industry and in agriculture. If ammonia is wasted into nature, it can cause problems because ammonia is a strong fertilizer and can therefore unbalance the natural equilibrium. Other problems with ammonia are that it contributes to acid rain, that it can damage your health and that it has a very irritating smell.

A solution to the ammonia problem can be the transformation of the ammonia by a catalyst into less harmful gases. A catalyst is a substance that influences the speed of a chemical reaction, without being consumed itself. An oxidation reaction of ammonia would give nitrogen and water in an ideal situation. Various types of catalysts have been tested for the ammonia oxidation: biological catalysts, metal oxide catalysts, ion-exchanged zeolites and metallic catalysts [1]. The majority of research on ammonia oxidation is done on platinum catalysts because of its high reactivity and high selectivity to nitrogen and low selectivity to nitrous oxide. The reaction can take place at low temperatures and at ambient pressure [2]. At temperatures below 400 K however, the platinum catalyst shows a considerable loss of activity as a function of time [1]. The process of the loss of activity of the catalyst is not yet fully understood, and it is the subject of this study. In this study oxidation on a Pt-sponge is examined to avoid influence of carrier material.

Several groups in the world are studying the ammonia oxidation process. Different methods are used for the investigation, for example infrared spectroscopy [3] or EELS [4]. In this study, the oxidation process is investigated by looking at concentration differences of the reactants in the reactor with Positron Emission Profiling (PEP). Interesting about this technique is that the kinetics of the labelled gas can be investigated in situ and at atmospheric pressure. To work with this technique, one of the reactants has to be labelled with a positron emitter. The activity in the reactor tube can be measured with PEP as a function of time and place. The production
method for $^{13}\text{N}\text{NH}_3$ is known [5] and it is used for the investigation of the elementary reaction steps. The goal of this project is to produce $^{15}\text{O}\text{O}_2$ and to use it for the study of the oxidation process.

An introduction to the measuring instruments that are used is given in chapter 2. The production method for $^{15}\text{O}\text{O}_2$ from a reaction of deuterons with nitrogen is described in chapter 3. Because of the installation of the new cyclotron facility that cannot accelerate deuterons, an explorative study for the production of $^{15}\text{O}\text{O}_2$ from a reaction of protons with oxygen is described in chapter 4. The analysis of the ammonia oxidation process is discussed in chapter 5.
Chapter 2

Measuring Instruments

2.1 The PEP detector

The PEP detector is designed to follow radioactive labelled gas in a reactor tube. Labelled molecules emit a positron that can annihilate with an electron to form two $\gamma$-photons. They can be detected with the PEP detector. A full description of the detector has been given by Mangnus et al. [6], here only a brief description is given.

Before annihilation of the positron and electron takes place, the positron quickly loses kinetic energy during scattering events with atomic electrons. When it approaches thermal equilibrium it will annihilate with an electron. The maximum range of a positron emitted by $^{15}$O in Pt sponge is about 1 mm, as is explained in chapter 3. The two photons that are formed in the annihilation each have an energy of 511 keV and they travel in opposite directions. Then they can be detected by a BGO crystal ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$-crystal) of the PEP detector.

The principle of PEP is the coincident detection of these two $\gamma$-photons. To allow coincident detection, there are two rows of each nine BGO-crystals. In figure 2.1 a schematic representation of the detector is given. In this project the distance between the detector banks is 80 mm. During an experiment the catalyst is situated in the middle. If a photon enters a BGO-crystal electrons are excited. When the electron de-excites a photon is emitted in the visual range. The signal of the BGO-crystal is amplified by a photomultiplier. The position of the annihilation can be reconstructed if a $\gamma$-photon is detected at the same time in both a crystal in the upper detection bank and a crystal in the lower detection bank. A straight line can be drawn between those two detector crystals to determine the annihilation position at the intersection of the line with the reactor axis. The reactor is considered to be one-dimensional. With this set-up there are 17 unique reconstruction positions, the distance between each measuring position is 3.25 mm [2, 7].

Because the position of the positron emitters can be determined with help of
the detectors a concentration profile can be made of the labelled molecules in the catalyst.

The average time resolution for the detection of two 511 keV gamma rays in coincidence is 23 ns. The maximum reconstruction rate for a binning time of one second is 35,000 reconstructions per second [8].

In the middle of the detector banks the reactor tube is placed. It is made of quartz and has an inner diameter of 4 mm. Inside this reactor tube is the catalyst. An oven is mounted around the reactor tube to keep it at a fixed temperature during the experiments. The oven can be heated to a maximum temperature of 673 K. The outside of the oven is cooled with water to protect the BGO-crystal from heating up. For the calibration of the counts that are measured with the PEP detector during the experiments with the catalyst a $^{22}\text{Na}$ tube with known activity is used.

2.2 The mass spectrometer

A Quadstar 422 mass spectrometer (MS) from Balzers Instruments is used to determine the composition of the flow that leaves the reactor.

A sample of the gas flow is led to the MS. There the incoming gas molecules are ionized to a positive charge. They are deflected by oscillating electric fields of four rod-shaped electrodes. The amplitudes of almost all oscillations escalate so that ultimately the ions will make contact with the rods. Only ions with a certain ratio of mass to charge m/e can pass through the system. The ions are detected with a Faraday cup. The dwell time per mass-to-charge ratio is set to 50 ms. The data are collected by a computer program that is supplied by Balzers.
In the ionization process molecules can be stripped into fragments. For example, the H_2O molecule can be measured with mass 18, 17, 16 and 1 because the hydrogen atoms can be stripped from the oxygen atom. Because of this phenomenon corrections have to be made for all signals. Mass 17 for example is used as signal for ammonia, but water gives also a small signal with mass 17. This has to be subtracted in order to get the true ammonia signal.

A difference in the degree of ionization leads to different mass to charge ratios measured with the MS. Correction factors for fragmentation and difference in ionization are supplied by Balzers.

Gases with known concentrations were measured to determine conversion factors for the calculation to concentrations from intensities, and to determine the background level of impurities.

### 2.3 Gas chromatography

Gas chromatography (GC) is a technique used to separate components of a gas or liquid sample. The components move through a column at different velocities and leave the column at different times. In this project the separation of gases is used to determine if a gas component is labelled with a radionuclide.

The Molecular Sieve 13X column (80-100 mesh, 1.86 m * 1/8" * 2 mm SS) is used to separate oxygen from nitrogen. The column contains a zeolite with a pore diameter of about 1.3 nm, the X indicates the type of crystal structure [9]. Zeolites are porous crystalline aluminosilicates which comprise assemblies of SiO_4 and AlO_4 tetrahedra joined together through the sharing of oxygen atoms. The crystal structure of the Mol. Sieves contains fine pores that form a series of interconnecting tunnels. Small molecules entering these pores pass through easily, larger molecules pass with more difficulty and thus more slowly. Elution is usually in order of increasing molecular size. According to Thompson [10] carbon dioxide (CO_2) is strongly retained by the Mol. Sieve columns. If the CO_2 is present in sufficiently high concentration it might cause interference with the light gases from a later sample injection. The Molecular Sieve column is deactivated by moisture [10]. The column can be used at room temperature. The flow that comes out of the column is analyzed by the MS.

The Hayesep columns are made of porous polymers with a uniform structure and pore widths. Columns made of porous polymers show a low affinity to strongly polar compounds, and therefore allow the separation of strongly polar samples. A Hayesep N (80-100 mesh, 1.8 m * 1/8" * 2 mm SS) and a Hayesep P column (80-100 mesh, o.d. 1/8 SS [5]) are used for separation of N_2O from other components in the gas.

The retention times of the gases of interest are given in chapter 3 and 4.
Chapter 3

Production of labelled oxygen with nitrogen target

3.1 Theory

3.1.1 Introduction

The main use of $^{15}$O-labelled oxygen is as a radiopharmaceutical. The $[^{15}O]_{2}$ is inhaled and then attached to the hemoglobin in the blood. The oxygen metabolism can be studied using positron emission tomography (PET) in hospitals. For this application research has been done on the production of $[^{15}O]_{2}$ [11, 12, 13, 14].

$[^{15}O]_{2}$ can be produced using different nuclear reactions, [15].

$$^{14}N(d,n)^{15}O$$ \hspace{1cm} (3.1)

$$^{15}N(p,n)^{15}O$$ \hspace{1cm} (3.2)

$$^{12}C(\alpha,n)^{15}O$$ \hspace{1cm} (3.3)

$$^{13}C(^{3}He,n)^{15}O$$ \hspace{1cm} (3.4)

$$^{16}O(p,pn)^{15}O$$ \hspace{1cm} (3.5)

The $^{14}N(d,n)^{15}O$ reaction is a well known reaction and mostly applied. It has been used before at the Eindhoven cyclotron facility by Jansen and Van der Linde to produce $[^{15}O]_{2}$O [16, 7]. This reaction is also used in this project. The use of enriched $^{15}$N is rather expensive, therefore reaction 3.2 is not used. Reactions 3.3 and 3.4, in which $\alpha$ and $^{3}$He particles are used, require a solid target. This has some disadvantages compared to a gaseous
target, for example that it is hard to get the labelled products out of the target. The last reaction that is mentioned is the $^{16}\text{O}(p,pn)^{15}\text{O}$ reaction. This reaction will be discussed in chapter 4, because this reaction will be used in the new cyclotron facility. The new cyclotron is incapable of accelerating deuterons, therefore an explorative study is done on this production process for PEP applications.

### 3.1.2 Yield

To calculate the threshold energy for a certain reaction $X(a,b)Y$, the difference in masses which is known as the Q value ($J$) of the reaction has to be known. Equation 3.6 \[Q = (m_{\text{initial}} - m_{\text{final}})c^2\] is the required equation, where $m_{\text{initial}}$ (kg) is the sum of the rest masses for the initial reaction products $X$ and $a$, and $m_{\text{final}}$ is the sum of the rest masses of the final reaction products $Y$ and $b$. The constant $c$ is the speed of light, $3 \times 10^8$ m·s$^{-1}$.

$$Q = (m_{\text{initial}} - m_{\text{final}})c^2 \quad (3.6)$$

The threshold energy ($J$) can then be calculated using equation 3.7.

$$E_{\text{th}} = \frac{(-Q)(m_Y + m_b)}{m_Y + m_b - m_a} \quad (3.7)$$

If $Q$ is larger than zero there is no threshold energy, the reaction will take place if the energy is large enough to overcome the Coulomb barriers. The Q value for the $^{14}\text{N}(d,n)^{15}\text{O}$ reaction is 5.065 MeV and therefore the reaction has no threshold energy.

To determine the optimal incident energy of the deuterons and to calculate the amount of radionuclides that are produced the excitation function is used. The excitation function shows the cross sections as function of incident energy and is given in figure 3.1. The data in this figure is based on the literature data given in [18], these data originate from multiple authors.

The activity that is produced in the target can be calculated using equation 3.8, [2].

$$A = (1 - e^{-\lambda t})n\int \frac{I}{q E_f} \sigma(E) \left(\frac{dE}{d(\rho x)}\right)^{-1} dE \quad (3.8)$$

where
- $A$ is produced activity (Bq)
- $\lambda$ is decay constant (s$^{-1}$)
- $t$ is radiation time (s)
- $n$ is number of target nuclei per unit of mass (kg$^{-1}$)
Figure 3.1: *Excitation function of the interaction of deuteron with nitrogen* [18].

I is beam current (A)
q is charge of projectiles (C)
E\(_i\) is initial energy of projectiles (MeV)
E\(_f\) is final energy of projectiles (MeV)
\(\sigma(E)\) is reaction cross section (m\(^2\))
\(dE/dx\) is stopping power (MeV·m\(^2\)·kg\(^{-1}\))

The initial energy is the energy the deuterons have when they enter the target. In the collisions with the nitrogen atoms they lose some of their energy. The amount of energy they lose in this trajectory depends on the stopping power of the nitrogen atoms.

The half life of \(^{15}\)O is 122.24 s, so 2.04 min [19]. The reaction that takes place in the decay process is:

\[
^{15}\text{O}_7 \rightarrow ^{15}\text{N}_8 + \beta^+ + \nu
\]  
(3.9)

This reaction takes place because \(^{15}\)O has an unfavourable ratio of neutrons to protons. The nucleus in fact has a superfluous amount of energy and wants an energetically more stable situation. In the \(^{15}\)O atom a proton is converted into a neutron which makes it a \(^{15}\)N atom. At the same time a positron and a neutrino are emitted. The neutrino has no electric charge. The maximum energy of a positron that is emitted by the \(^{15}\)O-atom is 1.72 MeV. The average energy of the positrons is 729 keV.

The range of positrons in a material can be estimated by using the rule of thumb in equation 3.10 which is known as the rule of Feather [20]. The
rule of Feather only gives a good estimation for $R_{\text{max}}$ (cm) if $E_{\text{max}}$ (MeV) is higher than 0.6 MeV. In this equation $\rho$ is the density in g·cm$^{-3}$.

\[ R_{\text{max}} \simeq \frac{0.542 \cdot E_{\text{max}} - 0.133}{\rho} \tag{3.10} \]

The density of pure platinum is 21.5 g·cm$^{-3}$, for the Pt sponge as used in the reactor tube the density is about 8 g·cm$^{-3}$. This means that the maximum range in pure Pt is 0.4 mm, in the Pt sponge it is 1 mm.

The positrons lose energy due to interactions with electrons in a material. The range of a positron depends on its energy and the density of the material in which it is emitted. When the positron is slowed down, it will annihilate with an electron. If the total momentum of the electron and positron is zero, two gamma's are formed each with an energy of 511 keV [17]. The total energy needs to be 1022 keV because of conservation of energy. The two photons will travel in opposite directions because of conservation of momentum. A deviation in energy of 2 keV FWHM and a deviation in angle distribution of 0°24' FWHM are the result of the average remaining momentum [21].

3.1.3 Purity

Several contamination products are formed when deuterons are used to irradiate nitrogen for labelled oxygen production. The contaminants can be divided into radionuclidic and radiochemical impurities.

Radionuclidic purity

Radionuclidic impurities that can be formed are $^{11}$C, $^{13}$N and $^{16}$N.

$^{11}$C is formed by the $^{14}$N(d,αn)$^{11}$C reaction. The threshold energy for the $^{14}$N(d,αn)$^{11}$C reaction is 5.9 MeV [11], the half life of $^{11}$C is $t_{1/2}=20.39$ min.

$^{13}$N is formed by the $^{14}$N(d,t)$^{13}$N reaction. The threshold energy for the $^{14}$N(d,t)$^{13}$N reaction is 4.9 MeV [11], the half life of $^{13}$N is $t_{1/2}=9.97$ min. For energies below 8 MeV, the cross-sections for these reactions are not found in literature. $^{11}$C and $^{13}$N are both $\beta^+$ emitters.

In nature 0.37 % of all nitrogen is $^{15}$N. In a collision with a deuteron $^{15}$N is formed. This reaction has no threshold energy, and has high cross-sections for low energies. For 2.6 MeV deuterons the cross section is 890 mb [18]. This is a large cross section in comparison to the reaction of deuterons with $^{14}$N. $^{15}$N decays with $\beta^-$ and $\gamma$ emission. The half life of $^{15}$N is 7.10 s [22].

Radionuclidic impurities found in literature are given in table 3.1. In this table the incident energy of the deuterons and the beam current are given. Also the amount of oxygen that is added to the target gas is given.
The addition of oxygen improves the radiochemical purity as is explained in the next section.

Table 3.1: Radionuclidic impurities in literature.

