APPLICATION OF

POSITRON EMISSION PROFILING

IN CATALYSIS

SIMON VAN DER LINDE
APPLICATION OF

POSITRON EMISSION PROFILING

IN CATALYSIS

THE DECOMPOSITION OF N₂O

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College voor Promoties aangewezen,

op dinsdag 2 november 1999 te 16.00 uur

door

Simon Comelis VAN DER LINDE

doctorandus in de scheikunde
geboren te Kaldenkirchen, Duitsland
Dit proefschrift is goedgekeurd door de promotoren:
Prof. dr. J.A. Moulijn
Prof. dr. F. Kapteijn

Samenstelling promotiecommissie:

Rector Magnificus voorzitter
Prof. dr. J.A. Moulijn Technische Universiteit Delft promotor
Prof. dr. F. Kapteijn Technische Universiteit Delft promotor
Prof. dr. ir. J.J.M. de Goeij Technische Universiteit Delft
Prof. dr. h.c. ir. J.W. Geus Universiteit Utrecht
Prof. dr. R.A. van Santen Technische Universiteit Eindhoven
Dr. B.E. Nieuwenhuys Universiteit Leiden
Dr. L.J. van IJzendoorn Technische Universiteit Eindhoven

Het onderzoek beschreven in dit proefschrift werd financieel gesteund door de stichting Scheikundig Onderzoek Nederland (SON).

Copyright © 1999, S.C. van der Linde

ISBN 90-6464-014-9
Stellingen behorende bij het proefschrift:

**Application of Positron Emission Profiling in Catalysis**  
The Decomposition of N$_2$O

door Simon C. van der Linde

1. De hoge mobiliteit van zuurstof verhindert in het algemeen het gebruik van zuurstof isotopen voor het analyseren van processen die uitsluitend op het oppervlak van een oxidische katalysator plaatsvinden.

2. De engelse uitdrukking "seeing is believing", die gebruikt wordt om de mogelijkheden van tomografische technieken aan te geven, gaat niet op voor PEP.

3. De positron emissie simulatie procedure van Jonkers et al.$^1$ en Vonkeman$^2$ houdt geen rekening met de positieresolutie van de detector, hetgeen een oversimplificatie blijkt te zijn.$^2$


   $^3$Dit proefschrift.

4. Het onderzoek naar Monte Carlo codes die het transport van positronen beschrijven zou zeer gebeat zijn met nieuwe transmissie metingen, daar de enige in 1955 gepubliceerde resultaten$^4$ twijfelachtig zijn.


5. De PEP techniek is zeer geschikt voor metingen aan reacties waarbij het toegevoegde isotoop een lange retentie op het katalysatoroppervlak vertoont. Andere isotopische technieken die alleen de produktstroom analyseren ondervinden door de lange retentie problemen bij de detectie van het isotoop.

6. De directe isotopische uitwisseling van het zuurstof atoom in N$_2$O met geadsorbeerde zuurstof atomen, zoals beschreven door Valyon et al.$^5$, is onwaarschijnlijk, daar tijdens deze uitwisseling de binding tussen N$_2$ en O verbroken en weer gevormd zou worden, wat thermodynamisch onmogelijk is.


7. Computational science kan de grens tussen model en werkelijkheid doen vervagen, en dient dus te allen tijde getoetst te worden met experimenten.

8. Doordat kaon deeltjes onderscheid kunnen maken tussen verleden en toekomst, wat een volledige annihilatie in de weg stond, is er nu materie.
9. Gezien de grote maatschappelijke commotie rondom de stier Herman en het schaap Dolly, mogen de laconieke reacties op groen fluorescerende laboratoriumdieren, zoals muizen en kikkervisjes, opmerkelijk worden genoemd.  


Internet www.welc.cam.ac.uk/~ea3/  

10. Veel treinreizigers zouden al gelukkig zijn, als de Nederlandse Spoorwegen zijn slogan “ieder z’n trein” zou kunnen waarmaken in de vorm van “ieder z’n zitplaats”.  

11. De economische wetmatigheid dat spoorvervoer efficiënter wordt naarmate de schaal groter wordt, staat haaks op de drang van de overheid om de markt van het spoorvervoer te verdelen over meerdere vervoorders.  

12. Veel bezwaren tegen het sluiten van loketten op stations zijn gebaseerd op de veronderstelling dat 65-plussers onnozele mensen zijn.  

13. De vernieuwde extra-hygiënische schoonmaakmiddelen, waarvan de reclame zegt dat zij 99.9% van de schadelijke bacteriën doden, laten dus 0.1% resistente bacteriën leven; deze zullen zich door exponentiële groei binnen enkele uren weer vermenigvuldigen tot de omvang van de beginpopulatie.  

14. Bij een sollicitatiegesprek is het EQ (emotional quotient) van de sollicitant belangrijker dan diens IQ.  

15. Hoewel de uitdrukking luidt “spreken is zilver, zwijgen is goud”, is voor een goede relatie spreken vaak belangrijker dan zwijgen.
Today

Look well to this day
for it is life
the very life of life!
For yesterday is but a dream
and tomorrow is only a vision,
but today well-lived makes
every yesterday
a dream of happiness
and every tomorrow
a vision of hope.

Look well therefore to this day!
Preface

Positron emission profiling (PEP) is an in-situ analysis technique for studying heterogeneous reactions and is closely related to the medical technique positron emission tomography (PET). The technique consists of addition of minute amounts of a positron emitting molecule to the reaction mixture of a catalyst operating under steady-state conditions. Subsequently, the course of this isotope through the catalyst can be followed with a specially designed detector (PEP detector). The basis of the technique has been laid down by Vonkeman and Jonkers. In their initial study they used a standard medical tomograph to follow the positron emitters in a catalytic reactor. This detector had a limited time and position resolution, therefore, a new detector has been designed and constructed specifically for catalysis research. The research project concerning the new PEP detector was initiated by the Departments of Technical Physics and Chemical Engineering of the Eindhoven University of Technology. The objective of this research was to increase both the spatial and temporal resolution of the detector, and to obtain a better understanding of the detection process by Monte Carlo simulations.

The major aim of the research resulting in this thesis was the development of a method to interpret transient data obtained with the PEP detector, and subsequently demonstrate the developed procedure for data evaluation. In the study by Vonkeman and Jonkers the PEP technique was mainly used to give a qualitative description of the reactions examined. To exploit the full potential of the PEP method and to obtain quantitative data, the measured PEP profiles have to be fitted with a mathematical model. The decomposition of N₂O over Pt/Al₂O₃ has been used as a system to show the potential of the PEP technique both qualitatively and quantitatively.

Chapter 1 gives an overview of various imaging and transient techniques for analyzing the mechanism and kinetics of a catalytic reaction. The emphasis is placed on techniques that use radioisotopes. The relation of PEP to these other techniques is explained in this chapter. The PEP technique requires the availability of positron emitting molecules. Relevant information related to the catalytic reaction can only be acquired when the positron emitting element is incorporated into the reactant. Chapter 2 describes the preparation of the positron emitting tracers ^¹⁵NO and ^¹¹CO. These tracers are prepared by proton irradiation of water or nitrogen gas respectively, using a cyclotron. Since PEP is a new and elaborate technique, most of the relevant experimental procedures are given in the same chapter.

The major part of this thesis is dedicated to the decomposition of N₂O, and the preparation of N₂^{^¹⁵}O is described in chapter 3. A new synthesis method for N₂^{^¹⁵}O has been devised to obtain a radioactive product with a high specific activity. The method is based on deuteron irradiation of gaseous nitrogen. The underlying target chemistry which results in the production of N₂^{^¹⁵}O and several labeled and non-labeled by-products is also discussed.
The next two chapters deal with the procedure to extract quantitative information from a PEP profile. The developed method can be divided into two main areas: 1. mathematical description of the reactions, and 2. assessment of the effects of the detection process on the measured PEP profile. The mathematical treatment focuses on the description of the transient processes taking place after addition of a labeled pulse to the catalyst. The model should describe the concentration of the labeled reactant and products as a function of both time and position. This automatically leads to a system of partial differential equations (PDE) describing the reactions taking place. The mathematical model should also describe the steady-state, because the catalyst is operating under steady-state conditions before the radioactive tracer pulse is added. The steady-state is given by a system of ordinary differential and algebraic equations (DAE) describing the gas phase and surface concentrations. The numerical methods used to solve both the DAE and PDE are discussed in chapter 4. Chapter 5 deals with the understanding of processes affecting the accuracy of the detection process. The mathematical model gives the tracer concentration at a specific position in the reactor. However, the PEP detector does not determine the concentration with such a precision but is limited by the spatial resolution which can be obtained. This limited resolution has an averaging effect on the real tracer distribution along the axial direction of the catalyst bed. This averaging effect is described by a sensitivity profile for each detection position. These profiles were simulated with the Monte Carlo code EGS4, describes the transport of positrons and photons through matter.

The decomposition of nitrous oxide over Pt/Al₂O₃ and ZSM-5 catalysts is the subject of chapters 6, 7 and 8. Chapter 6 gives a qualitative description of the decomposition of N₂¹⁵O over Pt/Al₂O₃. The emphasis is placed on the unusual behavior of oxygen on the catalyst surface. Only the oxygen atom of N₂O is labeled and therefore, it is possible to follow its pathway after the dissociation. The next chapter gives a quantitative description of the decomposition reaction. The procedure developed in chapters 4 and 5 has successfully been applied here to obtain kinetic data on the decomposition reaction.

The behavior of oxygen formed during the decomposition of N₂¹⁵O over ZSM-5 is described in chapter 8. The results are treated in a qualitative manner because the reactive nature of oxygen prevents a thorough quantitative description.

Reduction of NO by CO over Pt/Al₂O₃ is the topic of chapter 9. Using nitrogen labeled ¹⁵NO it was possible to focus on the fate of nitrogen during reduction by CO. Insight in the behavior of ¹⁸NO on this Pt/Al₂O₃ catalyst is obtained. The reduction of NO by CO is directed by the limiting dissociation rate of NO on platinum. In addition, formation of a ¹⁵N containing support species occurs under reaction conditions.

The possibilities and limitations of the PEP technique are evaluated in chapter 10.
## CONTENTS

**Preface**

**Chapter**

1. General Introduction ................................................................. 1

2. Experimental Procedures ......................................................... 15

3. Production of $^{15}$O-$N_2$O by Deuteron Irradiation of Nitrogen .......... 37

4. Mathematical Treatment of Transient Kinetic Data ......................... 53
   Combination of Parameter Estimation with Solving
   the Related Partial Differential Equations

5. Properties of the PEP Detector .................................................. 81
   Prediction of the Detector Response by Monte Carlo
   Simulations to Aid the Data Interpretation

6. Decomposition of $N_2^{15}$O over Pt/Al$_2$O$_3$ .......................... 121
   I. Spill-over of $^{15}$O Formed During the Decomposition

7. Decomposition of $N_2^{15}$O over Pt/Al$_2$O$_3$ .......................... 137
   II. Modeling

8. Decomposition of $N_2^{15}$O over Ion-exchanged ZSM-5 Catalysts ........ 161

9. The Reduction of $^{13}$NO by CO over Pt/Al$_2$O$_3$ ........................ 175

10. Evaluation of Positron Emission Profiling .................................. 185

**Appendix: Sensitivity Matrices** ................................................. 193

**Samenvatting** ................................................................. 199

**Dankwoord** ................................................................. 203

**List of Publications** ......................................................... 205

**Curriculum Vitae** ............................................................. 207
1

GENERAL INTRODUCTION
1 INTRODUCTION

In kinetic studies the reactor is usually operated under steady-state conditions. In this case the catalyst is treated as a black box and only the reactor entrance and exit concentrations are determined. Kinetics are deduced by varying the steady-state conditions like temperature, and reactant concentrations and monitoring the effect on the exit concentrations of the products and remaining reactants. The data obtained in this way only contain averaged information about the overall process. Several techniques have been developed which also take into account the processes occurring on the catalyst. These techniques can roughly be divided into two main areas:

1. Transient techniques.
2. Imaging (spectroscopic) techniques.

A short description of both fields is given below.

1. Transient. The technique consists of introducing a perturbation of one or more experimental variables such as gas concentration, reaction temperature or pressure. The system responds to this perturbation by relaxing into a new steady-state. The dynamic response of the system to this change allows determination of the time constants of the surface processes. Thus, processes on the catalyst can be evaluated. An interesting variation on this theme is the use of isotopes to introduce the perturbation. In this case the steady-state is actually not disturbed, but transient information can be obtained from the behavior of the isotope. This class of techniques is often referred to as Steady-State Isotopic-Transient Kinetic Analysis (SSITKA) [1-5].

2. Imaging. The term imaging has been used to address the methods that detect species on the catalyst surface. Most of these spectroscopic techniques can only be used under (ultra-)high vacuum conditions. Moreover, they usually require the use of model catalysts. Although much quantitative information on the reaction mechanism and kinetics can be obtained, they fail to be used under normal operating conditions. Several analytical techniques capable of obtaining such information are for example fourier transform infrared (FTIR), Mössbauer, nuclear magnetic resonance (NMR), and isotopic techniques. Again, isotopes can be used to determine the amount of a specific species on the catalyst surface. If the spatial resolution of the detector is high enough it should be possible to determine its distribution over the catalyst(-bed).

Positron emission profiling (PEP) is a method based on the use of radioisotopes that combines the possibilities of both techniques described above. In short, it consists of introducing a pulse of labeled molecules, positron emitters, to the reaction mixture of a catalyst operating under steady-state conditions (transient information). The position of the positron emitters can be monitored as they pass through the catalytic reactor (imaging). These two aspects make PEP a powerful technique. Like the methods mentioned above PEP also makes use of isotopes to examine the reaction mechanism and kinetics.

Isotopes have long been used as an efficient means to study the reaction mechanism and the kinetics. The possibilities of using isotopes in transient and imaging techniques in the field of catalysis research will be discussed in this chapter. The emphasis will be placed
on the use of isotopes within these methods, since PEP is also an isotopic analysis method. At the end the properties and potential of the PEP technique will be given.

2 ISOTOPIC LABELING

The use of isotopic labeling can provide an effective means for determining the mechanism and kinetics of a (catalytic) reaction. Isotopes are defined as elements having the same atomic number but a different atomic weight. There are two types of isotopes: radioactive and stable isotopes. Radioactive atoms have a neutron/proton ratio which differs from the stable ratio. For light elements an equal amount of neutrons and protons implies a stable configuration. The nucleus of a radioisotope is unstable and can spontaneously undergo a nucleus change (break-up). This process is also known as decay. Decay of a radioactive nucleus produces nuclear fragments (nuclear radiation) and a new nucleus of a another element. The most common fragments resulting from nuclear decay are, α-particles (helium nucleus), β-particles (electrons and positrons), and γ-rays (high energy photons).

The chemical properties of these isotopes are practically identical to their stable counterparts. It is possible to label a reactant with an isotope and following it through a sequence of chemical or physical changes. The use of such tracers has been applied in various fields, such as chemistry, biology, and medicine. This is one of the few methods for distinguishing two atomic species of the same element, with a similar chemical form. It is assumed that the isotope containing molecule behaves identically to the original molecule. This is not the situation for hydrogen/deuterium exchanges, because of the kinetic and thermodynamic differences arising from the relatively large differences in mass and bonding energies [6]. This is referred to as the isotopic effect. The isotopic effect lessens as the mass of the isotope increases, and therefore the isotopic effects of the isotopes used for PEP (\(^{12}\text{C}/^{13}\text{C}, \^{14}\text{N}/^{15}\text{N}, \text{or } ^{16}\text{O}/^{18}\text{O}) will be minimal [2].