<table>
<thead>
<tr>
<th></th>
<th>$E_i$ (MeV)</th>
<th>$I$ (µA)</th>
<th>$O_2$ addition</th>
<th>$^{15}$N</th>
<th>$^{11}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jansen [16]</td>
<td>7</td>
<td>0.5</td>
<td>-</td>
<td>0.5 %</td>
<td>0.004 %</td>
</tr>
<tr>
<td>Vonkeman [23]</td>
<td>7</td>
<td>15</td>
<td>0.05 %</td>
<td>2 %</td>
<td>-</td>
</tr>
<tr>
<td>Welch [12]</td>
<td>6.2</td>
<td>40</td>
<td>2 %</td>
<td>1 - 2 %</td>
<td>-</td>
</tr>
<tr>
<td>Mackay [13]</td>
<td>3.5</td>
<td>40</td>
<td>0.5 %</td>
<td>0.15 %</td>
<td>-</td>
</tr>
<tr>
<td>Clark [11]</td>
<td>6.1</td>
<td>30</td>
<td>-</td>
<td>&lt; 0.1 %</td>
<td>-</td>
</tr>
</tbody>
</table>

Radiochemical purity

For a better understanding of the formation of radiochemical impurities we look at the formation of $[^{15}\text{O}]_2$ as described by Ferrieri and Wolf [14]. He described the formation of $[^{15}\text{O}]_2$ by a hot atom process. He gave reaction 3.11 as the formation route for $[^{15}\text{O}]_2$. The * sign indicates a hot atom. In most cases the $[^{15}\text{O}]_3$ falls apart to $[^{15}\text{O}]_2$, but it can also be a stable contaminant. The $^{15}\text{O}^*$ atom can also react with $\text{N}_2$ to form $[^{15}\text{O}]\text{N}_2\text{O}$.

$$^{15}\text{O}^* + O_2 \rightarrow [^{15}\text{O} - O - O]^* \rightarrow ^{15}O_2 + O$$ (3.11)

In literature therefore often a mixture of nitrogen and oxygen is used as target gas. The amount of oxygen used varies from 0.5 % [13] to 2 % [12]. If some oxygen is added to the target gas, the radiochemical purity of $[^{15}\text{O}]_2$ is higher. The disadvantage of this is that the specific activity is decreased, because the ratio of labelled to unlabelled oxygen is decreased. Therefore, in this study the target gas is nitrogen 5.0 with an oxygen concentration below 5 ppm.

Contaminants can be expected from irradiation of the target material, or from impurities in the sweep gas. Contaminants that are found in literature are $^{18}\text{O}$ labelled $\text{N}_2\text{O}$, $\text{NO}_2$, $\text{CO}$, $\text{CO}_2$ and $\text{O}_3$, and some $[^{15}\text{N}]\text{N}_2$ [11, 16]. During irradiation also non-labelled $\text{CO}_2$ and $\text{N}_2\text{O}$ are formed [16], Ferrieri and Wolf [14] also found $\text{NO}_2$ and $\text{O}_3$ as trace chemical impurities. The trace chemical impurity $\text{CO}_2$ most likely arises from radiolytic oxidation of organic impurities [14]. In table 3.2 the impurities found in literature are given, the beam settings can be found in table 3.1.

To purify the flow from the contaminants, adsorbers are used. In literature mostly soda lime and activated charcoal are used [11, 12, 24]. Sometimes

---

1 Data subject to wide variations due to variable losses of products in the gas flow system.

---

17
Table 3.2: Radiochemical impurities in literature

<table>
<thead>
<tr>
<th></th>
<th>$^{15}$O$N_2$O</th>
<th>$^{15}$O$NO_2 + ^{15}$O$O_3$</th>
<th>$^{15}$O$CO$</th>
<th>$^{15}$O$CO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jansen [16]</td>
<td>9 %</td>
<td>&lt;4 % (^2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vonkeman [23]</td>
<td>0.5 %</td>
<td>-</td>
<td>&lt; 0.3 %</td>
<td>&lt; 0.3 %</td>
</tr>
<tr>
<td>Welch [12]</td>
<td>-</td>
<td>-</td>
<td>&lt; 0.5 %</td>
<td>&lt; 0.5 %</td>
</tr>
<tr>
<td>Mackay [13]</td>
<td>7 - 10 %</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Clark (^3)[11]</td>
<td>1.4 %</td>
<td>61 %(^4)</td>
<td>&lt; 0.1 %</td>
<td>&lt; 1 %</td>
</tr>
</tbody>
</table>

a silica gel is used to dry the gas [25]. Sodalime is used for the removal of NO$_2$, CO$_2$ and O$_3$ [12, 25]. Activated charcoal is used for trapping of N$_2$O [25]. These traps are used at room temperature and are replaced regularly. For the separation of labelled N$_2$O a cooled mordenite trap is used for the trapping of N$_2$O [16].

For the production of pure $^{15}$O$O_2$ the oxygen has to be separated from the target gas N$_2$. For medical applications the oxygen is not separated from the nitrogen since the $^{15}$O$O_2$ is taken in by inhalation. Jansen [16] studied various possibilities for this separation. He ruled out cryogenic separation because the boiling-point of oxygen at 90 K is close to the boiling-point of nitrogen at 77 K. He therefore tested several adsorbers at different temperatures. He found no metal at which the oxygen adsorbed well at a temperature higher than 77 K and desorbed well below 600 K. He mentioned decomposition of $^{15}$O$N_2O$ as a possible production of $^{15}$O$O_2$, but stated that the specific activity will be low because of the decomposition of unlabelled N$_2$O. He recommended the injection of minute amounts of target effluent, with the disadvantage of a lower specific activity and the introduction of nitrogen in the experiment.

3.2 Experimental

The 30 MeV AVF cyclotron of the Eindhoven University of Technology is used for acceleration of the projectiles. The beam of deuterons is directed to the nitrogen target for labelled oxygen production.

3.2.1 Schematic overview of set-up

Figure 3.2 shows a schematic overview of the test set-up.

In the irradiation bunker the nitrogen gasbottle is situated. From this bottle the nitrogen is continuously flowing to the target where it is irradiated

\(^2\)Value only for NO$_2$. O$_3$ was non detectable.

\(^3\)Data subject to wide variations due to variable losses of products in the gas flow system.

\(^4\)Value indirectly determined.
by the deuterons. The flow is controlled to 75 ml·min\(^{-1}\) so the average irradiation time is one minute. From here the gas is transported through tubes of 40 m length to the radiochemical lab. Here the gas is led through the adsorbers and is injected afterwards into a GC column with the use of a 6-way valve. The adsorbers and the GC columns that are used for each experiment are given in the Results section. After the GC column the flow is led to the PEP detector and then analyzed with a mass spectrometer. In the experiments for the determination of the composition of the target effluent the MS is placed directly after the column. NaI detectors measure the activity of the flow. In figure 3.2 five possible positions for NaI detectors are indicated, the positions of the NaI detectors will be given if their results are used for analysis. The deadtime for these detectors is experimentally determined to be 1.3·10\(^{-6}\) s [5].

### 3.2.2 Target

The target is made of aluminum, a schematic representation is depicted in figure 3.3. The target is cylindrical and has a length of 150 mm and a diameter of 25 mm. The gas volume inside the target is about 75 cm\(^3\). The nitrogen flows from the gas inlet (indicated with 1 in the figure) to the gas outlet (3). The beam enters from the left side (4) of the target. It has already passed one foil of Duratherm 600 before the beam hits a second Duratherm 600 foil. This is indicated as number 4 in the figure. The two foils have a thickness of 25 µm. The composition of Duratherm 600 is given in table 3.3 [16]. The density of the foil is 8.45 g·cm\(^{-3}\). Duratherm is a good heat conductor with a high melting point of 1620 K [20].

The beam that is used for the production of the labelled oxygen has an energy of 9.2 MeV, this way the same settings for the cyclotron that were
used in the project of Jansen [16] could be used in this project. By going through the first foil, the beam loses energy so that the average energy of the beam after the foil is 8.18 MeV, with an energy spread between 8.09 and 8.28 MeV. This is calculated with use of SRIM [26]. If the beam then goes through a second Duratherm foil the energy drops to 7.1 MeV, with an energy spread between 7.0 and 7.2 MeV [26].

Table 3.3: Composition of Duratherm 600 foil.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>41.5</td>
</tr>
<tr>
<td>Ni</td>
<td>25.5</td>
</tr>
<tr>
<td>Cr</td>
<td>12.5</td>
</tr>
<tr>
<td>Fe</td>
<td>10.1</td>
</tr>
<tr>
<td>Mo</td>
<td>4.0</td>
</tr>
<tr>
<td>W</td>
<td>3.9</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0</td>
</tr>
<tr>
<td>Be</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The gas in the target is nitrogen 5.0, the purity of the nitrogen is ≥ 99.999 vol%. The contaminations are: O₂ < 5 vpm, H₂O < 5 vpm and CₓHᵧ < 0.2 vpm. If the pressure in the target is 5 bar, the projected range of the deuterons with an energy of 7 MeV in the target is 76 ± 3 mm. Since the length of the target is 150 mm, all the deuterons will be stopped inside the target and Eᵦₐₙₙₐₜ = 0 MeV. The lateral straggling is 1.8 mm [26].

With equation 3.8 the produced activity can be calculated. For the calculation the half life τ₁/₂ = 122.24 s is used, so λ is 0.34 min⁻¹. The
radiation time that is used is 1 min, with a beam current of \( I = 0.5 \mu A \). The number of nitrogen atoms per kg is \( n = 4.30 \times 10^{25} \) atoms·kg\(^{-1}\).

With the cross sections that are shown in figure 3.1 and the stopping powers \( \frac{dE}{dx} \) that are given in table 3.4 [26], the produced activity can be calculated.

Table 3.4: Stopping powers for deuterium in nitrogen.

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>( \frac{dE}{dx} ) (MeV·m(^{-2})·kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>9.14</td>
</tr>
<tr>
<td>6</td>
<td>10.26</td>
</tr>
<tr>
<td>5</td>
<td>11.75</td>
</tr>
<tr>
<td>4</td>
<td>13.87</td>
</tr>
<tr>
<td>3</td>
<td>17.29</td>
</tr>
<tr>
<td>2</td>
<td>23.65</td>
</tr>
<tr>
<td>1</td>
<td>37.57</td>
</tr>
</tbody>
</table>

The total activity of the \( ^{15}O \) atoms is \( A = 290 \) MBq after one minute of irradiation. The amount of \( ^{16}N \) that is produced is estimated to be 22 MBq. This estimation is given because the cross sections for the production of \( ^{16}N \) with energies above 2.6 MeV are not known. For the calculation the cross sections are assumed to have a constant value of 900 mb which is about the cross section for 2.6 MeV.

For \( ^{13}N \) and \( ^{11}C \) no estimations can be given since no cross sections are found in literature for the relevant energies.

3.2.3 Absorbers

The traps that are used in literature for the production of \( ^{15}O\)O\(_2\) are sodalime and activated charcoal as mentioned before.

The sodalime (made of sodium hydroxide and potassium hydroxide) that is used in this project is delivered by Merck with a particle size of 2 to 5 mm. The sodalime adsorber is used in order to remove the labelled nitrogen oxide \( ^{15}O\)NO\(_2\) and labelled ozone \( ^{15}O\)O\(_3\). Also CO\(_2\) is adsorbed on the sodalime. The trap adsorbs \( ^{15}O\)NO\(_2\) and decomposes \( ^{15}O\)O\(_3\) into \( ^{15}O\)(O\(_2\)+O*) [16]. The * marks the adsorbed state. The sodalime has to be replaced every 30 hours according to Van der Linde [7] who used settings similar to the ones used in this project. According to Clark [11] the volume of the trap is not critical. The volume of the trap that is used in this project is 7.5 cm\(^3\).

The activated carbon trap is used in order to remove the \( ^{15}O\)N\(_2\)O. If the volume of the charcoal trap is too large, some \( ^{15}O\)O\(_2\) is lost [11]. The particle size of the charcoal is in the order of 5 mm. The initial volume of
the trap is 15 cm$^3$. It is changed during the experiments as is explained in the section Results.

Van der Linde [7] used an H-mordenite trap to trap $^{15}$O$\text{N}_2\text{O}$. In this project an H-mordenite trap is tested for the removal of $^{15}$O$\text{N}_2\text{O}$ from the flow. Mordenite is one of many types of zeolites. The formula of a typical unit cell for H-mordenite is $\text{H}_8[(\text{AlO}_2)\text{S}_4\text{O}_{40}]$ [27]. The H-mordenite is made for our purpose from $\text{NH}_4^+$-mordenite powder. The mordenite has been calcined by flowing a mixture of 80\% N$_2$ and 20\% O$_2$ at 100 ml·min$^{-1}$ over the mordenite at a temperature of 570 K for 2 hours followed by 820 K for $9\frac{1}{2}$ hours. The powder is then pressed with a pressure of 10,000 kg for 1 minute. One gram of mordenite grains of a size larger than 0.5 mm were put in a stainless steel tube, which has the disadvantage that the thermal conductivity is low. The stainless steel tube has an inner diameter of 4 mm and the thickness of the wall is 1 mm. For the use of a cold trap it is important that the gas used is dry, otherwise ice may block the trap.

3.3 Results

3.3.1 System characteristics

When the irradiation is started it takes some time before the activity is transported to the radiochemical lab from the target in the bunker. This is shown in figure 3.4. The figure also shows the effect of the build-up of activity after the start of the irradiation. It is important that the residence time in the target and the transporter tubes is short, because of the short half life of $^{15}$O.

![Figure 3.4: Activity measured in the radiochemical lab after start irradiation.](image-url)
Figure 3.4 shows the activity entering the radiochemical lab. If the flow would be ideal this would take less than half a minute since the speed of the flow is 75 ml·min$^{-1}$ and the distance is 40 m with a volume of 0.8 ml per meter. At time $t = 0$ s the irradiation is started and after about 210 s the first activity is detected in the lab. Note that it takes over ten minutes before steady state is reached.

The activity that enters the lab is measured with the PEP detector. An empty reactor tube is placed in the detector and the target effluent is flowed through it. The activity from this flow is determined with use of a calibration sample of $^{22}$Na. This calibration sample has the same dimensions as the reactor tube. The activity of the $^{15}$O flow is $A = 0.83$ MBq·ml$^{-1}$ at steady state production. The theoretical calculated activity in the target is 290 MBq for 75 ml or 3.9 MBq·ml$^{-1}$, after transportation to the PEP detector in 210 s would be decayed to 1.2 MBq·ml$^{-1}$.

In total three effects are observed. First, the transportation time of the labelled products to the PEP set-up is longer than theoretically expected. Second, the build-up of activity takes longer than expected. And third the produced activity is less than calculated. Reasons for these effects that are mentioned in literature are the loss of some $^{15}$O hot atoms on the walls of the target before they form $[^{15}\text{O}]_{2}$ and the flow dynamics inside the target [7]. If the flow pattern is not ideal this leads to a lower amount of $^{15}$O in the flow. A reason for the slow transportation of the labelled oxygen through the tubes can be a sticky behavior of oxygen.

### 3.3.2 Radionuclidic purity

Decay curve analysis is performed on the target effluent gas. The measurements are performed in the radiochemical lab and the flow has gone through the transportation tubes before analysis. This means that nuclides with a longer half life have comparatively less decayed than nuclides with a short half life. Since the half life of $^{16}$N is only 7.10 s, all $^{16}$N will have decayed before it is transported to the radiochemical lab.

For the experiment the gas is flushed into an empty tube which is closed at the ends by two three way valves. Helium is flushed through the supply tubes to lower the background activity. The activity is measured as a function of time with a NaI detector. From the experiments with the decay curve analysis it appears that the decay time of the gas is not the decay time of pure $^{15}$O. There is another emitter that has a longer half life present in the flow. This can be a positron emitter like $^{13}$N or $^{14}$C, or an emitter of $\gamma$'s or high energetic $\beta$'s.

For the decay curve analysis the data are fitted with equation 3.12 in Microcal Origin 6.0.
where \( \frac{N}{N_0} \) is the measured activity normalized to the activity at the first data point (-).

\( \lambda_O, \lambda_N \) and \( \lambda_C \) are the decay constants for respectively \(^{15}\text{O}, ^{13}\text{N}\) and \(^{11}\text{C}\) (s\(^{-1}\)).

\( a, b \) and \( c \) give the amount of the component present in the flow (-).

The fit gave a composition of 97.8 % \(^{15}\text{O}, 1.5 % ^{13}\text{N}\) and 0.9 % \(^{11}\text{C}\). The fit is shown in figure 3.5. The fit is accurate with an \( R^2 \) of 0.9997.

\[
\frac{N}{N_0} = a \cdot e^{-\lambda_O t} + b \cdot e^{-\lambda_N t} + c \cdot e^{-\lambda_C t}
\]  

(3.12)

---

**Figure 3.5:** Decay curve of the target effluent fitted with 0.9 % \(^{11}\text{C}, 1.5\% ^{13}\text{N}, \) and 97.8 % \(^{15}\text{O}\).