Isotopes are frequently employed to follow a reaction pathway and to determine the reaction mechanism. By applying this technique it is possible to identify the position of bond scission in a chemical reaction. For example, Polanyi and Szabo [7] have used \(^{18}\text{O} labeled water to determine the position of bond scission in the hydrolysis of esters as follows:

\[
\text{RCOO–R'} + \text{H}^{18}\text{O–H} \rightarrow \text{RCOOH} + \text{H}^{18}\text{OR'}
\]  \hspace{1cm} (1.1)

\[
\text{RCO–OR'} + \text{H}^{18}\text{OH} \rightarrow \text{RCO}^{18}\text{OH} + \text{HOR'}
\]  \hspace{1cm} (1.2)

Since only \(^{18}\text{O}-labeled carboxylic acids were found and no \(^{18}\text{O} could be detected in the alcohols, this clearly indicates that the reaction proceeds via the second reaction path. Another classic study, utilizing \(^{14}\text{C} labeled molecules gave an enhanced understanding of the reaction mechanism of the metathesis of propene:

\[
2 \text{C–C}=\text{C} \rightarrow \text{C}=\text{C} + \text{C–C}=\text{C–C}
\]  \hspace{1cm} (1.3)
The possible mechanisms can be divided into two categories:
1. Breakage of the C–C bond followed by an addition reaction.
2. Breakage of the C= C bond followed by an addition reaction.
The labeling experiment gave the following result:

\[ 2 \text{C}^{14}\text{C}=\text{C} \rightarrow \text{C}=\text{C} + \text{C}^{14}\text{C}=\text{C} \quad (1.4) \]

This directly proves that C= C bond breakage is involved in the metathesis reaction. Similarly, the distribution of isotopes in the products of a catalytic reaction can be utilized to determine the reaction mechanism. Nijhuis et al. [8] used \(^{18}\text{O}_2\) to examine the oxidation of CO over platinum. First, pulses of \(^{18}\text{O}_2\) were allowed to interact with the platinum metal, forming a layer of adsorbed \(^{18}\text{O}\). Subsequently, a pulse of \(^{16}\text{O}\) was admitted. The \(^{16}\text{O}\) reacted with the adsorbed \(^{18}\text{O}\) under formation of \(\text{CO}_2\). The isotopic composition of the produced \(\text{CO}_2\) was determined by mass spectroscopy. The analysis revealed the presence of three types of \(\text{CO}_2\): \(^{16}\text{O}_2\), \(^{16}\text{O}^{18}\text{O}\), and \(^{18}\text{O}_2\), whereas only \(^{16}\text{O}^{18}\text{O}\) was expected. The authors proposed that \(\text{CO}_2\) produced on the catalyst surface does not desorb instantaneously, but has fair chance of decomposing again to CO and \(\text{O}\) (reverse reaction). The decomposition of \(\text{CO}_2\) causes isotopic mixing to occur, redistributing the \(^{18}\text{O}\) among the three isotopic products.
Tracers can also be used to follow the pathway of a reactive species on the catalyst. For example, Van Wijk et al. [9] used \(^{18}\text{O}\) to evaluate the exchange of oxygen with the support during the oxidation of supported Cu particles. A model catalyst was prepared consisting of a \(^{16}\text{O}_2\)-oxidized Si surface, covered with 15 nm Cu particles. The particles were oxidized in \(^{18}\text{O}_2\) and subsequently reduced in hydrogen. After reduction, a significant amount of \(^{18}\text{O}\) was still present in the sample as observed by nuclear reaction analysis. The uptake of \(^{18}\text{O}\) was shown not to be due to the formation of an \(^{18}\text{O}\) adlayer or further oxidation of the support. Another mechanism was proposed, the \(^{18}\text{O}\) present in the oxidized Cu (CuO) particles exchanged with \(^{16}\text{O}\) from the support. The driving force for this process was that a maximum entropy was achieved by the mixing of \(^{16}\text{O}\) from the support with \(^{18}\text{O}\) located in the copper particles. Evidence for this conclusion followed from the fact that \(^{18}\text{O}\)-exchange also occurred during vacuum annealing of an oxidized sample. These results show that isotopic tracer analysis makes it possible to follow the pathway of oxygen during the oxidation of copper particles. If the tracer was not used only the uptake due to the oxidation of the copper particle would have been observed.

3 Steady-State Isotopic-Transient Kinetic Analysis

SSITKA is an isotopic method which is used to study the kinetics of heterogeneous catalytic reactions. This method, initially developed by Happel [10], Bennett [11], and Biloen [12], has been used to obtain information about the heterogeneous steps in a reaction mechanism under steady-state conditions. The technique is based upon the inclusion of a different stable isotope in one of the reactant species. For example, when studying the decomposition of nitrous oxide, it is possible to use \(\text{N}_2^{18}\text{O}\) instead of \(\text{N}_2^{16}\text{O}\).
The catalytic reaction is operated under steady-state with a particular isotopic label. Then the inlet feed stream is switched to another feed stream containing a different isotopic label in one of the reactants. During the switch the concentration of the reactants is kept the same. This results in the introduction of a step input of the new isotopic label (in the reactant) without influencing the steady-state reaction on the catalyst. As the labeled reactant progresses through the reactor, and reacts on the catalyst surface, the label is transferred to the product(s). Thus, the new isotopic label replaces the old one in the products of the catalytic reaction. The decaying response of the old label and the increasing response of the new label is monitored in the reactor effluent.

The shape of the transient response of the labeled and non-labeled species gives information about the reaction pathways of the labeled atoms. Figure 1.1 presents the transient responses for different irreversible reaction mechanisms. The response shows the behavior of the product. In SSITKA it is common to show the response of the isotope which is being replaced. The reaction on the catalyst surface can proceed by a single step process or by a multistep process. The most basic reaction processes are:

- Single reaction: \[ R \rightarrow I^* \rightarrow P \] (1.5)
- Serial reaction: \[ R \rightarrow I_1^* \rightarrow I_2^* \rightarrow P \] (1.6)
- Parallel reaction: \[ R \rightarrow I^* \rightarrow P \] (1.7)

Where, R is the reactant, I* is the intermediate adsorbed on the catalyst surface, and P is the product formed. In the single step mechanisms only one intermediate is involved. If all the catalytic sites are equally active (a homogeneous catalytic surface) the response for the single step reaction is obtained. On the other hand, if the surface contains sites
with different catalytic activities (a heterogeneous surface) the intermediate is converted with different rates allowing reactions to occur in parallel. Both curves show an immediate exponential decay of the isotope. The transient response of the parallel reaction displays a behavior given by the additive combination of exponentials. The serial reaction exhibits a completely different behavior, the curve has a S shape. This shape results because the isotope is distributed before it reaches the second step in the reaction pathway. The shape of the transient response can thus be used to verify the reaction mechanism of the catalytic reaction. A problem with this approach is that gas phase holdup and adsorption (readesorption) effects influence the transient response. These contributions to the transient response can interfere with the determination of the underlying kinetics of the catalyst surface.

It is also possible to obtain quantitative information from the transient response of the product. While the isotopic switch may also result in a transient behavior of the labeled reactant due to adsorption and desorption, the response of the product can be readily attributed to a residence time on the catalyst surface during reaction. The integration of the normalized step-decay response, as shown in figure 1.1, always yields the overall mean surface residence time of all the adsorbed surface intermediates which lead to this product. This quantity is equal to the area under the curves. The amount of surface species is easily deduced from the mean residence time by multiplication with the flow rate of the isotope containing molecule.

This method was used by Bajusz and Goodwin [13] to determine N₂ adsorption isotherms for the zeolite LiX under equilibrium conditions employing isotopic switches from ¹⁴N₂ to ¹⁵N₂. The uptake of N₂ by the zeolite at different temperatures was determined from the steady-state flow rate and the mean surface residence time of ¹⁴N₂. The isosteric heats of adsorption of N₂ as a function of coverage were calculated from the measured isotherms using the Clausius-Clapeyron equation. The value obtained (20 kJ/mol) was similar to those reported in literature for the same system. Thus, SITSKA can successfully be used to obtain such parameters. The use of multiple isotopic labels is not more difficult than use of a single label. Therefore, the results suggest that the technique can be used to evaluate the adsorption behavior of multicomponent mixtures.

4 IMAGING METHODS

Imaging techniques have long been used as a way to gain insight in processes that can not be sampled directly and are mostly used for the visualization of internal structures or processes. These techniques belong to the category of (process-) tomography methods [14-16] which use some type of radiation (γ-ray, X-ray, or neutron) to picture a cross section of a body or structure. For example, X-ray transmission tomography has been used to visualize flow patterns in a fluidized bed. The method consists of measuring the transmission of X-rays through the fluidized bed. The amount of attenuation of the incident radiation is a measure of the local mass density distribution along the path traversed by the beam. The measurement of several of such beams at different spatial and angular orientations to the test volume, followed by an image reconstruction
procedure, provides the density distribution in the measured slice [15]. In order to obtain a deeper understanding of the processes occurring on the surface of the catalyst, it is important to monitor these processes directly. This is impossible with the methods mentioned previously because only density distributions can be determined. Such information can only be obtained if the analysis method can follow the adsorbed molecules directly. Isotopic and non-isotopic techniques have been developed which allow direct observation of the processes on the catalyst surface.