To find out if the effluent gas consists of only positron emitters a test is performed to measure the energy of the radiation. This was tested with help of the Stralingsbeschermingdienst (SBD). Graph 3.6 shows a gamma spectrum taken of a sample of target effluent gas. The detector was shielded for \( \beta \)'s. The only energy line that is higher than the minimum detectable limit is the 511 keV line. This means that there are only positron emitters present in the flow. The counts on the left of the 511 keV line form the Compton edge.

### 3.3.3 Radiochemical purity

**Introduction**

The radiochemical purity of the target effluent is tested by GC analysis. The Hayesep N column and the Molecular Sieve 13X column are used for
the separation of the different components in the gas. The retention times of the gases in the columns are determined by injection of unlabelled gases in the columns. The gases are measured with an MS.

The Mol. Sieve 13X is used at room temperature for the separation of O₂ and N₂. At room temperature N₂ and O₂ are well separated, at higher temperatures the separation between N₂ and O₂ becomes more difficult. At 400 K one peak for both components is measured. The retention time of N₂O is very long at room temperature. According to Thompson [10] CO₂ is strongly retained on Mol. Sieves as is explained in chapter 2. From literature it is known that CO can be separated with the Mol. Sieve 13X column with a long retention time of about 7 minutes at 408 K [28].

The Hayesep N column is used at 373 K for the separation of N₂O from N₂ and O₂. It is known [16] that N₂, O₂, NO₂ and NO have the same retention time in the Hayesep N column.

The retention times for the columns are given in table 3.5.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mol.Sieve 13X (298 K)</th>
<th>Hayesep N (373 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>101 s</td>
<td>29 s</td>
</tr>
<tr>
<td>N₂</td>
<td>123 s</td>
<td>29 s</td>
</tr>
<tr>
<td>N₂O</td>
<td>-</td>
<td>62 s</td>
</tr>
</tbody>
</table>

The retention times for CO₂ are not determined because the gas was not available. The Mol. Sieve 13X column is tested with a helium carrier flow of 20 ml·min⁻¹ He, the Hayesep N column is tested with a carrier flow of 35 ml·min⁻¹.
Target effluent

The composition of the irradiated gas is determined with the GC columns. After the column the unlabelled gases are detected with an MS, the labelled gases are detected with a NaI-detector.

Figure 3.7: NaI and MS signal of target effluent after Hayesep N column. Scale of NaI response is not shown. Signal m/e 44 is N₂O or CO₂.

The Hayesep N column is used to determine the amount of N₂O that is produced during irradiation. Figure 3.7 shows a separation of the O₂ and N₂O. Together with the O₂ and N₂ peak also a peak for the mass-to-charge ratio 44 is observed. Since the retention time for N₂O is 33 s longer than the retention time of O₂ and N₂ this peak is most likely CO₂. Any NO or NO₂ present would have the same retention time as O₂ [16], these gases are not observed.

The peak in the NaI signal for the [¹⁵O]O₂ is at maximum about 1000 counts, the peak for [¹⁵O]N₂O is about 100 counts and the background is about 45 counts. From the surface area’s under the NaI signal the percentage of activity from [¹⁵O]N₂O is determined. Because of the short half life of ¹⁵O a correction is made for the [¹⁵O]N₂O signal. About 8% of the activity appeared to originate from the labelled N₂O. The N₂O peak from the MS signal indicates a production of unlabelled N₂O.

The target effluent is also analyzed with the Mol. Sieve 13X column which separates O₂ from N₂. Figure 3.8 shows a clear separation between oxygen and nitrogen. The NaI detector detected activity only during the oxygen peak. The maximum number of counts is about 1000, the background is about 50 counts. At the same time as the nitrogen peak a small
peak in m/e ratio 44 is detected. This can be the CO₂ effect that is discussed in chapter 2.

Any [13N]N₂ present in the flow would be detected with the NaI detector during the nitrogen peak. The signal of the NaI detector shows no peak for possible [13N]N₂. However, the N₂ peak is widely spread and the concentration level of [13N]N₂ can be similar to background noise. So still about 2 or 3 % [13N]N₂ can be present in the flow.

**Sodalime and activated carbon traps**

If the target effluent is flowed through the sodalime trap then 4 % of the activity is lost in the trap. This number is determined by comparing the activity in the flow led through a bypass around the trap with the activity in the flow led through the trap. The adsorbed activity consists of [15O]NO₂ and [15O]CO₂. The loss of activity is also caused by decay of the activity during the time the flow is inside the trap. After the flow was switched to the trap it took 15 s before the first activity was detected after the trap, in this time 8 % of the radioactive molecules has decayed. In steady state the flow goes faster through the trap and there is less than 8 % decay in the trap. The amount of [15O]NO₂ and [15O]CO₂ adsorbed in the trap is less than 4 % of the total activity.

The activated carbon trap is tested for trapping of N₂O. The initial volume of the trap was 15 cm³. With this initial set-up the activity after the trap is reduced to about 54 % of the original activity. It is not likely
that the activity in flow consists for 46 % of $[^{15}\text{O}]\text{N}_2\text{O}$ since in literature no percentages higher than 10 % are reported. The activity loss can be caused by adsorption of $[^{15}\text{O}]\text{O}_2$ or by decay of the activity in the flow in the trap. After the flow was switched to the trap it took 2 minutes before the first activity was detected after the trap, in this time 50 % has decayed. In steady state the flow probably goes faster through the trap, but the effect of decay in the trap is large. To lower this effect the trap was made half the original size. The volume effect was the same. After this the trap was made 4 cm$^3$. The activity of the flow after the trap is now reduced to about 72 % of the initial activity. One minute after the switch of the flow to the trap the first activity was detected. In this time 29 % has decayed. It can be concluded that the loss of activity in the carbon trap is mainly caused by decay of the activity in the flow when it passes the trap. The adsorption of $\text{N}_2\text{O}$ in the trap is tested by sending the flow from the trap to the Hayesep N column.

![Graph showing concentration of gases](image)

Figure 3.9: MS and NaI signals of irradiated gas that passed the activated charcoal trap and Hayesep N column. Scale of NaI response is not shown. Signal $m/e$ 44 is $\text{N}_2\text{O}$ or $\text{CO}_2$.

The signals from the MS and the NaI detector are shown in figure 3.9. The peak of the NaI detector for oxygen is at maximum 1075, the background is about 50 in this measurement. No clear $[^{15}\text{O}]\text{N}_2\text{O}$ peak is detected after charcoal trap, but some unlabelled $\text{N}_2\text{O}$ is detected with the MS. This means that the activated charcoal trap does not remove all $\text{N}_2\text{O}$.

Analysis with the Mol. Sieve 13X column of the gas that passes the sodalime and activated carbon trap showed that no $\text{N}_2\text{O}$ or $\text{CO}_2$ are present.
in the flow after this GC column. If this set-up is used for injection into the PEP detector the oxygen is well separated from the other gases.

H-mordenite trap

The H-mordenite trap is also tested for the trapping of N₂O. Mordenite that is cooled in a bath of ethanol (C₂H₅OH) and liquid nitrogen traps N₂O, but at too low temperatures oxygen is also trapped. At a temperature of 213 K [¹⁵O]N₂O is trapped and [¹⁵O]O₂ flows through, which is the desired situation. About 85% of the activity of the flow passes the cooled mordenite trap. As is shown in figure 3.10 no N₂O pulse is seen after the Hayesep N column. The peak in the signal m/e 44 from the MS is again probably CO₂. Only [¹⁵O]O₂ is detected by the NaI-detector. The peak of the NaI signal is about 1200 counts, the background is about 60 counts.

![Graph showing concentration of CO₂ and N₂O over time](image)

Figure 3.10: NaI and MS signal of the irradiated gas that passed the H-mordenite trap at 213 K and the Hayesep N column. Scale of NaI response is not shown. Signal m/e 44 is N₂O or CO₂.

To achieve pure [¹⁵O]N₂O pulses, the mordenite trap is flushed for 30 s with helium of 200 ml·min⁻¹ to flow out small amounts of oxygen that might be present. Then the trap is heated in a bowl of hot water and the N₂O desorbs. The pulse of N₂O is sent through the Hayesep N column. The result is shown in figure 3.11. With the NaI detector only [¹⁵O]N₂O is detected in the pulse, no [¹⁵O]O₂ is detected. For the [¹⁵O]N₂O the maximum detected with the NaI detector is about 200 counts, with a background of about 15 counts. The oxygen signal of the MS does not show a peak, but the N₂O signal does. This means that N₂O can be selectively adsorbed, but the
specific activity of the $N_2O$ pulse is not high. The specific activity can be optimized by making the adsorption time shorter because $^{15}O$N$_2O$ decays and stable N$_2O$ does not.

Even though the H-mordenite trap is more efficient in the removal of the $N_2O$ than the activated charcoal trap, it is not used for the catalytic experiments of chapter 5 because of the complexity of the set-up.

Composition of the flow

The total composition of the target effluent can be derived from the experiments described above. Remember that the experiments are done in the radiochemical lab and that the flow has gone through the transportation tubes.

The main gas in the flow is of course $N_2$. Other unlabelled gases that are detected are $O_2$ and $N_2O$. Experiments also indicate production of some unlabelled $CO_2$. No exact amounts could be determined for these gases, but it can be estimated that the amounts are $< 1\%$.

The percentages for the labelled products are displayed in table 3.6. The amount of $[^{15}O]O_3$ can not be determined. The $O_3$ is decomposed on the sodalime. The amount of $[^{15}O]CO_2$ and $[^{15}O]NO_2$ is determined indirectly by the activity lost in the sodalime trap. The $^{15}N$ and $^{11}C$ emitters are not detected with the GC analysis, the amounts are estimated from decay curve analysis.
Table 3.6: Composition of labelled products in the target effluent

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{15}$O labelled species</td>
<td>97.8 %</td>
</tr>
<tr>
<td>$^{13}$N labelled species</td>
<td>1.5 %</td>
</tr>
<tr>
<td>$^{11}$C labelled species</td>
<td>0.9 %</td>
</tr>
<tr>
<td>$[^{15}$O]O$_2$</td>
<td>± 85 %</td>
</tr>
<tr>
<td>$[^{15}$O]N$_2$O</td>
<td>8 %</td>
</tr>
<tr>
<td>$[^{15}$O]CO$_2$ + $[^{15}$O]NO$_2$</td>
<td>≤ 4 %</td>
</tr>
<tr>
<td>$^{13}$N$_2$</td>
<td>≤ 1.5 %</td>
</tr>
<tr>
<td>$[^{11}$C]CO / $[^{11}$C]CO$_2$</td>
<td>≤ 0.9 %</td>
</tr>
<tr>
<td>$[^{15}$O]O$_3$</td>
<td>?</td>
</tr>
</tbody>
</table>

3.4 Conclusions and recommendations

The $^{14}$N(d,n)$^{15}$O reaction can be well applied for production of $[^{15}$O]O$_2$ for PEP experiments. A 0.5 $\mu$A beam of 7.1 MeV deuterons on a target of 5 bar nitrogen gas gives sufficient yield for PEP measurements. The continuous production and short half life of $^{15}$O make serial measurements possible.

The purity in the target effluent towards $[^{15}$O]O$_2$ is about 85 %. A measurement of the gamma spectrum of the target effluent proved that only positron emitters were produced. The radionuclidic impurity of 1.5 % $^{13}$N is similar to what is found in literature [23, 12]. The 0.9 % $^{11}$C is higher than reported in literature [23]. The amounts of radiochemical impurities $[^{15}$O]N$_2$O (8 %), $[^{15}$O]CO$_2$ + $[^{15}$O]NO$_2$ (≤ 4 %) are in agreement with literature [16]. The amount of $[^{15}$O]O$_3$ could not be determined. As unlabelled contaminant N$_2$O is detected, this contaminant is not added to the target gas and must therefore be entirely radiolytic. Unlabelled oxygen and CO$_2$ are also detected in the target effluent.

To remove contaminants from the flow the sodalime trap (for NO$_2$, CO$_2$ and O$_3$) and the activated carbon trap (for N$_2$O) are used. A cooled H-mordenite trap can also be used to remove N$_2$O from the flow. The carbon trap is more practical to use than the H-mordenite trap. The carbon trap does not remove all N$_2$O, but if the Mol. Sieve 13X column is used for the separation of O$_2$ and N$_2$ the remainder of the N$_2$O is strongly retained in this column.

The use of a GC column for injection of the $[^{15}$O]O$_2$ in the PEP reactor has the disadvantage compared to direct injection that only a small amount of activity can be injected. The advantage is that the $[^{15}$O]O$_2$ is free of radiochemical and radionuclidic impurities. Only a small amount of carrier oxygen is present, no carrier is added. If large amounts of activity are needed
the flow can be injected directly into the PEP detector after it is purified by the adsorbers. The disadvantage is that a lot of N₂ is injected into the reactor.

It is also possible to inject $^{15}$O-labelled N₂O into the PEP reactor. For this purpose the sodalime trap and the cooled H-mordenite trap are used. After the H-mordenite trap is flushed with helium and heated the flow can be injected directly in the PEP set-up. Besides N₂O also some N₂ is injected. A problem with this method is the heating of the trap. It is necessary to heat the trap fast to get a sharp peak of N₂O. The heating of the stainless steel and the mordenite grains does not go fast and the pulse lasts over 20 seconds. To improve the production method of $^{15}$O$N₂O$ a smaller H-mordenite trap must be made and the heating method needs to be improved.

A recommendation for further analysis of the flow is to calibrate the GC columns for the CO₂ retention time.
3.5 Safety.

3.5.1 Radiation level in the lab

In daily life everyone is exposed to a certain very low amount of radiation from radioactive elements that are present in nature. Radioactivity can cause damage to persons that are exposed to the radiation. If a part of the human body is exposed to radiation, the extent of the exposure is expressed by a numerical value for dose. If the entire body is irradiated the exposure is given in effective dose, a weighted average of the damage to all organs. The unit for the quantity effective dose is the Sievert.

There are two types of health effects as a consequence of radiation, the deterministic and the stochastic effects. In case of exposure to high doses the health effects are acute and symptoms of disease will appear within hours to a few months. The threshold dose for the first observable effects is 300 mSv exposed to the body in a short time period. These are the deterministic effects and they have to be prevented at all times. In case of exposure to low doses the effects are called the stochastic effects. A low dose of radiation can still be carcinogenic and it can lead to genetic effects. The effects occur with distribution of probability. Because of this probability distribution extra care should be taken when working with radioactivity to keep the dose as low as reasonably achievable. The dose limit for a radiological worker is 20 mSv per year. All experimental set-ups should at least be protected in a way that this dose limit for the workers will not be exceeded. For the work in this project an estimation will be given of the exposure to radiation.

The radiation level due to the γ radiation of the radioactive gas that flows in the tubes can be estimated with formula 3.13 [29]. This rule of thumb is based on the assumption that all activity is located in one point.

\[
\frac{dH}{dt} = h \cdot \frac{A}{r^2}
\]

\[
h = \frac{1}{8} \Sigma f \cdot E
\]

where
\[\frac{dH}{dt}\] is dose tempo (µSv·h⁻¹)
\(h\) is gamma dose constant (µSv·h⁻¹ per MBq at 1 m distance)
\(A\) is activity (MBq)
\(r\) is distance (m)
\(f\) emission probability (-)
\(E\) energy (MeV)

For positron decay followed by the annihilation, the energy of the photons is \(E = 511\) keV with the emission probability of \(f = 2\).
The tubes that are used in the lab have an internal diameter of 1 mm. The volume of 1 meter of a tube is therefore about 0.8 ml. The activity is measured to be 0.83 MBq·ml⁻¹, so the activity inside this one meter tube is 0.65 MBq.

If the tube is in a straight line perpendicular to the person a geometrical correction should be made because the source is not a point source. The correction factor for a tube of 1 meter length that lies 1 meter away perpendicular to the person is 0.95. This means that the dose a person receives is a factor 0.95 lower than for a point source at the same distance. For a line source 30 cm away the correction factor is 0.70.