1. Non-isotopic. Qin and Wolf [17] have developed a method based on the detection of infrared (IR) radiation with a sufficient spatial resolution to monitor the coverage of adsorbed species. This method was used to study the spatial surface coverage of CO during its oxidation on a supported catalyst. The system consists of a position sensitive IR camera fitted with an IR filter which measures the transmission of an IR source after passing through a catalyst wafer with adsorbed CO. The 5% Rh/SiO$_2$ catalyst was pressed into a thin wafer of about 2.5 cm diameter. It was shown that linear adsorbed CO molecules on rhodium absorb IR radiation at the wavenumber of 2060 cm$^{-1}$. This suggests that if a narrow bandpass IR filter with the central wavenumber at 2060 cm$^{-1}$ is placed in front of the camera it is possible to measure the amount of linearly adsorbed CO. The intensity of the transmitted IR beam will change according to the concentration of linear bonded CO. Thus, the filtered IR images detected with the camera contain information about the surface concentration of CO at various points of the catalyst wafer. A map of the absorbence which is proportional to the surface concentration was constructed after image processing. The resulting image with 105 x 68 pixels, had a spatial resolution of 0.2 mm horizontally and 0.3 mm vertically. The images acquired during CO adsorption/desorption indicate that the technique depicts the surface coverage with sufficient spatial resolution.

The spatial resolution obtained with this technique is higher than that of PEP. However, its applicability is smaller because only a specific adsorbed form can be monitored. In this case it was shown that linear adsorbed CO was the most abundant species. Another requirement is that the adsorbed species should absorb IR radiation at a different frequency than the gas-phase molecules. With PEP, molecules in both the gas-phase and adsorbed on the catalyst surface can be monitored. Moreover, the PEP technique is independent of the process conditions and consequently the interpretation is more straightforward.

2. Isotopic. The use of isotopes allows the study of chemical surface processes at elevated pressure and in the presence of a working supported catalyst. The most often used isotopes for labeling ($^{13}$C, $^{35}$S, $^{3}$H) are soft $\beta$ emitters. The adsorption of this type of radiation in the catalyst is large, therefore, the radioactivity detector has to be in close vicinity of the source. Direct observation of surface processes on supported catalysts at normal reaction conditions are therefore difficult to obtain because of the limited durability of the measuring equipment at elevated temperatures. The use of $\gamma$-ray emitting sources, like positron emitters, does not have these limitations. However, these emitters have to be prepared with a cyclotron and safe handling of such tracers is more complicated. This is the benefit of using soft $\beta$ emitters, which can be bought in a bottle.
Schröder and Schön [18,19] developed a method based on the use of $^{14}$C to measure the desorption of CO from a Pd/Al$_2$O$_3$ catalyst in the presence of gasphase CO. The experimental setup is shown in figure 1.2. It consists of a flow cell with a scintillation crystal directly above the catalyst. The scintillator is connected to a photomultiplier via an externally cooled light conductor in order to decrease the risk of overheating the counter. The method developed here can only monitor the whole catalyst surface, and therefore the results do not contain any spatial information.

Using this technique they showed that the presence of CO in the gas-phase enhanced the desorption of adsorbed CO ($^{14}$CO). The enhanced desorption was shown to be much slower under these realistic conditions than at the vacuum conditions reported in literature. This shows that catalytic processes occurring under process conditions behave differently from processes under vacuum conditions. Moreover, this indicates the need for analysis techniques which can operate under realistic catalytic conditions. Such a technique is PEP as explained in the next section.

5 Positron Emission Profiling

PEP is an in situ analysis method closely related to the medical technique positron emission tomography (PET). This medical technique has been introduced as an non-invasive method to visualize internal structures of the living body. Minute amounts of an isotopically labeled molecule are admitted to a living organ. The isotope used for labeling is a positron emitter. These isotopes decay via the emission of a positron ($\beta^+$-decay). The positron, which is the antiparticle of an electron, combines with an electron which results in the annihilation of both particles. The total energy of the particles is
Figure 1.3. Schematic drawing of the PEP setup.
The PEP detector consists of two detection banks containing 9 scintillation crystals (BGO) capable of detecting 511 keV photons. The detection banks are placed on both sides of the oven/reactor system. The distance to the oven can be varied between 50 and 240 mm. For a PEP experiment a pulse of positron emitter labeled molecules is injected into the feed. The pulse can be followed through the reactor with the PEP detector. The photons emitted by the tracer are detected coincidentally by the detector. The position of the tracer can then be reconstructed from the intersection of the line which connects the two crystals that detected a photon, and the center of the reactor. The dashed lines show the two most simple reconstruction possibilities between opposite and opposite-adjacent crystals. Dimensions are given in millimeters.

converted into two 511 keV photons emitted in opposite direction. The energy of the photons is high enough to penetrate the body tissue. The location of this annihilation event can be determined via coincident detection of the emitted photons using a
cylindrical array of scintillation crystals. Tomographic reconstruction methods are then used to obtain a three-dimensional image of the distribution of the labeled molecules in the living organ. Currently it is possible to achieve a spatial resolution of 3 mm in each direction and a time resolution of 5 seconds [20,21].

The use of PET in heterogeneous catalysis has first been applied by Jonkers et al. [22]. A commercial PET camera (NeuroECAT [23]) was used to obtain a concentration profile of the labeled atom along the axial axis of the reactor. The technique was used to study the CO oxidation reaction over a cerium promoted platinum exhaust catalyst (Pt-CeO$_2$/Al$_2$O$_3$). The tomograph was operated in such a way that only the events that were coincident at detectors in both the opposing banks parallel to the reactor were registered. This means that only one of the three dimensions was used for the reconstruction procedure. This limitation was brought about by the design of the PET camera, which only allows a full 3D reconstruction every 60 seconds. The use of only one dimension is not a problem for catalyst research, because conditions can be chosen such that the major concentration variations only occur in the axial direction (plug flow reactor). Using this setup, a spatial resolution of 9 mm and a temporal resolution of 1.2 seconds were achieved. It was possible to determine the isotope concentration at 21 equidistant positions each separated by 11 mm.

In continuation of the initial study by Jonkers [22] and Vonkeman [24] a new detector has been designed and constructed specifically for catalysis research. This project based on the use of positron emitters within heterogeneous catalysis has been started by the Departments of Technical Physics, and Chemical Engineering of the Eindhoven University of Technology [25-28]. The detector has been optimized to measure in situ isotope profiles along the axial axis of a cylindrical plug flow reactor. The aim of this research was to increase both spatial and temporal resolution, and to obtain a better understanding of the detection process. An increased knowledge of the detection process will facilitate data interpretation. The technique based on the use of this detector has been designated as Positron Emission Profiling.

The PEP detector (figure 1.3) consists of two arrays of nine independent detection elements, which are placed on opposite sides of the reactor/oven [25,26]. Each detection element contains a bismuth germanium oxide (BGO) scintillation crystal coupled to a photomultiplier tube. The position of the annihilation event is deduced as follows. During annihilation two 511 keV photons are formed which are emitted under an angle of 180 degrees. The photons are detected coincidentally by two elements, one from each array. The position is reconstructed from the intersection of the line which connects the two elements that detected a photon, and the central axial axis of the reactor. Consequently, the activity (concentration) can be measured at 17 unique equidistant positions along the axial axis of the reactor. The distance between each measuring position is 3.25 mm. The optimal configuration consists of placing the detection elements tightly next to each other. The maximum spatial resolution which can be achieved with this “close-packed configuration” is 2.9 mm [29]. The actual spatial resolution depends on the positron emitter, catalyst density, and the reactor/oven configuration. Taking this into account the spatial resolution varies between 3 and 9 mm.
Data can be collected every 0.5 second, which leads to an identical value for the temporal resolution. The specifications for the constructed PEP detector are better than those for the NeuroECAT used previously and current state of the art PET detectors. PEP experiments are performed as follows. The catalyst is allowed to reach steady-state. Under these conditions a pulse of a positron emitter labeled molecule is injected into the reaction mixture going to the catalyst. The labeled molecule is the isotopic analogue of one of the reactants. The labeled molecules are followed with the PEP detector as they pass through the reactor containing the catalyst. The measured profiles contain information about the distribution of the isotope along the length of the catalyst bed as a function of time. Since the labeled molecule is converted as it advances through the reactor, the isotope is distributed among the reactant and products. The PEP detector only measures the amount of the radioisotope, it is impossible to determine the identity of the labeled molecules. At the exit the distribution can be determined by gas chromatography. Analysis of the PEP results is only possible with the aid of an mathematical model describing the reactions at hand. The outcome of the model is compared with the experimental results (fitting procedure).