A point source of 0.65 MBq at 30 cm gives a dose tempo of 0.92 µSv·h⁻¹, for a line source this gives 0.64 µSv·h⁻¹. If the distance to the point source is one meter, the dose tempo is 0.8 µSv·h⁻¹, for the line source this is still 0.8 µSv·h⁻¹.

The radiation level due to \(\beta^+\) radiation can also be estimated. The maximum energy of the \(\beta^+\) radiation is 1.72 MeV and the average energy is 729 keV. The maximum range of the positrons in the tube walls can be calculated by equation 3.10. The tube walls are 1 mm thick, and are made of teflon. The density of this material is about \(\rho = 2 \text{ g·cm}^{-3}\). This means that the maximum range in this material is 0.4 cm, and the average range is 0.13 cm. Most of the positrons are not stopped in the tube wall.

An estimation for the skin dose tempo \(\frac{dH_s}{dt}\) can be made with use of equation 3.15 [29]. This rule of thumb is valid if the distance to the radiation source is less than 10 % of the maximum range of the positrons in air. For the positrons with an average energy of 729 keV the range in air is 2.8 m, so the equation is valid to about 30 cm.

\[
\frac{dH_s}{dt} = 8f \frac{A}{r^2}
\]  
(3.15)

In equation 3.15 \(f\) is 1, because one positron is emitted in the decay of \(^{15}\text{O}\). For the calculation it is assumed that all positrons penetrate the tube wall, this gives a slight over-estimation of the dose. The skin dose due to positron emission at 30 cm of a one meter tube is 58 \(\mu\text{Sv·h}^{-1}\) for a point source, for a line source this is 41 \(\mu\text{Sv·h}^{-1}\). Equation 3.15 is used to determine an upper limit for the dose at 1 meter. For a point source this is 5.2 \(\mu\text{Sv·h}^{-1}\), for a line source this is 4.9 \(\mu\text{Sv·h}^{-1}\).

An example makes clear how safe it is to work in the lab. We assume that a person works for 5 hours per week for 45 weeks per year in the lab, so 225 hours per year. Constant work with a tube at 30 cm and a tube at 1 m gives a total dose of 47.34 \(\mu\text{Sv·h}^{-1}\). This gives a dose of almost 11 mSv per year, but remember that this is a slight over-estimation. In practice most
tubes near the PEP set-up are shielded with lead and give much lower doses. We can conclude that a person in the lab has to take care not to stand too close to the unprotected tubes, one step away from the tubes makes a lot of difference.

3.5.2 Radiation level during incident

If a tube is broken or by accident left open, the flow can do more harm. The inhalation and submersion close now have to be taken into account.

The concentration of activity in the lab can be calculated. The concentration depends on the activity that flows out of the tube, the decay time of the emitter and the ventilation in the lab. In this calculation it is assumed that the activity instantly spreads out over the entire volume of the lab. Three fume cupboards, each with a capacity of 800 m$^3$·h$^{-1}$, refresh the air in the lab with a volume of 400 m$^3$. If a tube is open, an activity of 0.83 MBq per ml enters the lab at a rate of 75 ml·min$^{-1}$. The values of the variables are given in table 3.7. Equation 3.16 gives the relation between these variables. The solved equation is given in 3.17.

$$\frac{dC}{dt} = \frac{F_{out}}{V}C(t) - \lambda C(t) + \frac{F_{in}}{V}C_{in}$$

(3.16)

$$C(t) = \frac{F_{in}C_{in}}{\lambda V + F_{out}} e^{-(F_{out} + \lambda) t} + \frac{F_{in}C_{in}}{\lambda V + F_{out}}$$

(3.17)

where

- $C(t)$ is the concentration of activity in the lab (MBq·m$^{-3}$)
- $C_{in}$ is the concentration of activity in the tube (MBq·m$^{-3}$)
- $t$ is the time (s)
- $\lambda$ is the decay constant of $^{15}$O (s$^{-1}$)
- $F_{in}$ is the flow from the tube (m$^3$·s$^{-1}$)
- $F_{out}$ is the flow caused by fume cupboards (m$^3$·s$^{-1}$)
- $V$ is the volume of the lab (m$^3$)

Table 3.7: Parameters for the calculation of the activity concentration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{in}$</td>
<td>$1.25 \cdot 10^{-6}$ m$^3$·s$^{-1}$</td>
</tr>
<tr>
<td>$F_{out}$</td>
<td>0.67 m$^3$·s$^{-1}$</td>
</tr>
<tr>
<td>$V$</td>
<td>400 m$^3$</td>
</tr>
<tr>
<td>$C_{in}$</td>
<td>$8.3 \cdot 10^{-5}$ MBq·m$^{-3}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$5.67 \cdot 10^{-3}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

The maximum level of activity that can be reached in the lab is 0.35 MBq·m$^{-3}$. The total amount of activity in the lab is at that time about 140
MBq. If the activity is inhaled this gives a certain dose, because the labelled oxygen flows into the lungs and is absorbed in the blood. The activity then spreads out over the entire body. An average person inhales 1.2 m$^3$ of air per hour [29]. If the concentration is 0.35 MBq·m$^{-3}$ the total amount of inhaled activity is 0.42 MBq in one hour. According to Hopkins [30] the dose a person receives after one hour of continuous inhalation of $[^{15}\text{O}]\text{O}_2$ is $1.59\text{ mrem} \cdot \text{mCi}^{-1}$ or $0.43\ \mu\text{Sv} \cdot \text{MBq}^{-1}$. The dose the person receives is therefore $0.18\ \mu\text{Sv} \cdot \text{h}^{-1}$.

Besides the inhalation dose, the dose to the outside of the body also has to be taken into account. This is called the dose from submersion. The effective dose conversion coefficient for air submersion is $4.91 \cdot 10^{-14}\ \text{Sv} \cdot \text{Bq} \cdot \text{m}^{-3}$. This coefficient is determined if skin is not taken into account. If skin is taken into account the coefficient is $4.96 \cdot 10^{-14}\ \text{Sv} \cdot \text{Bq} \cdot \text{m}^{-3}$ or $179\ \mu\text{Sv} \cdot \text{m}^3\text{MBq}^{-1}\text{h}^{-1}$ [31]. The dose conversion coefficient for the skin is higher than for the other organs because of positron radiation.

$$E_H = e \int C(t) dt \quad (3.18)$$

The effective dose ($E_H$) can be calculated using equation 3.18, in which $e$ is the dose conversion coefficient. In this case $e = 179\ \mu\text{Sv} \cdot \text{m}^3\text{MBq}^{-1}\text{h}^{-1}$. A stay of one hour in the contaminated lab with a radiation level of 0.35 MBq·m$^{-3}$ gives a dose of $E_H = 63\ \mu\text{Sv}$.

We can conclude that the dose from submersion is much higher than the dose from inhalation. A person who is working in the lab in the case of an unperceived incident next to a tube at 30 cm and a tube at 1 m is exposed to a dose of $110\ \mu\text{Sv} \cdot \text{h}^{-1}$. The annual dose limit for radiological worker is reached in about 180 hours in this situation. There is no risk for deterministic effects.

The activity is removed by the fume cupboards. The contaminated air flows through a coalfilter, which absorbs most of the activity. Because of the short half life of the labelled oxygen, the small amount of activity that passes the filter is harmless to the environment.
Chapter 4

Production of labelled oxygen with oxygen target

4.1 Theory

A second method of $^{15}\text{O}O_2$ production is analyzed. This is the $^{16}\text{O}(p,pn)^{15}\text{O}$ production method. This method is analyzed because the new cyclotron facility cannot accelerate deuterons, but only protons to an energy of 18 to 30 MeV. The old cyclotron is used for an explorative study with protons of 26 MeV. The $^{16}\text{O}(p,pn)^{15}\text{O}$ reaction is not found in literature for the production of $^{15}\text{O}O_2$.

4.1.1 Yield and purity

The $^{16}\text{O}(p,pn)^{15}\text{O}$ reaction has a threshold energy of $E_{\text{thres}}=16.7$ MeV. In figure 4.1 the excitation function is given for the $^{16}\text{O}(p,pn)^{15}\text{O}$ reaction [18]. From literature [32] it is known that the maximum cross section for this reaction is at about 50 MeV, the cross section is then 75 mb.

The gas in the target is not pure oxygen, but a mixture of oxygen and helium. No reactions are found in literature for protons with this energy reacting with helium.

Radionuclidic purity

Radionuclidic impurities that can be formed are $^{13}\text{N}$, $^{17}\text{F}$ and $^{18}\text{F}$.

$^{18}\text{F}$ can be formed if a proton hits a $^{18}\text{O}$-atom. In nature 99.76 % of the oxygen isotopes is $^{16}\text{O}$, 0.20 % is $^{18}\text{O}$ and 0.038 % is $^{17}\text{O}$. The threshold energy for the reaction of a proton with $^{18}\text{O}$ is $E_{\text{thres}}=2.59$ MeV with $\sigma=700$ mb at 5 MeV [2]. The reaction cross section for 26 MeV is not found. The half life of $^{18}\text{F}$ is 109.77 min.

Formation of $^{17}\text{F}$ can take place by a $^{17}\text{O}(p,n)^{17}\text{F}$ or $^{18}\text{O}(p,2n)^{17}\text{F}$ reaction [15], no reaction cross sections are found. The half life of $^{17}\text{F}$ is 66s.
$^{13}$N can also be formed as by-product in the production process of $^{[15]O}O_2$. The threshold energy for $^{16}$O(p,$\alpha$)$^{13}$N is 5.5 MeV. The half life of $^{13}$N is 9.97 min. In figure 4.1 the cross sections for the $^{13}$N production with protons are given [18]. The data only go up to an energy of 16 MeV while the energy of the protons used is 26 MeV. In [32] different cross sections are found. The maximum cross section that is given there is 19 mb at 23 MeV. At an energy of 26 MeV the cross section is about 15 mb.

Another reaction that can produce a by-product is the $^{16}$O(p,$\alpha p n$)$^{11}$C-reaction. The threshold energy is 27.5 MeV and will therefore not occur [32]. The $^{16}$O(p,2$\alpha p n$)$^7$Be-reaction has a threshold energy of 35.5 MeV [32].

Radiochemical purity

No literature data is found for the production of labelled oxygen with protons with an energy of around 26 MeV. However, the use of a proton beam on an oxygen target is used by Parks [33] and Stöcklin [34] for the production of $^{13}$N labelled species. Parks used a 10 to 15 atm high purity oxygen target with a 5 to 10 µA beam of 15 MeV protons. The produced labelled nitrogen atoms are found in the primary products $^{13}$N$_2$, $^{13}$N$_2$O and $^{13}$NO$_2$ with a ratio of 8:1:3.5. Any $^{13}$N$_2$O$_5$ that is formed is lost on the walls.

Due to N$_2$ radiolysis also nonradioactive N$_2$O, NO and NO$_2$ are formed according to Parks [33].

The disadvantage of this method of production of labelled oxygen is that the specific activity of the $^{[15]O}O_2$ will be very low since oxygen is used as the target gas.
4.2 Experimental

The same target that is used for the $^{15}\text{O}\text{O}_2$ production with deuterons is used for the $^{15}\text{O}\text{O}_2$ production with protons. Since not all energy is lost in the gas target, the beam is dumped on a carbon beamstop that is cooled with water.

With equation 3.8 the activity that is theoretically produced can be calculated. The target gas that is used is 4.93 vol% oxygen in helium. If the pressure in the target is 5 bar, the density is $0.0012 \text{ g cm}^{-3}$. The stopping power in this situation is $2.0 \text{ MeV m}^2 \text{ kg}^{-1}$ for 26 MeV protons. The protons have a projected range with this energy of about $6.0\pm0.2$ m. If they have an energy of 25.5 MeV the projected range is $5.8\pm0.2$ m [26]. The target length is about 15 cm, this means that the protons lose $0.5$ MeV of energy on average on this distance.

Table 4.1: Parameters for activity calculation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.327 min$^{-1}$</td>
</tr>
<tr>
<td>$n$</td>
<td>$1.12 \cdot 10^{25}$ atoms kg$^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>1.2 $\mu$A</td>
</tr>
<tr>
<td>$t$</td>
<td>1 min</td>
</tr>
<tr>
<td>$q$</td>
<td>$1.602 \cdot 10^{-19}$ C</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>63 mb [18]</td>
</tr>
<tr>
<td>$\delta E_{\text{abs}}$</td>
<td>$2.0 \text{ MeV m}^2 \text{ kg}^{-1}$</td>
</tr>
</tbody>
</table>

In table 4.1 the values are given for the calculation of the activity. Equation 3.8 is used to calculate the activity. The activity that is produced in the form of $^{15}\text{O}$ is $A = 37 \text{ MBq}$ and in the form of $^{13}\text{N}$ it is about $9 \text{ MBq}$. The activity per ml then becomes theoretically $0.6 \text{ MBq ml}^{-1}$. Due to high radiation levels near the target it is for safety reasons not possible to use a higher current for the production.

4.3 Results

The total activity in the flow is measured by the PEP detector. When the target effluent is flowed through an empty reactor tube the activity of the flow is $0.1 \text{ MBq ml}^{-1}$.

4.3.1 Radionuclidic purity

A decay curve analysis is performed on the target effluent in the same way as presented in chapter 3. The activity as function of time is measured with a NaI detector and corrected for deadtime. This decay curve is fitted
in Microcal Origin 6.0 with the half-lives of $^{15}\text{O}$, $^{13}\text{N}$ and $^{18}\text{F}$. For this fit equation 3.12 is used with the decay constant of $^{18}\text{F}$ instead of $^{11}\text{C}$. The result of the experiment is shown in the figure 4.2.

![Decay curve](image)

Figure 4.2: Decay curve of the target effluent fitted with 0.9 % $^{18}\text{F}$, 1.9 % $^{13}\text{N}$ and 97.3 % $^{15}\text{O}$.

The fit shows a composition of 0.9 % $^{18}\text{F}$, 1.9 % $^{13}\text{N}$ and 97.3 % $^{15}\text{O}$ with the $R^2$ of the fit 0.99958. The amount of $^{13}\text{N}$ measured is much smaller than theoretically expected. A cause can be an error in the cross sections for $^{13}\text{N}$ production, or sticky behavior of $^{13}\text{N}$ labelled products in the target and transportation tubes. It is not known in what compound $^{18}\text{F}$ is present in the flow.

### 4.3.2 Radiochemical purity

The radiochemical purity is tested with a Mol. Sieve 13X column and a Hayesep P column. The Mol. Sieve 13X column is used before in chapter 3, the retention times can be found in table 3.5. The retention times of the Hayesep P column are given in table 4.2. The NaI detector is pointed to the end of the GC column.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Hayesep P (383 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>35-40 s</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>35-40 s</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>40 s</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>70 s</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$</td>
<td>110 s</td>
</tr>
</tbody>
</table>
The sodalime trap removes NO\textsubscript{2}, CO\textsubscript{2} and O\textsubscript{3} from the flow. After the sodalime trap about 5 \% of the activity is lost. This is partly caused by adsorption of labelled NO\textsubscript{2} and CO\textsubscript{2} and partly caused by decay of the activity in the flow in the trap. About 6 seconds after the flow is switched to the sodalime trap the first activity is detected. In this time 3.4 \% of the \textsuperscript{15}O has decayed.

Figure 4.3: NaI and MS signals of target effluent after Mol. Sieve 13X column. Scale of NaI response is not shown.

The Mol. Sieve 13X column separates well the oxygen and nitrogen as is shown in figure 4.3. The maximum of the peak in the NaI signal is 200 counts, the background is about 40 counts. The signal of the NaI detector indicates that only the oxygen is labelled. The amount of \textsuperscript{13}N\textsubscript{2} is less than 1 \% of the labelled species. Together with the oxygen a small peak in the signal m/e 44 is observed, this can be the CO\textsubscript{2} problem as is discussed in chapter 2.