As mentioned, PEP combines the possibilities of transient isotopic and imaging methods. Transient information is obtained from the behavior of the labeled pulse as it passes through the reactor. In contrast to SSITKA, information about the surface occupancy and the residence time of the labeled molecules can not be obtained directly from the exit profiles. This is the result of mixing of the isotope among the reactant and products, and usage of labeled pulse instead of an isotopic switch. In addition, the use of a pulse instead of a concentration step complicates the data analysis. Information about the surface occupancy and residence time can only be obtained after modeling the PEP response. The imaging component of the PEP technique gives information about the distribution of the reacting molecules on the catalyst surface and in the gas phase. Such information can provide extra knowledge about the reaction at hand. As mentioned before, the data can only be extracted with a mathematical model. The model should describe the reactions taking place on the catalyst under steady-state and transient conditions. Since data are obtained as a function of time and position this automatically leads to a system of partial differential equations which needs to be solved numerically. Finally, the use of isotopes still gives information about the reaction pathway taken by the labeled molecule, as described in section 2.

6 CONCLUSION

Catalysis takes place on the active catalyst surface, which can differ considerably from the clean surface. Therefore, the properties of the surface under working conditions should be examined in order to understand the real nature of the heterogeneous catalytic reaction. The behavior of each chemisorbed species on the surface of the catalyst can be examined isotopically under working conditions. In this way not only the reaction path, but also the rate of each reaction step may be estimated, and the rate determining step may be elucidated.
PEP is an **in situ** technique that makes use of the transient response to a pulse of positron emitter labeled molecules. The distribution of these labeled molecules on the catalyst can be monitored with the PEP detector. The technique therefore combines the possibilities of isotopic, transient, and imaging analysis methods.

7 REFERENCES


EXPERIMENTAL PROCEDURES

ABSTRACT

Positron emission profiling (PEP) is a transient technique to study the reaction kinetics of catalytic reactions. The technique relies on the availability of positron emitting counterparts of the reactant molecules. Several exhaust catalysis related positron emitting reactant molecules like $^{11}$CO ($^{11}$CO$_2$), $^{13}$NO, $^{15}$O$_2$, and N$_2$$^{15}$O have been prepared. $^{11}$CO$_2$ has been produced by proton irradiation of high purity nitrogen, followed by reduction over zinc to yield $^{11}$CO. The product is further purified by passage through a soda lime trap. $^{13}$NO has been prepared by the reduction of $^{15}$NO$_3$, formed during proton irradiation of water, with VCl$_3$. The yield of $^{13}$NO can be maximized by increasing the reaction temperature (373 K), and by vigorously purging with helium. The formation of $^{15}$O labeled molecules is described in chapter 3. The experimental procedure to perform PEP experiments is given in conjunction with a description of the PEP detector. In addition, the preparation of ZSM-5 coated glass beads is described.
1 INTRODUCTION

The use of transient techniques in catalysis has become increasingly popular. In contrast to steady-state techniques, transient operation allows information to be obtained about reaction mechanisms and rates. Positron emission profiling (PEP) is a recent addition to this field, it allows in-situ monitoring of gas and surface concentrations in a catalytic reactor \[1\text{-}4\]. PEP is based on the popular three-dimensional technique positron emission tomography \[5\] used in medicine. The main difference is that PEP only uses one dimension (axial direction). The technique is made possible due to the special properties of positron emitters used. A positron is emitted when these isotopes decay. This positron has a short half-life in matter and annihilates with an electron, thereby producing two high energy photons travelling in opposite direction. These photons can be detected outside the reactor with a special detector deducing the position of the positron emitter. Just as the medical technique, PEP relies on the availability of positron emitters to make the technique feasible. Thus, a catalytic reaction can only be studied when a positron emitting counterpart of a reactant can be produced. The reactions studied here are all related to exhaust catalysis involving conversion of molecules like CO, N\(_2\)O and NO into less harmful species. Candidate positron emitting isotopes which may be used to label these molecules are \(^{11}\)C \((t_1=20.4 \text{ min})\), \(^{13}\)N \((t_2=10.0 \text{ min})\), and \(^{15}\)O \((t_3=2.0 \text{ min})\). If these positron emitting molecules are used with PEP they have to satisfy several requirements such as high specific activity, high radiochemical purity, and availability in a small gas volume (pulse). A high specific activity can be obtained when using isotopes with a short half-life, like the isotopes mentioned, and by not introducing any non-labeled counterparts during the synthesis. A high radiochemical purity is also required since small amounts of a strongly adsorbing impurity may cause a high degree of background noise in the resulting profile. A possible method to introduce the labeled molecules as a pulse is by adsorption at low temperatures (77 K –170 K) on a suitable adsorbent such as zeolites, and rapid desorption at elevated temperatures. This method has been employed here using molsieve 13X or mordenite as an adsorbent which has been cooled by liquid nitrogen or ethanol/liquid nitrogen.

The preparation of \(^{11}\)CO, \(^{11}\)CO\(_2\) and \(^{15}\)NO will be described in this chapter and the production of \(\text{N}_2^{15}\)O will be discussed in chapter 3. \(^{11}\)C labeled molecules have been prepared by proton irradiation of nitrogen gas. This produces mainly \(^{11}\)CO\(_2\) and small amounts of \(^{11}\)CO, and therefore, \(^{11}\)CO has been produced by reduction of \(^{11}\)CO\(_2\) with metallic zinc. Proton irradiation of water has been used to form \(^{13}\)N labeled nitrates which can be further reduced with VCl\(_3\) to give \(^{15}\)NO.

The use of zeolitic catalysts in catalytic processes is becoming increasingly popular. If zeolites are to be used in the current setup for PEP experiments they should be supported. Investigations[2] with non-supported zeolite crystals which were shaped into larger particles to achieve a low pressure drop have shown that the diffusion between the zeolite crystals in a particle can become rate limiting \[1\]. Therefore, using non-supported zeolite crystals does not allow the intrinsic reaction kinetics to be studied with PEP. To overcome this problem the zeolite (ZSM-5) was grown on non-porous glass beads, giving
a thin layer of the zeolite on a glass bead, thereby eliminating the need to form large particles. The preparation of these coated beads is also described. In addition, the experimental techniques involving the PEP experiments with the automated equipment will be discussed, followed by a basic description of the PEP detector.

2 PREPARATION OF $^{11}$CO AND $^{11}$CO$_2$

Carbon-11 labeled products were prepared by the $^4$N($p,\alpha$)$^{11}$C nuclear reaction [6,7]. A 12 MeV proton beam was used to irradiate nitrogen (Hoekloos 99.999%, 4 ppm O$_2$) at a pressure of 4 bar in a double foil cylindrical gas target, similar to the one used by Strijkmans et al. [8]. The two 25 µm thick foils (Duratherm 600) reduced the beam energy to around 10 MeV, at this energy the production of other radionuclides like $^{13}$N is severely suppressed. A schematic of the entire synthesis setup is shown in figure 2.1. Nitrogen gas was irradiated for 20 min in a closed target at a beam current of 300 nA. After irradiation the target was opened and continuously swept with fresh nitrogen at a flow rate of 400 ml/min. The target effluent containing both $^{11}$CO and $^{11}$CO$_2$ was mixed with helium at a flow rate of 500 ml/min and was led to a liquid nitrogen trap where $^{11}$CO$_2$ was collected. Helium was added to the target effluent to prevent condensation of nitrogen in the cold trap. Due to the high flow rate through the trap only $^{11}$CO$_2$ was trapped efficiently. The trap consisted of a double walled tubing, with the target effluent
flowing through the inner tube (i.d. 2 mm) while it was cooled by liquid nitrogen flowing through the outer tube (i.d. 10 mm, see figure 2.1). The trap was precooled with liquid nitrogen for six minutes before collection. After collection for 8 minutes the trap was warmed up by flowing air through the outer tube, and trapped \(^{11}\text{CO}_2\) was removed by continuously flushing the trap with a lower helium flow (50 ml/min). If \(^{11}\text{CO}_2\) was needed for PEP experiments the product was directly led to the adsorber (see figure 2.9). The adsorber consisted of an U-shaped stainless steel tube with an internal diameter of 0.15 mm. The tube was filled with a small amount of molsieve 13X and was cooled by immersing it in liquid nitrogen. At this temperature (77 K) both \(^{11}\text{CO}_2\) and \(^{11}\text{CO}\) were adsorbed efficiently. The isotope was desorbed by removing the coolant and allowing the adsorber to warm up to room temperature in 30 sec, after which the isotope was removed by flushing with helium (20 ml/min). \(^{11}\text{CO}\) was easily prepared by passing the \(^{11}\text{CO}_2\) containing gas through a tube containing metallic zinc which was heated to 673 K in an oven [7]. This procedure reduces \(^{11}\text{CO}_2\) to \(^{11}\text{CO}\) with an efficiency of 80%. Unreduced \(^{11}\text{CO}_2\) was removed by a trap containing soda lime and molsieve 13X, placed behind the zinc reactor. This trap completely removed \(^{11}\text{CO}_2\) and any other non-labeled nitrogen oxides which might be produced by radiolysis (see chapter 3). The resulting product, \(^{11}\text{CO}\), was sent to the adsorber (see figure 2.9) already mentioned earlier.