The target effluent is also analyzed with the Hayesep P column. The background for the NaI detector is relatively high in this measurement (about 800 counts) due to a different position of the NaI detector. Figure 4.4 shows a peak of O\textsubscript{2} and N\textsubscript{2}. This peak is also detected with the NaI detector with a maximum of about 1600 counts. With the MS no peaks are measured for NO, NO\textsubscript{2} or N\textsubscript{2}O. The m/e ratio 44 signal goes up a little during the O\textsubscript{2} peak, this indicates some CO\textsubscript{2} is formed. With the NaI detector a small peak is observed at the retention time of \textsuperscript{15}O\textsubscript{2}O. The peak has an area of less than 2 \% of the \textsuperscript{15}O\textsubscript{2} peak. A second test is performed to confirm that the peak is the \textsuperscript{15}O\textsubscript{2}O peak and not background noise, but the second test showed even more background noise. The signal of the NaI
Figure 4.4: \(\text{NaI and MS signal of target effluent after Hayesep P column. Scale of NaI response is not shown. Signal m/e 44 is } N_2O \text{ or } CO_2\).

detector showed no peak at the retention time of NO.

**Composition of the flow**

Since this is only an explorative study only an indication of the composition can be given. The flow consists of 4.93 \% \(O_2\) in helium. Measurements indicate some unlabelled \(N_2\) and \(CO_2\) are present in the flow, the amounts are less than 1 \%. An overview for the labelled compounds is given in table 4.3.

**Table 4.3: Composition of labelled products in the target effluent**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{15})O labelled species</td>
<td>97.3 %</td>
</tr>
<tr>
<td>(^{13})N labelled species</td>
<td>1.9 %</td>
</tr>
<tr>
<td>(^{18})F labelled species</td>
<td>0.9 %</td>
</tr>
<tr>
<td>([^{15})O]O_2</td>
<td>90 to 95 %</td>
</tr>
<tr>
<td>([^{15})O]N_2O or ([^{13})N]N_2O</td>
<td>(\leq 2 %)</td>
</tr>
<tr>
<td>([^{15})O]CO_2+ ([^{15})O]NO_2+ ([^{13})N]NO_2</td>
<td>(\leq 5 %)</td>
</tr>
<tr>
<td>([^{13})N]N_2</td>
<td>(\leq 1 %)</td>
</tr>
<tr>
<td>([^{15})O]O_3</td>
<td>?</td>
</tr>
<tr>
<td>([^{15})O]NO or ([^{13})N]NO</td>
<td>(\leq 1 %)</td>
</tr>
</tbody>
</table>

The amount of \([^{15}\O]O_3\) cannot be determined. However \(O_3\) is converted into \(O_2\) if the sodalime trap is used. The amount of \([^{15}\O]CO_2+ \([^{15}\O]NO_2\)
\[ ^{13}\text{N} \text{NO}_2 \] is only indirectly determined by determining the amount of activity lost in the sodalime trap. If the sodalime trap is not large enough the amount can be higher.

4.4 Conclusions and recommendations

The \( ^{16}\text{O}(p,pn)^{15}\text{O} \) reaction can be applied for the production of \( ^{15}\text{O}\text{O}_2 \) for PEP experiments. The target gas for this reaction is a mixture of oxygen in helium, this means that the specific activity of the labelled oxygen is low compared to the specific activity of the oxygen produced with the \( ^{14}\text{N}(d,n)^{15}\text{O} \) reaction.

The activity of the flow is 0.1 MBq·ml\(^{-1}\) with a 0.5 µA beam. This is low for injection in PEP experiments. Before a higher current can be used the target needs to be shielded better for safety reasons. For a higher yield of labelled products the oxygen percentage in the target gas can be raised from 4.93 vol % to for example 20 vol %.

Decay time experiments indicate that the radionuclidic contaminants are 1.9 % \( ^{13}\text{N} \) and 0.9 % \( ^{18}\text{F} \). GC analysis of the flow proved that less than 2 % of the activity is labelled N\(_2\)O. The amount of labelled N\(_2\) and NO is less than 1 % and the amount of O\(_3\) in the flow could not be determined. From the amount of activity trapped in the absorbers it was determined that less than 5 % of the labelled products is labelled CO\(_2\) or NO\(_2\). The use of sodalime and activated carbon removes most contaminants (NO\(_2\), CO\(_2\), O\(_3\) and N\(_2\)O).

More GC analysis needs to be done to make sure all contaminants are found. It is recommended to do a GC test with a column that can separate NO\(_2\) and CO\(_2\) from oxygen and nitrogen so the amounts of NO\(_2\) and CO\(_2\) present in the flow can be determined separately.

For injection of the labelled oxygen in PEP experiments no GC column is needed, the flow can be injected directly.
Chapter 5

Ammonia oxidation on Pt sponge

5.1 Theory

5.1.1 Introduction

The amount of ammonia wasted into our environment can be lowered by converting the ammonia into other gases that are environmentally friendly. Oxidation of ammonia can give nitrogen and water as reaction products. This reaction is given in equation 5.1. For ammonia oxidation a platinum sponge is found to be a good catalyst at temperatures higher than 400 K. At temperatures below 400 K the catalyst works for a period of minutes only. Experiments were done with low and stoichiometric concentrations of ammonia and oxygen. The process of deactivation of the platinum catalyst at low temperature provides us information about the ammonia oxidation at higher temperature.

The reaction given in equation 5.1 is highly exothermic with a reaction enthalpy ($\Delta H$) of -633 kJ·mol$^{-1}$[1].

$$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O \quad (5.1)$$

Nitrous oxide is a by-product at temperatures below 800 K on most catalysts [1]. Reaction 5.2 is also highly exothermic with a $\Delta H$ of -551 kJ·mol$^{-1}$ [1].

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (5.2)$$

At temperatures above 800 K nitric oxide (NO) is the main product, at temperatures above 1473 K the production of nitrogen is the main reaction [1].
The role of the catalytic surface is to provide an alternative reaction route for the gas-phase reaction, in which the activation energies for the separate steps are all significantly lower than for the uncatalyzed reaction [35]. This enhances the reaction rate, but the final equilibrium concentrations are not changed. If certain concentrations at certain pressure and temperature are predicted by thermodynamics this also applies to catalysis.

The ammonia oxidation reaction takes place on a platinum sponge. This is an example of heterogeneous catalysis, because the catalyst and the reactants are in different phases. The catalyst is in solid phase, and the reactants are in gas phase. The way molecules chemisorb, react and desorb on metal surfaces depends on a number of parameters such as the reactivity of the metal, the temperature at which the adsorption takes place, the structure of the substrate surface and the surface coverage of the adsorbate.

5.1.2 Surface structure

The lattice structure of platinum is the fcc structure. The low index faces of the structure are the (100), (110) and (111) planes. An atom in the (100) plane has four nearest neighbours in the surface, the (110) atom has only two nearest neighbours, and the (111) atom is in a close-packed structure with six nearest neighbours. The open surface of the (110) plane is generally most reactive [36].

Metals with an open structure have a higher reactivity on the surface. Also steps and defects in the material increase the reactivity. These surfaces form stronger bonds with adsorbates and the probability of molecules to dissociate is higher. A sponge catalyst exposes many different surfaces and all kinds of defects, therefore the heat of adsorption on a catalyst represents an average value [35]. The pure sponge catalyst is used here to avoid any influence of a catalyst carrier. Picture 5.1 [1] shows the structure of the Pt sponge.

Figure 5.1: SEM image of Pt sponge. Particle size 250 - 350 µm. Size of non porous particles 1 - 5 µm [1].
5.1.3 Reaction mechanism

Platinum catalysts show a considerable loss of activity as a function of time in the low temperature ammonia oxidation reaction. The loss of activity of the platinum catalysts is attributed in literature to oxidation of the platinum surface or to inhibition of the surface with reaction intermediates also called poisoning. A molecule is called poison if it blocks active sites on the surface of the catalyst and thus reduces the reaction rate. Before we go to the reaction mechanism, we first discuss the adsorption of oxygen and ammonia.

Adsorption

UHV experiments performed by Gland [37] prove that oxygen dissociation on platinum is activated. Oxygen can exist in molecularly bound form or as oxygen atoms on the surface.

\[ O_2 \rightarrow 2O \]  

(5.3)

The dissociation of oxygen as given in equation 5.3 is severely limited by preadsorbing atomic oxygen. On a stepped surface the adsorption of oxygen is substantially more probable than adsorption on a Pt(111) surface. This is most likely caused by a decreased activation energy for atomization on the stepped surface. The dissociated oxygen forms islands on the surface, this island growth mechanism is proven with LEED experiments even at low coverages [37].

Wintterlin et al. [38] proved the existence of a hot atom mechanism for the dissociation of \( O_2 \) on Pt(111). STM experiments at 160 K revealed that dissociation of \( O_2 \) creates hot atoms. The hot atoms show non thermal transient motion that can even induce chemical reactions.

In literature the formation of less reactive oxygen species is reported under various conditions. This is attributed to subsurface oxygen which is less reactive than oxygen adsorbed on the surface. Subsurface oxygen is found on Pt from 520 K [39].

Bradley et al. [40] did experiments on adsorption of ammonia. Ammonia adsorption is believed to be molecular on most Pt single crystal planes. At higher temperatures (>400 K) some ammonia dissociation is observed on Pt(100). They found that NH\(_3\) adsorption is not blocked by preadsorbed oxygen. It is therefore assumed that oxygen atoms occupy hollow (or three-fold) sites and ammonia occupies on-top (or one-fold) sites. Coadsorption with oxygen shows that O adatoms enhance the dissociation of NH\(_3\) [40].

For the reaction products that are formed during the ammonia oxidation it is known that nitrogen interacts weakly with Pt, and does not dissociate.
H₂O interacts weakly with most metal surfaces and desorbs readily upon formation under reaction conditions [35]. On clean Pt(111) H₂O desorbs at 180 K and hydroxyl groups recombine at 215 K [41]. N₂O adsorbs weakly on Pt [7], the desorption of N₂O is found at 86 K on Pt(111) [42].

The thermal desorption spectrum of NO is complex. On Pt(111) three distinct desorption processes are observed. At temperatures above 350 K desorption competes with dissociation [43].

Reaction steps

Studies of the reaction mechanism of the ammonia oxidation are performed under different reaction conditions. For example Mieher and Ho [4] and Bradley et al. [40] used high vacuum, Van den Broek [1] used ambient pressure and Fahmi et al. [41] did theoretical calculations. Several reaction steps are proposed. Since the reaction conditions are not the same at high vacuum and at ambient pressure also the reaction mechanism can differ.

The theory of Mieher and Ho [4] for ammonia oxidation on Pt(111) at UHV is based on three keypoints.

1. Oxygen atoms are the agents that are responsible for N-H bond cleavage. N-H bond cleavage becomes more difficult as more H atoms are removed.

2. All hydrogen from reacting ammonia eventually forms water, not H₂ or NH₃.

3. Oxygen will react preferentially with hydrogen rather than nitrogen, except in case of very high nitrogen concentrations when coverage dependent effects become important.

Supported by the stable intermediates NH, NH₂ and OH that were identified by EELS, Mieher and Ho come to the following reaction mechanism for water formation.

\[
\begin{align*}
NH_3 + O & \rightarrow NH_2 + HO \quad (5.4) \\
NH_2 + O & \rightarrow NH + HO \quad (5.5) \\
NH + O & \rightarrow N + HO \quad (5.6) \\
2OH & \rightarrow H_2O + O \quad (5.7) \\
OH + NH_3 & \rightarrow H_2O + NH_2 \quad (5.8) \\
OH + NH_2 & \rightarrow H_2O + NH \quad (5.9) \\
OH + NH & \rightarrow H_2O + N \quad (5.10)
\end{align*}
\]

They rule out equation 5.8 as main reaction for water formation and say that equation 5.9 and 5.10 are the rate limiting steps. The choice for
water formation is between OH + OH and OH + NHX. Mieher and Ho also recognize the existence of hot O* atoms created by O2 dissociation. They are reactive and can be important in the initial creation of OH species at low temperatures.

For the formation of NO they propose the following reactions:

\[ N + O \rightarrow NO \quad (5.11) \]
\[ NH + O \rightarrow NO + H \quad (5.12) \]

Mechanism 5.12 seems unlikely because water formation is the dominant reaction. They also state that there is no evidence to suggest that free H atoms occur at any time on the platinum surface. They conclude that there is a coverage dependent effect if there is an overabundance of N-containing species that favors NO formation. Since O2 recombination occurs at higher temperatures than N2 and NO formation Mieher and Ho conclude that O is not the mobile species.

For N2 formation they claim that equation 5.13 is the most likely mechanism.

\[ 2N \rightarrow N_2 \quad (5.13) \]

Nitrogen formation increases as the availability of O for NO formation decreases.

Bradley et al. [40] studied ammonia oxidation at Pt(100) at UHV. They attribute a part of N2 production to NO dissociation. On Pt(111) the NO does not dissociate readily but does on defect sites. NO dissociation is suppressed at higher oxygen coverages due to either site blocking or a change in adsorption energy. For NO production they propose mechanism 5.14 and 5.15.

\[ NH_3 + O \rightarrow NO + 3H \quad (5.14) \]
\[ NH + 2O \rightarrow NO + OH \quad (5.15) \]

Since the energy required for NO desorption is higher than for NO dissociation the NO desorption can only compete with dissociation at higher surface temperatures.

Theoretical calculations performed by Fahmi and Van Santen [41] confirm that atomic oxygen activates all the N-H bond cleavages. Preadsorbed atomic oxygen forms a strong basic site which activates N-H bond cleavage and forms the hydroxyl group. The fragments that arise by the dissociation
process interact strongly with the metal. They calculated that reactions of OH with NH\textsubscript{X} are endothermic reactions. They determined that the reaction species bind at different sites: OH 1-fold, NH and NH\textsubscript{2} 2-fold, H, O and N 3-fold.

Experiments by Van den Broek [1] at atmospheric pressure gave N\textsubscript{2}O production instead of NO production. For the NO formation he gives mechanism 5.16 besides 5.15 and 5.11. N\textsubscript{2}O can be formed from NO according to mechanism 5.17.

\[ NH + 2OH \rightarrow NO + H_2O \]  
\[ NO + N \rightarrow N_2O \]  

From TPD experiments he concluded that the concentration of NH species is higher than the concentration of NH\textsubscript{2} species on the surface after deactivation. The concentration of OH species is comparable to the concentration of NH species. With a deuterium experiment he showed that no O\textsubscript{ads} and N\textsubscript{ads} are present on the surface. He poses that the reaction of NH with OH is the rate determining step, and that NO dissociation is not taking place. His propositions are in agreement with Mieher and Ho [4].

### 5.1.4 Conversion and selectivity

To compare the activity of the catalyst under different conditions some quantities are defined. These are conversion (X), yield (Y), selectivity (S) and Turn Over Frequency (TOF).

The conversion rate is the ratio of transformed to initial species. The conversion is defined as:

\[ X_A = \frac{100 \cdot (A_{in} - A_{out})}{A_{in}} \]  

where

- \(X_A\) is the conversion of species A (\%)  
- \(A_{in}\) is the concentration of species A that goes in the reactor tube (vol %)  
- \(A_{out}\) is the concentration of species A measured after the reactor tube (vol %)

For species A both NH\textsubscript{3} and O\textsubscript{2} can be filled in.

The yield is the ratio of reaction products to reactants. For the ammonia oxidation two types of yields are defined. The factors 2 and \(\frac{3}{2}\) originate from the stoichiometric equations given in equations 5.1 and 5.2.
\[ Y_{\text{NtoNH}_3} = \frac{2(N_{2,\text{out}} + N_{2O,\text{out}})}{\text{NH}_3,\text{in}} \]  
\[ (5.19) \]
\[ Y_{\text{NtoO}_2} = \frac{2N_{2O,\text{out}} + \frac{3}{2}N_{2,\text{out}}}{\text{O}_2,\text{in}} \]  
\[ (5.20) \]

The selectivity towards the wanted reaction product N\(_2\) compared to the by-product N\(_2O\) is defined as:

\[ S_{\text{N}_2} = \frac{100 \cdot N_{2,\text{out}}}{N_{2,\text{out}} + N_{2O,\text{out}}} \]  
\[ (5.21) \]

The selectivity towards N\(_2O\) is defined in a similar way.

For the turnover frequency of NH\(_3\) is the total number of formed moles of N\(_2\) and N\(_2O\) per surface site per second. The equation for the TOF is:

\[ \text{TOF} = \frac{2(N_{2,\text{out}} + N_{2O,\text{out}}) \cdot F}{n} \]  
\[ (5.22) \]

where

- F is the total flow (mol·s\(^{-1}\))
- n is the total number of surface sites (mol)

It is assumed that the total flow remains constant during the entire experiment.

### 5.2 Experimental

#### 5.2.1 Catalyst preparation

The experiments are performed with the PEP set-up that is described in chapter 2. The experiments are done at ambient pressure and with low and stoichiometric concentrations of reactants. The concentration of the gases in the flow are measured with the MS. The MS is calibrated every few months, the factors determined for different calibrations vary 15 to 20\%. One should be careful with comparing concentrations of gases measured in different experiments.

To examine the reaction process on platinum a sample of 1.8 g of pure platinum sponge is used as the catalyst. The platinum sponge is acquired from Johnson Matthey and has a purity of over 99.9\%. The catalytic bed has a length of 4.0 cm. The reaction flow used in all experiments is 46.5 ml·min\(^{-1}\) and the gas hourly space velocity (GHSV) is 5600 hr\(^{-1}\). The GHSV is the flowspeed divided by the total catalyst volume. The total amount of free
sites was determined with the BET method to be $5.39 \times 10^{18}$ [5], this is equal to $8.95 \times 10^{-6}$ mol.

Before each experiment the catalyst is reduced in situ. A mixture of 10 vol % H$_2$ in He at 46 ml·min$^{-1}$ is flown over the catalyst for at least four hours at 673 K. Then the catalyst is flushed with He for 20 minutes at 673 K. Under the He flow the temperature is lowered to the reaction temperature. Then the reaction flow is turned on. The reaction flow contains 2 vol % NH$_3$, and 1.5 vol % O$_2$ in helium. In PEP experiments pulses of labelled oxygen and labelled ammonia are injected into the flow. The preparation and injection of labelled ammonia and labelled oxygen are described in the next sections.

For some experiments the platinum surface is pretreated with oxygen before the reaction flow is turned on. This means that after reduction the catalyst is cooled to a temperature of 373 K. A flow of 1 vol % O$_2$ in helium of 48 ml·min$^{-1}$ is turned on for exactly one hour. After this hour the catalyst is cooled or heated to the reaction temperature.

After the reaction took place a temperature programmed desorption (TPD) experiment can be performed. Fifteen minutes after the deactivation of the catalyst the reaction flow is switched to a helium flow. The helium flow of 40 ml·min$^{-1}$ is on for two hours before the catalyst is heated. The catalyst is heated with 10 or 20 K per minute. The compounds that desorb from the catalyst surface are measured with the MS.

The results of the experiments with the labelled molecules are presented in PEP pictures. The pictures show the distribution of activity over the position of the catalyst bed in time. The concentration is represented by intensity of the signal. A more intense signal indicates a higher concentration of labelled molecules. The results of the PEP experiments are also shown in graphs of the total amount of activity over all positions per second. The PEP measurements were corrected for the radioactive decay of $^{15}$N or $^{15}$O.

### 5.2.2 Labelled oxygen for PEP experiments

The method that is used for $^{15}$O$_2$ production for the PEP experiments is described in chapter 3. The sodalime trap and the activated carbon trap are used as absorbers. The labelled oxygen is injected into the PEP reactor after the Mol. Sieve 13X column. The activity of the flow in the tubes is monitored with NaI detectors at positions 1, 3 and 5 as indicated in figure 3.2.

The injected volume of the gas to the GC column is determined by the volume of the sample loop. The activity of the target effluent is 0.83 MBq·ml$^{-1}$, after the traps this is reduced to about 0.6 MBq·ml$^{-1}$. The
volume of the sample loop that is used is 0.5 ml, this contains an activity of about 0.3 MBq. By flushing of the sample loop not all activity is flushed out. It is estimated that about 80 % is flushed, which leads to an injected activity of about 0.25 MBq. The oxygen pulse is injected in 6 seconds. The concentration of the injected oxygen is estimated from the analysis with the Haysep N column to be at maximum 0.15 vol % in helium, this is 10 % of the concentration of oxygen in the reaction flow (1.5 vol %).

5.2.3 Labelled ammonia for PEP experiments

Besides experiments with labelled oxygen in ammonia oxidation on Pt, also experiments with labelled ammonia are performed. The production method of gaseous $^{15}$N$\text{NH}_3$ is described elsewhere by Sobczyk et al. [5], here only a short description is given.

Water is irradiated with high energetic protons of 16 MeV. The nuclear reaction for the production of $^{15}$N is the $^{16}$O(p,$\alpha$)$^{15}$N reaction. From this $^{15}$N labelled nitrates and nitrites are formed. The reduction of the nitrates and nitrites to ammonia is done by the De Varda’s alloy method. The alloy consists of 50% Cu, 45% Al and 5% Zn. NaOH is added to the alloy to make the environment basic in order to convert the produced NH$_4^+$ into NH$_3$. Aluminum in a basic environment dissociates water and catalyses hydrogen formation. Copper and zinc catalyze the reduction of nitrates to ammonia. The powder is put in a glass reactor and the irradiated water is added. The evolving gas is transported via a NaOH filter to reduce the amount of water vapour in the flow. The gas is led through a Haysep P column to filter the ammonia from hydrogen, nitrogen, oxygen and water. The pulse that is formed in this way is not carrier free, the activity of the pulse is 7 $\pm$ 1 MBq·ml$^{-1}$. A pulse time of 10 seconds is used to inject the radiolabelled gaseous ammonia into the reactant stream. The concentration of ammonia in the pulse is low enough not to disturb the ratio of ammonia and oxygen in the reaction flow.

5.2.4 Calibration experiments

Retention of oxygen and ammonia in PEP set-up

The retention time of oxygen and ammonia from the flow switch through the reactor tube to the MS is determined. The reactor tube is filled with small quartz balls of diameter of 1 mm. The reaction conditions in this experiment are exactly the same as in the experiments with the Pt catalyst.

At the moment the helium flow is switched to the oxygen and ammonia flow in helium it takes 12.5 s before a rise in the oxygen signal is detected by the MS. Figure 5.2 shows a small retardation of 4 seconds of the NH$_3$ gas in comparison to the O$_2$ signal. The NH$_3$ signal is stabilized after about 1 minute, for the O$_2$ signal this takes over 2 minutes.
Figure 5.2: Concentrations of NH$_3$ and O$_2$ in calibration experiment with the reactor tube filled with quartz balls. Switch from He to NH$_3$/O$_2$ flow at $t=0$ s.

Due to a small leakage in the system the N$_2$ and H$_2$O signal also go up after the switch. The N$_2$ signal arrives at the same time at the MS as the O$_2$ signal. The H$_2$O signal goes up after about 6 seconds after a small initial dip. After one minute a maximum value is reached for the water concentration. Since this water signal was due to leakage another test is performed for the retention time of water.

The profiles of the concentrations after switching to NH$_3$/O$_2$ flow is taken into account in the analysis of the experiments.

Retention of water in PEP set-up

The response of the system to a water signal is tested. A water signal is generated by flowing helium through a water reservoir (298 K) before it is sent to the PEP set-up. The helium flow then contains water vapour. The water signal is sent through a Pt catalyst at 373 K that is not reduced. The water signal is put over the catalyst for 12.5 minutes, then the flow is switched to a pure helium flow. This can be seen in figure 5.3.

At $t = 0$ seconds the flow is switched to the helium saturated with water. There is a retardation of 16 s before H$_2$O increases compared to a N$_2$ increase caused by an intentional small leakage in the system.

For the decrease the difference in the two signals is 79 s. A possible explanation can be the condensation of H$_2$O in the tube to the MS because the tube is not heated. Another explanation can be that the MS cannot pump out the H$_2$O quickly enough and gives a delayed signal.
Figure 5.3: Calibration of water signal through Pt sponge at 373 K. Switch to $H_2O$ signal at $t=0$ min, switch to helium flow at $t=12.5$ min.

Labelled oxygen pulse in empty reactor tube

In figure 5.4 a labelled oxygen pulse through an empty reactor tube is shown as detected with the PEP set-up. As expected, the pulse is clearly visible even though no reaction is taking place.

Figure 5.4: Labelled oxygen pulse in empty reactor tube

A pulse of 6 seconds moved within 6 seconds through the empty tube. This means that labelled oxygen that flows through the bed in the gas phase can be seen with the PEP set-up. The maximum total activity that is measured is lower if the labelled oxygen flows through the bed than if the labelled oxygen adsorbs at the surface, because if the labelled oxygen flows through the first part of the activity has left the PEP detector before the last part of the activity enters.
5.3 Adsorption of NH$_3$ and O$_2$ on Pt

The adsorption of oxygen is tested by pulsing $^{15}$O$_2$ in a helium flow on the platinum surface at 323 K. Figure 5.5 shows the result. About ten seconds after the pulse the flow is changed to an oxygen/helium flow for one minute.

![Figure 5.5: Labelled oxygen pulse on Pt sponge at 323 K, 10 s after the pulse the flow is switched to an oxygen flow for 1 min.](image)

The total sum of activity for all positions remains constant when the oxygen flow is turned on. Remember that the data are corrected for decay. There is hardly any exchange between the adsorbed oxygen on the surface and the oxygen in the flow, there is no equilibrium for adsorption and desorption. This can indicate oxygen dissociation or strongly bound molecular oxygen on the surface. A small part of the activity moves through the bed after the flow is switched back from the oxygen flow to helium. This can be molecularly bounded oxygen that desorbs from the surface and adsorbs again further on.

In a second experiment the Pt catalyst is reduced and then pretreated with oxygen. After 15 minutes of oxygen flow the $^{15}$O$_2$ is pulsed in a helium flow. Figure 5.6 shows the result of the experiment.

Since only 5% of the activity remains on the surface, it appears that there are hardly any free sites for the adsorption of oxygen left. No activity stays on the surface after a pulse of labelled oxygen in the oxygen/helium flow.

To examine the adsorption of NH$_3$ on platinum, the catalyst is reduced and a pulse of $^{13}$N$_2$NH$_3$ is injected in the helium flow.

Figure 5.7 shows that 22% of the $^{13}$N remains at the surface. A large part of the ammonia passes the catalyst in a few seconds and is detected with the MS. It can be that the ammonia adsors for a short time at the surface, but it desorbs quickly. Some $^{13}$N$_2$NH$_3$ remains at the surface, this can be caused by oxygen on the surface that is left after reduction or from an
Figure 5.6: *Labelled oxygen pulse on Pt sponge pretreated with oxygen at 373 K*

Figure 5.7: *Labelled ammonia pulse on Pt sponge at 313 K*
oxygen impurity in the helium flow. A small amount of $^{13}$N labelled species desorb from the surface, this is most likely desorption of reaction products.

To test the activation of ammonia adsorption by oxygen a pulse of $[^{13}\text{N}]\text{NH}_3$ is injected over a Pt sponge at 313 K that was pretreated for 2.5 hours at 313 K with oxygen. Figure 5.8 gives the result of this experiment.

![Figure 5.8](image)

Figure 5.8: *Labelled ammonia pulse on Pt pretreated with oxygen at 313 K*

The total activity signal as function of time shows that over 85% of the activity stays on the surface and does not form reaction products that desorb from the surface. The 15% decrease in the total activity signal is caused by the desorption of reaction products from the surface. Comparing figure 5.8 to figure 5.7 we can conclude that more ammonia remains on the Pt surface that is first covered with oxygen. Figure 5.8 shows the adsorption of the ammonia is in the beginning of the bed. We conclude that the adsorption of ammonia is activated by oxygen. This is an indication that oxygen atoms on the surface cause of N-H bond cleavage as is suggested in literature [4, 41].

### 5.4 Reaction process

#### 5.4.1 Initial deactivation

At low temperatures there is an initial deactivation of the catalyst after a few minutes, after this initial deactivation the ammonia conversion is reduced to 10 to 20%. The initial deactivation time is defined as the time until the $\text{N}_2$ production sharply decreases. In experiments the time to the initial deactivation is determined at different temperatures. Experiments are performed on both freshly reduced platinum and platinum pretreated with oxygen. The results are given in table 5.1.

For the reduced platinum it is determined that deactivation takes 16.5 hours at 398 K. For temperatures higher than 400 K the catalyst was not observed to deactivate. The experiments at 423 K are stopped after 20 hours of reaction.
Table 5.1: Initial deactivation times for Pt catalyst

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pt</th>
<th>Pt pretreated with oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.6 min</td>
<td>0.2 min</td>
</tr>
<tr>
<td>348</td>
<td>1.0 min</td>
<td>0.8 min</td>
</tr>
<tr>
<td>373</td>
<td>13 min</td>
<td>5 min</td>
</tr>
<tr>
<td>423</td>
<td>&gt; 20 hrs</td>
<td>&gt; 20 hrs</td>
</tr>
</tbody>
</table>

Two effects are found:

1. At higher temperatures the initial deactivation takes longer.

2. Preadsorption of oxygen causes a faster deactivation at temperatures below 398 K.

A possible explanation for the longer deactivation time at higher temperature is that the species are more mobile at higher temperature. More diffusion of the species over the surface cause more reaction products to be formed. It is likely that at higher temperatures more types of surface reactions can take place.

An explanation for the faster deactivation of Pt pretreated with oxygen is that there are less sites available for ammonia adsorption. Or perhaps there are no sites for the reaction products that are formed during the ammonia oxidation since the different reaction species bind at different sites. If oxygen atoms are adsorbed at the surface in oxygen islands it can be that the oxygen in the middle of the islands is not available for reaction. If the ammonia does react with the oxygen, NH₂, NH, NO and OH can be formed. If these species surround each other it is possible that they cannot react and deactivate the surface. Mieher and Ho [4] state that the reactions of NH and NH₂ with OH are the rate determining reactions. This effect can be worse for Pt pretreated with oxygen than for clean Pt because the ammonia molecules may adsorb closer to each other on the Pt pretreated with oxygen. It is possible that the reaction goes faster.

Another possible cause for the faster deactivation is the presence of a non reactive oxygen species on the surface. There are several forms of non reactive oxygen imaginable. One form can be molecularly bound oxygen that cannot dissociate because it is situated for example on a defect site. Perhaps the oxygen atoms need to be hot atoms to take part in the reaction. Oxygen hot atoms are mentioned in literature [4, 38] but their effect in reactions is not investigated. Another explanation for the faster deactivation is subsurface oxygen. It is possible that subsurface oxygen changes the structure of the Pt surface and therefore changes the adsorption sites.
To find out the effect of the amount of catalyst used, a catalyst bed with half the original size is tested. A catalyst bed of 2 cm is made which contains 0.9 g platinum, this is half the amount of catalyst of the normal 4 cm bed. There are half the amount of reactive sites on the surface. Figure 5.9 shows the turn over frequency for the two situations.

![Figure 5.9: Turn over frequency for platinum catalyst with reactor length of 4 and 2 cm at 373 K](image)

The short catalyst bed deactivates in less than half the deactivation time of the original bed at the same temperature. The conversion in the reactive time period is still over 90%. The yield of nitrogen containing species as defined in equation 5.19 is about 1.1 before initial deactivation in both experiments. The yield is determined higher than 1 due to inaccurate calibration of the MS. Because the conversion is the same in both experiments and there are less surface sites on the short bed, the turn over frequency per site is calculated to be higher for the short bed. But since the two experiments are performed with the same catalyst material the turn over frequency per active site is expected to be equal. From the difference in turn over frequency we can conclude that not all sites are active at the same time. The calculated turn over frequency is in fact an apparent turn over frequency, there must be a reactive zone that moves through the bed in time. This is confirmed by PEP experiments in section 5.4.4.