3 Preparation of \(^{13}\text{NO}\)

3.1 Introduction

Synthesis methods for \(^{11}\text{CO}\) with a high specific activity are well known [7], however, this is not the case for \(^{13}\text{NO}\). A method was developed for production of \(^{13}\text{NO}\) with a short synthesis time, high radiochemical purity, and a high specific activity which are all required for catalyst research with PEP. A possible synthesis route is the reduction of \(^{13}\text{NO}_3^-\) which is produced by proton (p) irradiation of natural water, inducing the following nuclear reaction [9-13]:

\[
^{16}\text{O} + p \rightarrow ^{13}\text{N} + \alpha
\] (2.1)

According to literature, nitrates are reduced efficiently to nitrogen monoxide in the presence of copper or vanadium [14,15]. This method, using vanadium (V\(^{5+}\)), has been mentioned in literature [15], but no data concerning the radiochemical purity or the exact synthesis route have been given. The reduction of nitrates has been employed here to obtain non-carrier added and carrier added \(^{13}\text{NO}\) depending on the additive present during the reduction step.

3.2 Production of \(^{13}\text{NO}_3^-\)

A Philips cyclotron producing 16 MeV protons was used to irradiate a natural abundance water target. The target was a flow-through dual-foil (Duratherm 600, thickness 15 \(\mu\)m) brass target with a water chamber volume of 0.7 ml (see figure 2.2). A second water reservoir was connected to the target allowing a total volume of 6 ml of water to be
irradiated. All connecting tubes were made of Teflon tubing. The water was continuously pumped through the target by a peristaltic pump fitted with silicone tubing to allow all the water to be irradiated and to avoid boiling. Before loading the target with water it was flushed with helium. The water used was taken from a reservoir containing helium outgassed distilled water and was filled off with 0.5 bar helium overpressure. The target was irradiated at a beam current of 300 nA for 5 minutes. After irradiation the water was removed from the target by flushing the system with helium and was stored in a transport vessel. The interior of this vessel was made of Teflon surrounded by a lead lining to reduce radiation exposure during transport. The Teflon insert with a volume of 15 ml had an airtight sealing, and the in- and outlet connectors were self closing with a small dead volume (0.1 ml, Swagelok QM series).

3.3 Reduction of $^{13}$NO$_3$:

Reduction with copper powder was performed as follows. Copper powder (1 g, Merck, $d_p$ 10 μm) was thoroughly mixed with 5 ml of distilled water and was placed in a 50 ml 3-necked flask fitted with a water cooler, helium inlet, and an outlet for liquid waste (see figure 2.3). The copper suspension was continuously flushed with helium. After addition of 6 ml of irradiated water, 400 μl 36% HCl (Merck), or 500 μl of an 1% HNO$_3$ (Merck)
Figure 2.3. $^{13}$NO$_3^-$ reduction setup.
The transport vessel containing irradiated water was emptied by flushing with helium as indicated in the figure after which VCl$_3$ was added to the irradiated water by opening the reservoir. After reduction of $^{15}$NO$_3^-$ to $^{15}$NO valve V1 was closed and the waste was removed by purging with helium while opening valve V2. The gaseous reaction products were removed from the solution with helium and were sent to the adsorber in (figure 2.9) to be collected for a PEP experiment.

solution was added to the suspension. The concentration of the nitric acid solution was lower to prevent formation of large amounts of non-labeled NO. When other acids were used they were first diluted to 36% and 400 µl of this dilution was added. The reaction mixture was subsequently brought to a boil. A total synthesis time of 6 minutes was achieved. Liberated (radioactive) gases were led through a 5 ml NaOH column to remove water and HCl. The loss of activity in the reaction vessel was monitored by a NaI detector to determine synthesis efficiency.

Reduction with VCl$_3$ (Merck) was performed in a similar way. Briefly, irradiated water (6 ml) was added to a solution containing 5 M HCl and 0.5 M VCl$_3$ and was heated to 373 K. This solution had been previously outgassed with helium and was taken from a helium pressurized (0.5 bar overpressure) glass container. Gaseous reaction products were dried over a NaOH column.
Figure 2.4. Conversion of $^{13}$NO$_3^-$ to $^{13}$NO.
The conversion levels of several Cu(s)/acid systems are compared with the V$^{5+}$/HCl system. Equal concentrations of acid were used when copper was used as a reductant.

3.4 Product analysis

Gaseous products produced during reduction were trapped in an adsorber emerged in liquid nitrogen (77 K). The adsorber (see figure 2.9) consisted of an U-shaped Teflon tube with an internal diameter of 1 mm. Trapped products were released by allowing the adsorber to warm up to room temperature after which it was flushed with helium. Subsequently, the products were led through an 1 ml sample coil monitored by a NaI detector. At maximum activity the sample was injected on a Haysep N/molsieve 13X (Chrompack) column. Non-labeled products were analyzed by a thermal conductivity detector and labeled products by a flow-through NaI detector.

3.5 Results and Discussion

The presence of radionuclidic impurities in proton irradiated water has been determined by decay analysis. Only minor contributions (<1%) could be assigned to impurities such as $^{18}$F and $^{11}$C (due to traces of nitrogen gas). The analysis resulted in a half-life of 606 s for the nuclide produced, which is in good agreement with literature values of 597.6 s – 613 s [9] for the half-life of $^{13}$N. The main product formed during proton irradiation of water has shown to be $^{13}$NO$_3^-$ [7,11-13], which can be reduced with copper metal or V$^{5+}$ ions to yield $^{13}$NO. Both methods have been evaluated in this study.

Nitrate reduction with copper metal only occurs with high efficiency in acidic solutions, therefore, its reduction efficiency has been assessed for several acids. The conversion of $^{13}$NO$_3^-$ was determined by monitoring the decrease in activity of the $^{13}$NO$_3^-$ solution which was continuously swept with helium to remove gaseous $^{13}$NO. The conversion levels of the acids used are shown in figure 2.4. As can be seen, HCl and HNO$_3$ are the most active acids for this system, the conversion level without added acid is negligible (<1%). The low conversion levels with H$_3$PO$_4$ and H$_2$SO$_4$ are probably due to the formation of
Figure 2.5. Radio GC analysis of $^{13}\text{NO}$ produced by reduction of $^{13}\text{NO}_3$ with the Cu(s)/HCl system.

NO and N$_2$O were separated with the Haysep (Chrompack) column. A molsieve (13X, Chrompack) column was used in series with the previous column to also separate N$_2$ and NO. The amount of radioactivity was recorded with a NaI detector.

Insoluble copper salts on the surface of the metal. The salts formed when HCl (CuCl and CuCl$_2$) is used are soluble in water, therefore, this is the only suitable system for the production of carrier free $^{13}$NO when using copper as reductant. Addition of HNO$_3$ also produces $^{13}$NO with a high efficiency, however, in this case $^{13}$NO is not carrier free. A similar conversion level is obtained when VCl$_3$ is used as reductant (see figure 2.4), giving carrier free $^{13}$NO.

The radiochemical purity of $^{13}$NO produced by HNO$_3$-HCl/Cu(s) and V$^{3+}$/HCl has been determined by GC analysis. Using two columns it was possible to identify the following products: NO, N$_2$, NO$_2$, and N$_2$O. Figure 2.5 shows the analysis for the HCl/Cu(s) system. As can be seen, only $^{13}$NNO is present as an impurity and further reduction to $^{13}$NN does not occur. To perform analysis with the molsieve column it was necessary to add some NO to the sample because $^{15}$NO could not be detected otherwise. This is a known problem when zeolites are used as column material since small quantities of NO remain irreversibly adsorbed [16,17]. This confirms that produced $^{13}$NO is carrier free. The analysis results for the other systems are given in Table 2.1. In contrast to the Cu(s) systems, further reduction to N$_2$ does occur when V$^{3+}$/HCl is used. This difference is probably caused by the fact that V$^{3+}$ is a more potent reductant than Cu(s). Removal of $^{13}$NNO from the gas stream with known adsorbents like active charcoal and zeolites [18].