The reason that the 2 cm catalyst deactivates in less than half the time of the 4 cm catalyst and not in exactly half the time is not sure. The difference in time is rather large to be a coincidence. The short bed deactivates in 4 minutes instead of the expected 6 to 7 minutes. It can be that the 2 cm bed was covered with more oxygen due to a leakage.
5.4.2 Conversion rates

The reaction is followed with the MS to determine the conversion rates as a function of time. The profiles of the main species are displayed in figure 5.10. The concentration profile of N$_2$O is discussed in the next section. No H$_2$, NO$_2$ or NO are detected with the MS.

![Figure 5.10: Concentrations for O$_2$, NH$_3$, N$_2$ and H$_2$O for ammonia oxidation at 373 K on Pt sponge](image)

The H$_2$O signal that is measured before initial deactivation is not the 3 vol % that is expected for reaction 5.1. This can be caused by an inaccurate calibration factor for H$_2$O or by a delay in the H$_2$O signal. The difference in concentration is too large to be caused only by OH species deactivating the surface. The concentration of H$_2$O is high for over ten minutes after the initial deactivation. This is partly caused by the instrumental effect that is discussed in section 5.2.4 which can be influenced by the detection of ammonia and oxygen. It can also be partly caused by some water production after the initial deactivation.

A comparison of ammonia and oxygen conversion for platinum without preadsorbed oxygen to platinum with preadsorbed oxygen shows a difference. The conversion patterns for experiments at 373 K are displayed in figure 5.11.

After initial deactivation the conversion of ammonia decreases sharply on pure platinum, but the oxygen conversion decreases more slowly. The oxygen conversion is determined only from the amount of oxygen measured with the MS, so the delay of the H$_2$O signal is irrelevant for the determination of the conversion. From the calibration experiment in section 5.2.4 we know that stabilization of the oxygen signal takes about 2 minutes. The decrease in the conversion of oxygen on Pt takes over 15 minutes and can therefore not be caused by stabilization of the signal.
From the slow decrease in oxygen conversion for Pt we conclude that there are still sites available after initial deactivation for oxygen adsorption, and some water or N₂O can be formed. H₂O and N₂O production after decrease of the H₂O signal cannot account for the calculated oxygen conversion. There must be adsorption of oxygen at the surface that does not form reaction products. It is possible that subsurface oxygen is formed. For Pt pretreated with oxygen the slow decrease in oxygen conversion is not observed. After deactivation of the catalyst the conversion of ammonia sharply decreases and also the conversion of oxygen sharply decreases to a constant value of about 20%. Apparently there are less free sites for oxygen adsorption on Pt pretreated with oxygen than on Pt not pretreated with oxygen. It is likely that for the pretreated platinum these sites were already taken during the pretreatment.

Another remark about the conversion rates is the decrease in conversion for NH₃ from nearly 100% to about 90% after one or two minutes after the start of the reaction. Apparently not all ammonia is converted at the surface. It seems that there is not enough oxygen for activation of ammonia adsorption and further ammonia conversion. A cause can be that the ratio of ammonia to oxygen in the flow is not completely stoichiometric, or part of the adsorbed oxygen is non reactive. The yield of oxygen containing species is less than 1 because as we saw in figure 5.10 the yield of H₂O is not as high as expected and there is almost no N₂O production before initial deactivation. A yield of oxygen species lower than 1 means that there can be oxygen species remaining on the surface. Since the drop in conversion of NH₃ is faster for Pt pretreated with oxygen than for Pt, it is unlikely that the formation of subsurface oxygen is the cause. It seems more likely that
OH or NO species on the surface are blocked for further reaction. It is unclear why this effect appears only after a few minutes. Perhaps there is some oxygen left on the Pt surface after reduction and the ammonia adsorbs next to these oxygen atoms.

5.4.3 Selectivity to N₂ or N₂O

The selectivity to N₂ or N₂O changes in time during the reaction. The concentration profile of N₂ and N₂O for a reaction at 373 K on clean Pt is shown in figure 5.12.

![Figure 5.12](image.png)

Figure 5.12: Concentration profiles of N₂ and N₂O for ammonia oxidation at 373 K

The profile that is observed in this experiment is a general profile that is found in all experiments for both clean Pt and Pt pretreated with oxygen at temperatures below 400 K. The process of the N₂O production can be divided in three regions.

1. The first region is the start of the ammonia oxidation. There is a high selectivity towards nitrogen (> 98 %) and a small peak of N₂O or CO₂ that disappears after about 6 seconds.

2. In the next period selectivity to nitrogen is about 98 %. The conversion level of ammonia and oxygen is still high.

3. A few minutes before the initial deactivation the N₂O production increases. The nitrogen selectivity decreases and N₂O selectivity increases to 15 to 25 %. For a reaction at 323 K this third period is reached after only 40 seconds.

The N₂O or CO₂ peak in the first region may be caused by an artificial effect because in some measurements it is not observed.
The rise in N₂O production in the third region indicates a coverage dependent effect. A cause can be that the NO that is formed in for example reaction 5.15 or 5.16 cannot dissociate at a higher surface coverage. It can also be that NO is only formed at a higher surface coverage because in this situation reaction 5.11 is taking place because for example the mobility of the nitrogen atoms is too low to form N₂. N₂O can then be formed like in reaction 5.17. If we assume a reactive zone that moves through the catalyst bed then N₂O is produced not long after the start of the ammonia oxidation, already in the second period that was described above. The N₂O is not detected with the MS because it adsorbs again on the Pt and probably dissociates.

5.4.4 Labelled experiments

In this section experiments with both labelled ammonia and labelled oxygen are discussed. They are performed to see if the deactivation of the catalyst is mainly caused by N-containing or O-containing species. First the results of experiments at 323 K are presented and at the end of the section the influence of temperature is discussed.

Labelled ammonia pulses in reaction flow

The first type of experiment is a pulse of labelled ammonia in the reaction flow. In figure 5.13 a pulse of [¹⁵N]NH₃ is injected in the reactor tube at 323 K within 2 seconds after the reaction flow was started.

![Figure 5.13: Labelled ammonia pulse about 2 seconds after start ammonia oxidation at 323 K](image)

It is clear from the picture that not all ammonia forms reaction products that desorb from the surface. Some N-containing species remain on the surface, this can be N, NO or NHₓ with X is 1 to 3. At the positions of the catalyst bed where the highest activity was measured about 27 % of the activity stayed on the surface. The percentages are determined for the sites
where the most labelled atoms stayed on the surface because this is the place
where the catalyst is mostly deactivated. If the labelled ammonia pulse is
given later than 2 seconds after start of the ammonia oxidation the positions
of main deactivation moved through the bed. This is a second indication
of a reactive zone that moves through the bed. The first indication was
the shorter deactivation time for a shorter catalyst bed, this is explained in
section 5.4.1.

The influence of temperature is shown in table 5.2 on page 68.

In a second type of experiment the ammonia pulse is given after the initial
deactivation. Figure 5.14 shows a PEP experiment of a labelled ammonia
pulse 42 minutes after start of the reaction.

![Figure 5.14: Labelled ammonia pulse 42 minutes after start ammonia oxida-
tion at 323 K](image)

Most of the labelled ammonia flows through the reactor tube in less than
15 seconds in this experiment, this is about the same as for the experiment
that is shown in figure 5.13. This is comparable to the pulse width of 10
seconds, some diffusion or short adsorption can cause the longer retention
time. Only 3 % or the labelled ammonia remains adsorbed at the surface.
Apparently there are not enough free sites for all of the ammonia to adsorb.
A part of the ammonia that does adsorb forms reaction products that desorb
from the surface. This is in agreement with the fact that the ammonia
conversion is not zero after initial deactivation.

The first type of experiment is repeated but now the platinum is pre-
treated with oxygen. This experiment is only meaningful with labelled am-
onia, not with labelled oxygen because not enough labelled oxygen adsorbs
on platinum with preadsorbed oxygen.

Figure 5.15 shows the result for a labelled ammonia pulse in the reaction
at 323 K. The pulse is given in the beginning of the reaction. At this
temperature 28 ± 3 % of the activity stays on the surface, this is comparable
to the activity that stays on the surface in an experiment with platinum that
is not pretreated with oxygen. From a comparison of figure 5.15 to figure 5.13 we conclude that the labelled ammonia adsorbs more in the beginning of the bed if the platinum is pretreated with oxygen. This is in agreement with figure 5.8 that shows activation of ammonia adsorption by oxygen.

Labelled oxygen pulses in reaction flow

Besides nitrogen species the catalyst can also be poisoned by oxygen species. Because oxygen adsorbs well on a freshly reduced catalyst, experiments are performed by first pulsing labelled oxygen and then starting the reaction flow. Picture 5.16 shows a pulse of $^{[15]O}_2$ on a reduced platinum catalyst at 323 K. One minute after the $^{[15]O}_2$ pulse is injected the reaction flow is started.

Almost 90% of the preadsorbed labelled oxygen reacts very fast and desorbs from the surface. At the positions where the highest amount of activity was adsorbed 11% of the activity stayed on the surface. At other
temperatures this amount is about the same as is presented in table 5.2. This experiment is another indication of an non reactive oxygen species at the surface. This is discussed before for the faster initial deactivation of platinum pretreated with oxygen and for the ammonia conversion of 90% before initial deactivation. The same types of non reactive oxygen that were mentioned before can be the cause of the remaining labelled oxygen at the surface, like subsurface oxygen, adsorption on defect sites, OH-species or NO-species that are site-blocked and oxygen islands.

For a good comparison with the labelled ammonia experiments also pulses of labelled oxygen are injected in the reaction flow. In figure 5.17 a pulse is given before and after the initial deactivation.

![Figure 5.17: Labelled oxygen pulse in ammonia oxidation before and after initial deactivation at 323 K](image)

From the pulse in the reaction flow before the initial deactivation 3% of the labelled oxygen stays behind on the surface, for the pulse after the initial deactivation this is 2%. From this experiment it seems that oxygen is not the main deactivating species since only a small part of the oxygen pulse is irreversibly adsorbed before the initial deactivation. It is surprising that of the oxygen pulse after initial deactivation only 2% of the labelled oxygen remains on the surface. Figure 5.11 on page 62 showed that oxygen conversion is much higher than ammonia conversion for some minutes after initial deactivation. At the pulse time of the labelled oxygen after initial deactivation the oxygen conversion was 17% and the ammonia conversion was about 1%. From the oxygen conversion and water and N₂O production after initial deactivation was concluded in section 5.4.2 that some oxygen has to remain adsorbed on the platinum. The results for the two experiments do not seem to agree because the 2% labelled oxygen that remains on the platinum is too low to explain the high oxygen conversion. A possible explanation can be that the detected water or N₂O signal is not high enough, or that the labelled oxygen pulse is not mixed well in the reaction flow.
Influence of temperature

The results of the experiments described above are summarized in table 5.2 and 5.3. The experiments are repeated at different temperatures, the PEP pictures of experiments at higher temperature look similar to the pictures of the experiments at 323 K. Table 5.2 shows the percentage of activity that stays on the surface after labelled ammonia and labelled oxygen pulses in the reaction. Also the activity is determined if the labelled oxygen is adsorbed at the surface before the start of the reaction. The numbers given are an average over the position where most activity remained at the surface.

Table 5.2: Percentage of labelled species remaining at catalyst after pulse before or in reaction flow

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$^{13}$N in reaction</th>
<th>$^{15}$O in reaction</th>
<th>$^{15}$O preadsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>27 ± 3 %</td>
<td>3 ± 1 %</td>
<td>11 ± 2 %</td>
</tr>
<tr>
<td>348</td>
<td>16 ± 2 %</td>
<td>2 ± 1 %</td>
<td>10 ± 2 %</td>
</tr>
<tr>
<td>373</td>
<td>17 ± 2 %</td>
<td>4 ± 1 %</td>
<td>12 ± 2 %</td>
</tr>
</tbody>
</table>

An important feature in this table is the high amount of N-containing species that poison the surface in comparison to O-containing species. The amount of nitrogen containing species that remain on the surface seems to be a temperature dependent effect. At higher temperatures less $^{13}$N remains on the surface which is in agreement with the longer deactivation time at higher temperatures. The amount of O-containing species that remain on the surface is much lower. From the difference in N and O containing species that remain on the surface we conclude that the initial deactivation is mainly caused by nitrogen containing species like NH and NH$_2$. For platinum pretreated with oxygen the amount of labelled ammonia that remained on the surface is 28 ± 3 % at 323 K, at 373 K this is 23 ± 3 %. These numbers are comparable to the labelled ammonia that remained on the platinum that was not pretreated with oxygen.

If the labelled oxygen is preadsorbed about 10 % of the labelled oxygen remains on the surface. This is not a temperature dependent effect. Possible explanations for the oxygen remaining at the surface were given by the discussion of figure 5.16.

Experiments after initial deactivation show that not more than 2 % of the labelled oxygen adsorbs irreversibly on the surface and not more than 3 % of the labelled ammonia remains on the surface. In table 5.3 a comparison is made for the amount of labelled oxygen on the surface and the conversion determined with the MS at the same moment.

Table 5.3 shows that the amount of $^{15}$O remaining on the platinum of a pulse after initial deactivation is about equal for different temperatures.
Table 5.3: Percentage of labelled oxygen remaining at catalyst for pulse after initial deactivation compared to NH$_3$ and O$_2$ conversion at the pulse time.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>NH$_3$ conversion</th>
<th>O$_2$ conversion</th>
<th>$^{15}$O remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>1 %</td>
<td>17 %</td>
<td>2 %</td>
</tr>
<tr>
<td>348</td>
<td>10 %</td>
<td>20 %</td>
<td>2 %</td>
</tr>
<tr>
<td>373</td>
<td>5 %</td>
<td>5 %</td>
<td>2 %</td>
</tr>
</tbody>
</table>

The possible causes for this effect were discussed after figure 5.17.

**High temperature**

At temperatures above 400 K no irreversibly adsorbed species are found for both labelled ammonia and labelled oxygen. However if we pulse labelled oxygen in a NH$_3$ flow some labelled oxygen remains at the surface. Figure 5.18 shows a labelled oxygen pulse in an ammonia flow at 423 K.

![Figure 5.18: Labelled oxygen pulse in ammonia/helium flow at 423 K](image)

About 5 % of the activity remains on the surface. This means that a small part of the oxygen or the OH or NO that is formed is not mobile on the surface and can therefore not react further. Formation of subsurface oxygen is not likely since the effect is not observed if the labelled oxygen is pulsed in a reaction flow. A possible cause can be that OH species are not accessible for other OH species because they are surrounded by for example NH$_2$. The blocked OH species cannot form H$_2$O. Another cause can be that NO is formed and blocked by NH$_X$ species, then the NO cannot dissociate or form N$_2$O.

If the temperature is lowered and $[^{15}$O]$O_2$ pulses are given in NH$_3$ flow the retention time of the pulses becomes longer. At 393 K the peak is 10 seconds and at 317 K this is 25 seconds. An explanation can be that the surface reactions at low temperature are slower or that desorption of the
reaction products is slower. The amount of labelled oxygen that remains on the surface after the initial peak of activity is the same for all temperatures, it is 3 to 5 %.

5.4.5 Temperature programmed reaction

To see the effect of temperature on the initial deactivation a temperature programmed reaction is performed. First the ammonia oxidation is started on Pt pretreated with oxygen at 323 K. After the catalyst is deactivated it is heated with 10 K per minute. The reaction flow is still on during the heating of the sample. The result for the N\textsubscript{2} and N\textsubscript{2}O concentrations is given in figure 5.19.

![Graph showing concentration of N\textsubscript{2} and N\textsubscript{2}O during temperature programmed reaction starting at 323 K on Pt pretreated with oxygen.]

Figure 5.19: Concentration of N\textsubscript{2} and N\textsubscript{2}O during temperature programmed reaction starting at 323 K on Pt pretreated with oxygen

The irregularities are caused by a non uniform heating curve. At a temperature of about 373 K the conversion of NH\textsubscript{3} is rising, and at a temperature of 408 K the conversion of NH\textsubscript{3} reached 90 %. This is the highest conversion that is reached in this experiment. The production of both N\textsubscript{2} and N\textsubscript{2}O increase if the temperature rises, until at 405 K the N\textsubscript{2}O production decreases fast. The N\textsubscript{2} production is constant above this temperature. The selectivity to N\textsubscript{2} increases from 80 % below 373 K to nearly 100 % at temperatures above about 405 K.

An temperature programmed reaction for platinum that was not pretreated with oxygen experiment gave the same result. It can be concluded that the catalyst is reactivated as the temperature rises. Because reactivation is a slow process and the platinum is heated quickly, the actual reactivation temperature is somewhere between 373 and 405 K.

Possible explanations for a longer time to initial deactivation at higher
temperatures were already discussed in section 5.4.1. These were the mobility of the species and the possibility of other surface reactions taking place at higher temperatures. From the abrupt decrease in $\text{N}_2\text{O}$ production above 405 K we conclude that above this temperature almost no $\text{NO}$ is formed and NO that was already formed dissociates on the surface. It is possible that the nitrogen atoms on the surface are so mobile at this temperature that they almost always form $\text{N}_2$. Another explanation is that the surface reaction of for example NH and OH is possible at this higher temperature. The reaction products that are formed from this reaction desorb from the surface and clear sites that become available for other surface reactions.

5.4.6 Temperature programmed desorption

To examine the adsorbed species left on the catalyst after ammonia oxidation a temperature programmed desorption or TPD is carried out. First an ammonia oxidation experiment is done at 323 K, followed by a TPD with a raise of 10 K per minute.

![Figure 5.20: TPD after ammonia oxidation on Pt sponge at 323 K](image)

The result of the experiment is shown in figure 5.20. It can be seen that already at 363 K the signals of the $\text{N}_2$, $\text{H}_2\text{O}$ and $\text{N}_2\text{O}$ are rising. The first peak is of $\text{N}_2\text{O}$, the maximum desorption rate of $\text{N}_2\text{O}$ is at 384 K. The first $\text{N}_2$ peak is at 393 K, for $\text{H}_2\text{O}$ the first maximum is at 406 K.

If the temperature is raised further a second desorption maximum is observed for all species. The second $\text{N}_2$ peak is around 438 K. A third $\text{N}_2$ peak is concomitant with the second $\text{N}_2\text{O}$ and $\text{H}_2\text{O}$ peaks. The third $\text{N}_2$ and the second $\text{N}_2\text{O}$ peak are at 473 K. The second $\text{H}_2\text{O}$ peak is at 483 K. All $\text{N}_2$ and $\text{N}_2\text{O}$ is desorbed at 513 K, for $\text{H}_2\text{O}$ this is at 573 K.

Before we come to any conclusion we first compare the first TPD to a
TPD for platinum with preadsorbed oxygen (not shown in a figure). The TPD for Pt pretreated with oxygen is performed after a reaction at 348 K. In comparison to the TPD after deactivation of Pt at 323 K the amount of desorbing species is lower. The N₂O peak is not as clearly visible as for the first TPD. The N₂ and H₂O peaks are similar to the peaks of the first TPD.

The fact that H₂O, N₂ and N₂O are desorbed from the surface does not mean that they were present in this form on the surface before heating. Surface reactions can take place during the heating. Before heating the surface is covered with for example N, O, NO, OH and NHₓ species. In table 5.4 the amounts that are desorbed from the surface are given.

Table 5.4: Amount of desorbed species from Pt sponge during TPD

<table>
<thead>
<tr>
<th></th>
<th>Pt (from 323 K)</th>
<th>Pt pretreated with oxygen (from 348 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (10⁻⁶ mol)</td>
<td>0.87</td>
<td>0.69</td>
</tr>
<tr>
<td>N₂ (10⁻⁶ mol)</td>
<td>0.96</td>
<td>0.68</td>
</tr>
<tr>
<td>N₂O (10⁻⁶ mol)</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>N total (10⁻⁶ mol)</td>
<td>2.22</td>
<td>1.48</td>
</tr>
<tr>
<td>O total (10⁻⁶ mol)</td>
<td>1.02</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Remember that with the BET method the total amount of sites is determined to be 9·10⁻⁶ mol, the same order of magnitude as the amounts the are desorbed from the surface. From table 5.4 it is clear that for both TPD's the total amount of nitrogen species that desorb from the surface is twice as high as the total amount of oxygen species that desorb from the surface. It is possible that not all oxygen desorbs from the surface because the oxygen only desorbs as H₂O and N₂O and not as O₂. The total amount of species desorbed from the platinum that was pretreated with oxygen is lower than for the platinum that was not pretreated with oxygen. An explanation for this can be that on platinum pretreated with oxygen there are less sites available for adsorption of ammonia. This would agree with the faster deactivation of Pt pretreated with oxygen as described in section 5.4.1.

The fact that reaction products desorb at higher temperatures can be caused by a higher mobility of the surface species at higher temperatures or more surface reactions taking place at the surface. It is possible that non reactive oxygen like subsurface oxygen or oxygen in the middle of oxygen islands becomes available for reaction at higher temperatures.

It is clear from figure 5.20 that the first and third N₂ peaks are both accompanied by a slightly retarded H₂O peak. This suggests reactions take place at these temperatures that produce both nitrogen and water. These can be the same reactions that are responsible for the reactivation of the
catalyst as the temperature rises, as was explained in section 5.4.5. The peak at the lowest temperature can be for example reaction 5.10, the reaction of OH and NH. The second peak can be caused by reaction 5.9, the reaction of OH and NH₂. The amount of desorbed species cannot only be described by these 2 reactions, because of the N to O species ratio. An intermediate reaction is needed which produces N₂ in favour of H₂O. Possible reactions are given in equation 5.23 and 5.24. The OH that is formed in reaction 5.23 can react with another OH to form water as in equation 5.7.

\[
\begin{align*}
NO + NH & \rightarrow N_2 + OH \\
NO + NH_2 & \rightarrow N_2 + H_2O
\end{align*}
\]  

(5.23)  
(5.24)

This suggests that there is a relatively large amount of NO on the surface. This contradicts with the labelled oxygen experiments in ammonia oxidation of section 5.4.4. The amount of labelled oxygen that stayed on the surface was low. Another explanation can be that the high N₂ peaks are partly caused by recombination of N atoms on the surface.

The recombination of N atoms on the surface can also be the cause of the second N₂ peak that seems not to be accompanied by H₂O or N₂O.

TPD's are also performed with labelled oxygen and ammonia. First a reaction is carried out on platinum that was not pretreated with oxygen at 348 K, after the initial deactivation the flow is switched to a helium flow. Before the start of the TPD the labelled oxygen is pulsed in the helium flow, the result is shown in figure 5.21. One minute after the pulse the platinum is heated with 20 K per minute.

![Figure 5.21: TPD after ammonia oxidation at 348 K. Labelled oxygen pulse in helium flow before start TPD](image)

From figure 5.21 it is clear that after initial deactivation there are free sites for oxygen adsorption. The labelled oxygen reacts and desorbs from the surface as the temperature increases. The picture shows two different slopes
for temperatures below and above 393 K. This is another indication that there are two different reaction mechanisms that start working at different temperatures.

A similar experiment with labelled ammonia also showed reaction and desorption as temperature increased.

5.4.7 NO and N₂O experiments on Pt

Some additional experiments were performed with NO and N₂O to clarify their role in the deactivation process.

**NO**

An experiment with NO is performed to see if NO can react with the surface species that are formed during ammonia oxidation. First a reaction is carried out at 348 K, then after deactivation a labelled oxygen pulse is injected in a helium flow. About 30 s later the helium flow is switched to a NO flow of 0.5 vol % NO in helium. This is shown in figure 5.22.

![Figure 5.22](image_url)

Figure 5.22: *After ammonia oxidation at 348 K labelled oxygen is injected in helium, then start NO flow at time t=130 s.*

A large part of the labelled oxygen desorbs from the surface after the start of the NO flow. This means that the NO from the flow is reacting with species at the surface. This can also be concluded from the MS measurements. With the MS peaks are observed after the start of the NO flow for N₂O and N₂, both peaks had about the same height. Also a rise in the NO and H₂O signal is measured.

The N₂O that is formed is most likely a reaction of N and NO, equation 5.11. For the formed nitrogen one can think of reactions like 5.23 and 5.24. The OH that is formed can react with OH on the surface to form water. This can be the reason that the labelled oxygen desorbs from the surface.

The fact that NO can react with other species on the surface implies that there is not a large build-up of NO species on the surface and that NO
is not the main deactivating species.

\[ \text{N}_2\text{O} \]

In figure 5.23 a pulse of \([^{15}\text{O}]\text{N}_2\text{O}\) in helium is shown over a Pt catalyst at 423 K. The catalyst was used in a reaction at 348 K and deactivated. It was not reduced in between.

Figure 5.23: Pulse of \([^{15}\text{O}]\text{N}_2\text{O}\) in helium at 423 K after ammonia oxidation

As can be seen in the picture the \(\text{N}_2\text{O}\) either dissociates and reacts very quickly at the surface, or it does not react at all. No labelled oxygen species are left at the surface after the pulse, there is no trace of any inactive oxygen. The first small radioactive pulse that can be seen in the total activity signal is an impurity due to the not fully optimized production method of the labelled \(\text{N}_2\text{O}\).

A pulse of \([^{15}\text{O}]\text{N}_2\text{O}\) in a reaction flow instead of a helium flow at this temperature gives the same result. A pulse in a helium flow at 348 K after a reaction also shows only a small peak in activity. It is not possible this way to discriminate between a peak in activity caused by a fast reaction at the surface and a peak in activity without any reaction. A decomposition of \(\text{N}_2\text{O}\) to \(\text{N}_2\) and atomic oxygen can lead to a fast reaction of the oxygen to water that desorbs quickly from the surface. To know if the \(\text{N}_2\text{O}\) reacts the outcoming pulse has to be analyzed with a GC column to discriminate between labelled \(\text{N}_2\text{O}\) and labelled water.
5.5 Conclusions and recommendations

5.5.1 Conclusions

The aim of the project was to gain further insight in the ammonia oxidation process on a Pt sponge catalyst. PEP experiments provide additional insights in the reaction mechanism. Both labelled ammonia and labelled oxygen were successfully used to examine adsorption and desorption processes on the platinum.

Adsorption

With PEP experiments it was found that oxygen adsorbs well on platinum. The fact that there was hardly any interaction between the oxygen on the surface and oxygen in the flow is an indication that most oxygen dissociates on the surface. Dissociation of oxygen on platinum is also reported in literature [37]. The adsorption of ammonia was found to be activated by preadsorption of oxygen. This agrees with the statement of Bradley et al. [40] that oxygen adatoms enhance dissociation of NH₃.

Initial deactivation

For temperatures below 400 K the catalyst shows an initial deactivation. At the start of the reaction there is a small N₂O or CO₂ peak, this is probably an artifact because it is not observed in all measurements. At 373 K the ammonia conversion drops from nearly 100 % to about 90 % after one or two minutes, the oxygen conversion stays about 100 %. About 13 minutes after the start of the reaction the conversion of ammonia drops further to about 15 %. The N₂O production rises and nitrogen production decreases. The selectivity to nitrogen after initial deactivation is about 80 %. At lower temperatures the deactivation was faster. An explanation is that as temperature rises the species become more mobile at the surface, and reactions go faster. A rise in temperature can also mean that more types of surface reactions become available. Possible rate limiting steps are discussed below.

Experiments with labelled ammonia and labelled oxygen indicated that the deactivation is mainly caused by nitrogen containing species. After injection of labelled ammonia in the reaction flow at 323 K over 25 % of the labelled nitrogen remained on the surface. For oxygen this is only 3 %. After deactivation the conversion of oxygen is about 40 % for a few minutes for platinum that was not pretreated with oxygen, but this oxygen conversion cannot be explained by H₂O and N₂O production only. A part of the oxygen has to remain on the platinum, but if labelled oxygen is injected almost no activity remains at the surface. These two measurements are contradictory.
Either the measured H$_2$O or N$_2$O signal is too low or the labelled oxygen is not well mixed with the oxygen in the reaction flow. For Pt that was pretreated with oxygen the oxygen conversion drops at the same rate as the ammonia conversion after initial deactivation.

Preadsorption of oxygen before start of the reaction results in a faster deactivation that can be caused by a non reactive type of oxygen on the platinum. A PEP experiment with labelled oxygen preadsorbed on the platinum catalyst before start of ammonia oxidation also showed that a part of the labelled oxygen remained on the surface. An explanation can be that part of the oxygen adsorbs as molecular oxygen that cannot dissociate because it is adsorbed for example on a defect site, or that the oxygen is dissociated but trapped in the middle of an oxygen island. Oxygen island formation is proven with LEED experiments by Gland [37], but their influence on oxidation reactions was not investigated. In literature [39] the formation of subsurface oxygen is reported. Subsurface oxygen is said to be less reactive, but its formation is reported only from 520 K on platinum. It is possible that the subsurface oxygen changes the surface structure of the platinum and therefore influences the reaction mechanism. A last possible explanation is that there are less surface sites available for the reaction products of the ammonia oxidation. Adsorption of oxygen and ammonia can cause a shortage of free sites that blocks the reaction process.

The non reactive oxygen on the surface was confirmed by TPD experiments that proved that less species remained on the surface after deactivation of Pt pretreated with oxygen, perhaps caused by the fact that there are less surface sites available for reaction.

It is possible that the drop in ammonia conversion from nearly 100 % to 90 % in a few minutes is also caused by non reactive oxygen. It seems that there is not enough oxygen available for activation of ammonia adsorption or for complete oxidation to reaction products.

**Reaction zone**

Evidence is found that the deactivation of the catalyst proceeds by deactivation of the reaction zone that moves through the catalyst bed. A catalyst bed of half the original size deactivated in less than half the time of the large bed. It is not clear why the deactivation time was not exactly half the original time. It is possible that a leakage in the system caused preadsorption of oxygen on the platinum and therefore a faster deactivation.

PEP experiments also show a shift in the main deactivating positions on the catalyst in time.
Rate determining steps

Heating the catalyst under reaction flow after the initial deactivation showed a reactivation probably caused by surface reactions that only take place if the temperature is high enough. A TPD showed two nitrogen desorption peaks accompanied by water peaks at temperatures of about 400 and 475 K. This gives reason to believe the surface reactions that start taking place at higher temperature are the reactions of NH and NH\textsubscript{2} with OH, which is in agreement with literature [4, 41]. The amount of nitrogen containing species that desorb from the surface is too high compared to the amount of water species to be explained by the two reactions that are mentioned above. Another reaction producing nitrogen must take place. This can be recombination of nitrogen atoms on the surface. This can also be an explanation of another nitrogen desorption peak in the TPD spectrum 438 K. The nitrogen atoms can originate from NO dissociation. From literature [43] it is known that NO dissociation starts around 350 K. It is not likely that NO is present in large amounts on the surface at low surface coverage since NO is found to react with other surface species at this temperature. \textsubscript{N}2O production seems to take place at relatively high surface coverage, most likely because NO cannot dissociate at higher surface coverage. From the experiments it did not become clear if during the reaction large amounts of NO are formed and later dissociated or that it is not formed at all before initial deactivation.

5.5.2 Recommendations

More information can be obtained from the labelled experiments if the reaction products are analyzed with a GC to determine which reaction products are labelled.

More experiments with different lengths of the catalyst bed can prove if the time to initial deactivation is linearly correlated to the length of the bed, or that it is more complicated.

The surface of the platinum can be studied with surface techniques like LEIS and SIMS. LEIS is a technique that has a high surface sensitivity. Measurements with LEIS on a clean Pt sample and Pt pretreated with oxygen can prove if the oxygen is adsorbed on the surface of the platinum or that is has also diffused subsurface or into the bulk. The difference between platinum that is just initially deactivated and platinum that stayed over 30 minutes after initial deactivation in the reaction flow can show if any oxygen adsorbs at the surface or diffuses into the bulk. This can prove the slow decrease in oxygen conversion for platinum after initial deactivation.

SIMS measurements on for example platinum that is deactivated and platinum that is used at temperatures above 400 K give an indication of the
surface complexes formed during the experiment.

More unlabelled NO and N$_2$O experiments can be done to prove that NO and N$_2$O dissociate at the surface. It might be useful to produce $[^{15}\text{N}]\text{NO}$ or $[^{15}\text{O}]\text{NO}$ to see if for example a part of the NO remains on the surface and cannot react with the other surface species.
Acknowledgements

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Bibliography