<table>
<thead>
<tr>
<th>Component</th>
<th>Product distribution per system [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu(s)/HNO$_3$</td>
</tr>
<tr>
<td>$^{13}$NO</td>
<td>99.1</td>
</tr>
<tr>
<td>$^{13}$N$_2$O</td>
<td>0.9</td>
</tr>
<tr>
<td>$^{13}$N$_2$</td>
<td>0.0</td>
</tr>
</tbody>
</table>
has not been successful. Although $^{15}$NNO is removed by these traps a substantial amount (>70%) of the $^{14}$NO produced is also adsorbed, and therefore, these traps should only be used when very high purity $^{15}$NO is required.

In an attempt to decrease the synthesis time, the effect of increasing the reduction solution temperature and the flushing rate have been investigated. When the mixture is not heated reduction of $^{15}$NO$_2$ does occur since a rise in the activity of the effluent (containing $^{15}$NO) is observed directly after addition of the reductant. The total conversion of this system is much lower than when the mixture is brought to a boil, therefore, heating increases the amount of $^{15}$NO which can be liberated from the reaction solution. Thus, removal of $^{15}$NO from the solution seems to be limiting the synthesis time. Indeed, increasing the flow rate of the helium flush through the reduction solution increases the removal of $^{15}$NO. This removal is further enhanced when a mixture of helium and nitrogen oxide (0.5%) is used as flushing gas. In this way a conversion of 90% could be obtained, which also shows that removal of $^{15}$NO is the limiting factor in the production procedure.

3.6 Conclusion

Irradiation of water with high energy protons mainly produces $^{15}$N which is present as $^{15}$NO$_2$. This can be reduced to $^{15}$NO using either copper or vanadium. Copper is only active in the presence of HCl and is in this case just as active as vanadium. With both systems carrier free $^{15}$NO is the main product and $^{15}$NNO is present as a minor impurity (< 1%). Production of small quantities of $^{15}$NN (1%) only occurs when vanadium is used. The synthesis is most efficient at elevated temperatures and when a high helium flush flow rate is used, resulting in a rapid removal from the reduction solution.

Since the preparation of $^{15}$NO with vanadium only requires handling of liquids this method was chosen to produce $^{15}$NO for the PEP experiments. The reaction liquid was continuously flushed with helium at a high flow rate (300 ml/min) to efficiently remove $^{15}$NO from the solution. To further increase the $^{15}$NO removal the mixture was heated to 373 K. A total synthesis time of 5 min could be achieved by which the decay of $^{15}$NO was minimized.

4 Preparation of ZSM-5 Coated Glass Beads

4.1 Introduction

ZSM-5 is an aluminum containing zeolite and its structure (MFI) is similar to that of silicalite-1 which does not contain aluminum. The preparation of ZSM-5 has been described extensively in literature [19], however, most studies are based on $^{15}$- or preparation of non-supported ZSM-5 crystals. A review by Jacobs and Martens [19] gives a thorough overview of the influence of the various synthesis components (i.e. silica, template, water) on the crystallization behavior of ZSM-5. It has been shown that it is possible to grow A-type zeolite on quartz plates and quartz wool [20]. Since the composition of glass is similar to that of quartz it is expected that ZSM-5 will also grow on
To stimulate the growth of ZSM-5 crystals on the glass surface instead of in the solution a diluted synthesis mixture was used [20-22]. This mixture has been allowed to crystallize at 443 K in the presence of glass beads in an autoclave. To prevent association of the beads due to growth of crystals between several beads the autoclaves were rotated during the synthesis.

### Table 2.2. Composition of the ZSM-5 synthesis solution for 20 g glass beads.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount [g]</th>
<th>Concentration [mmol]</th>
<th>Component/Si This study</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS</td>
<td>13.72</td>
<td>65.9</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TPA-OH</td>
<td>1.36</td>
<td>6.7</td>
<td>0.1</td>
<td>0.04-0.55</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>0.28</td>
<td>3.4</td>
<td>0.05</td>
<td>0.07-1.18</td>
</tr>
<tr>
<td>Water</td>
<td>68</td>
<td>3774</td>
<td>57</td>
<td>7-144</td>
</tr>
</tbody>
</table>

Glass beads. The synthesis solution described here was used to synthesize 20 grams of ZSM-5 coated glass beads with a Si/Al ratio of 19. The composition of the synthesis solution is summarized in Table 2.2. Sodiumaluminate (NaAlO₂, Merck) and Tetra-ethyl-orthosilicate (TEOS, Merck) were used as sources for aluminum and silica. NaAlO₂ (0.28 g) was first dissolved in distilled water (68 g). Care was taken to ensure that all the NaAlO₂ was dissolved since further dissolution did not occur after this step. The template containing aqueous solution (40% Tetrapropylammoniumhydroxide, TPA-OH, 1.36 g) was added to this solution, and the resulting mixture was stirred for 2 minutes. After addition of 13.7 g TEOS the two-phase system was allowed to age (hydrolysis of TEOS) under shaking at room temperature for at least 20 hours. The resulting solution should be clear (or slightly opaque) and most importantly, it should be a single phase. Synthesis solutions containing two phases usually resulted in the formation of large amounts of free ZSM-5 crystals and gel.

### 4.2 Synthesis solution

The synthesis solution described here was used to synthesize 20 grams of ZSM-5 coated glass beads with a Si/Al ratio of 19. The composition of the synthesis solution is summarized in Table 2.2. Sodiumaluminate (NaAlO₂, Merck) and Tetra-ethyl-orthosilicate (TEOS, Merck) were used as sources for aluminum and silica. NaAlO₂ (0.28 g) was first dissolved in distilled water (68 g). Care was taken to ensure that all the NaAlO₂ was dissolved since further dissolution did not occur after this step. The template containing aqueous solution (40% Tetrapropylammoniumhydroxide, TPA-OH, 1.36 g) was added to this solution, and the resulting mixture was stirred for 2 minutes. After addition of 13.7 g TEOS the two-phase system was allowed to age (hydrolysis of TEOS) under shaking at room temperature for at least 20 hours. The resulting solution should be clear (or slightly opaque) and most importantly, it should be a single phase. Synthesis solutions containing two phases usually resulted in the formation of large amounts of free ZSM-5 crystals and gel.

### 4.3 Pretreatment of glass beads

The surface of the beads was cleaned before the synthesis procedure. Glass beads with an average diameter of 650 μm were obtained from Tamson and were first washed with tap water at room temperature. Washed beads were further cleaned by stirring them in a 20% HNO₃ solution at 373 K for one hour. The beads were then rinsed with a 1% HNO₃ solution followed by distilled water at room temperature. The dried beads were calcined at 825 K for 24 hours. This was necessary to prevent cracking of the outer surface into small splinters (grit) at elevated temperatures (>373 K) after the ZSM-5 synthesis. This would result in loss of the zeolite coating because the splinters hold the zeolite crystals. Furthermore, the use of non-calcined beads gave irreproducible results, due to gelation of the synthesis solution. This is probably caused by dissolution of the glass beads in the
Experimental Procedures

![Diagram of ZSM-5 coating on glass beads setup.](image)

Figure 2.6. ZSM-5 coating on glass beads setup.

synthesis solution. With the calcined beads the viscosity of the synthesis solution was the same before and after the synthesis.

4.4 ZSM-5 synthesis

Figure 2.6 shows a schematic of the synthesis setup with the rotating autoclaves. The autoclaves (volume 60 ml, height 10 cm, diameter 5 cm) were made of stainless steel with a Teflon insert (volume 45 ml) and a screwcap. The autoclaves without the inserts were pre-warmed at 443 K in an oven. The glass beads (10 g) were placed in the insert and the synthesis solution was added, the inserts were filled for 90%. The filled inserts were placed in the pre-heated autoclaves and the lid of the autoclave was screwed on hand-tight. The autoclaves were fastened to a horizontal rotating spindle in the oven. The system was allowed to crystallize for 16 hours at 443 K, during this time the autoclaves were rotated 3 times in 2 seconds every 30 min. After the synthesis, the solution was removed and the beads were washed with distilled water and dried at 373 K. The beads were calcined a second time for 32 hours at 825 K to remove template molecules from the zeolite structure. Calcination was performed in a quartz tube heated in a furnace at a rate of 3 K/min to the final temperature of 825 K. Template molecules were oxidized with a stream of 80% N₂ and 20% O₂. After heating, the furnace was allowed to cool down to room temperature. The ZSM-5 coated beads were analyzed by X-ray diffraction, nitrogen adsorption, and scanning electron microscopy. This analysis was performed after sputtering the coated beads with platinum.
4.5 Ion-exchange

Metal (Cu, Fe, Co) loaded zeolites were prepared by ion-exchange. Zeolite coated beads (1 g) were added to a solution (1 l) containing the desired metal ion at a concentration of 0.15 mol/l. Cu-acetate, Fe(NO₃)₃, and Co-acetate were used to prepare the Cu-, Fe-, and Co-exchanged zeolites. This was allowed to exchange for 72 hours at room temperature for Cu, and at 330 K for the other metals. The beads were washed after this procedure by immersing them in distilled water for 24 hours. The resulting beads were dried and calcined at 825 K to remove any residual counter ions still present in the zeolite structure, respectively. The use of glass beads as a carrier for the ion-exchanged ZSM-5 made it impossible to accurately determine the exchange levels for the used metals because of interfering silica.

Figure 2.8. XRD profile of ZSM-5 coated glass beads.
Arrows indicate the diffraction angles belonging to ZSM-5.
### Table 2.3. Properties of the ZSM-5 layer on the glass beads.

<table>
<thead>
<tr>
<th>Property</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen adsorption</td>
<td></td>
</tr>
<tr>
<td>ZSM-5 coating</td>
<td>0.1 mmol/g beads</td>
</tr>
<tr>
<td>ZSM-5 pure</td>
<td>3.59 mmol/g</td>
</tr>
<tr>
<td>ZSM-5 layer</td>
<td></td>
</tr>
<tr>
<td>thickness (average)</td>
<td>21 µm</td>
</tr>
<tr>
<td>weight percentage</td>
<td>2.86 %</td>
</tr>
<tr>
<td>crystals (l x w x h)</td>
<td>2 x 8 x 4 µm</td>
</tr>
<tr>
<td>Glass beads</td>
<td></td>
</tr>
<tr>
<td>average diameter</td>
<td>650 µm</td>
</tr>
<tr>
<td>number of beads</td>
<td>2300 beads/g</td>
</tr>
</tbody>
</table>

### 4.6 Analysis results

Figure 2.7 shows SEM pictures taken from the surface of the coated glass beads. As can be seen, the whole surface is covered with crystals. The average crystal size, as determined by SEM, is around 8 µm. The XRD profile in figure 2.8 indicates that the crystalline phase is indeed ZSM-5, due to the low coverage the peak intensity is low. The amount of ZSM-5 present on the beads has been determined by nitrogen adsorption, which resulted in an adsorption of 0.1 mmol nitrogen per gram of coated beads. Since the amount of adsorbed nitrogen by pure ZSM-5 is known (3.59 mmol N₂/g ZSM-5) the amount of ZSM-5 on the beads can easily be deduced. This value is given in Table 2.3, together with other properties of the ZSM-5 layer and the beads. The thickness of the ZSM-5 layer was derived with the following formula:

\[ Layer \ thickness = \frac{A_{ZSM-5}}{\rho_{ZSM-5} S_{bead}} \]  

(2.2)

where,

- \( A_{ZSM-5} \) Amount of ZSM-5 on the beads (g)
- \( \rho_{ZSM-5} \) ZSM-5 density (1.8 g/cm³)
- \( S_{bead} \) Bead surface area (cm²)

### 5 PEP Experiments

#### 5.1 Equipment

PEP experiments were carried out with an automated continuous flow apparatus with a quartz fixed-bed flow reactor (i.d. 10 mm) operated at ambient pressure as shown in figure 2.9. The gases CO, O₂, CO₂, N₂O and NO were obtained from Praxair and helium was obtained from Hoekloos (99.999%). The gases were premixed with helium to give the following concentrations 5% CO, 2% O₂, 5% N₂O, and 0.5% NO. All gases were used
without further purification unless stated otherwise. The flow of the individual gases was controlled by mass flow controllers (Brooks). A valve was placed behind each mass flow controller to prevent leakage of small amounts of gas through the mass flow controller when the gas was not needed (zero flow). All the tubing was made of stainless steel except the tubing going to and coming from the adsorber and the reactor, which were made of Teflon. The multi-position valves were obtained from Valco and were switched either electrically (six-way valves) or pneumatically (four-way valves and GC sampling valves). The temperature of the reactor was controlled by a cylindrical water-cooled aluminum oven. The oven consisted of a large aluminum block which was heated with two electrical heating rods. This provided a constant temperature over the whole reactor (catalyst bed). The aluminum block was surrounded by isolation followed by a cavity through which water could flow in order to cool the outer surface of the oven (see figure 5.4). The temperature of the oven was controlled by a West temperature controller. The radioactivity at various points, as shown in figure 2.9, was monitored with lead shielded (collimated) NaI detectors. To measure the activity in the tubing the tubing was coiled (1 winding) around the detector to increase the detection sensitivity. The cylindrical detectors, obtained from Scionix, consisted of a NaI crystal connected to a photomultiplier tube. If the voltage pulse (energy of the detected photon) from the photomultiplier exceeded a certain cut-off level a logical pulse was generated. These pulses were accumulated during intervals of 0.5 seconds. The cut-off level was determined experimentally with a $^{133}$Ba source, which emits photons with an energy of 356 keV.

5.2 Experimental procedure

A typical PEP experiment was performed as follows. The quartz reactor was loaded with the desired catalyst resulting in a bed length of 4 cm, and was further filled up with glass beads (diameter 0.65 mm) on both sides of the bed. The reactor was placed in the oven and was allowed to reach the reaction temperature while flowing with helium (50 ml/min). The pressure drop over the reactor was negligible as determined by two pressure sensors placed at the inlet and outlet of the reactor. The reactants were mixed followed by further mixing with the helium stream going to the catalyst, the resulting flow was 40 ml/min. The catalyst was allowed to reach steady-state for at least 10 hours. Upon subsequent changes (raise) in temperature the catalyst reached steady-state in less than an hour, as determined by analysis of the effluent. The appropriate positron emitter was then prepared and collected at low temperature in the adsorber shown in figure 2.9. The adsorber consisted of an U-shaped tubing which was cooled by immersing it in an ethanol/N$_2$(l) bath (173 K) or liquid nitrogen (77 K) using a pneumatically controlled container. The exact characteristics of the adsorber are mentioned in the experimental sections. The amount of radioactivity adsorbed was monitored with a NaI detector. After adsorption, any residual activity still present in the tubing was removed by flushing with helium at 500 ml/min. The positron emitter was removed by raising the temperature of the adsorber while flushing with the helium stream (usually 20 ml/min) going to the
catalyst. The adsorption-desorption parameters like the adsorbent type and the temperature are mentioned in the sections describing the preparation of the positron emitting isotope. This procedure resulted in a pulse of activity (4-40 MBq) with a width of 24 seconds, which was injected in the reaction feed mixture flowing over the catalyst. The distance between the detection banks of the PEP detector was adjusted such that the number of reconstructions (counts) per second never exceeded 28000. Above this
maximum the number of counts recorded by the detector is no longer linear with the activity [23]. The distance between the banks was based on the amount of adsorbed radioactivity. The radioactivity distribution of the isotope in the feed and effluent was recorded by collimated NaI detectors.

5.3 Analysis

The composition of the reactor effluent was determined by gas chromatography using a Chrompack CP9001 chromatograph fitted with Haysep N/molsieve 13X columns. These packed columns with a length of 1.5 m were obtained from Chrompack. The columns were maintained at 393 K. Helium was used as a carrier gas at a flow rate of 20 ml/min. The reactor effluent was led through a 1 ml sample coil monitored by a NaI detector. The products in the sample were separated with the Haysep column, and further separation of N$_2$ and O$_2$ was performed with the molsieve column placed in series with the Haysep column. With this setup it was possible to separate N$_2$O, O$_2$, NO, N$_2$, NO$_2$, CO, and CO$_2$. Non-labeled and labeled products were analyzed by a thermal conductivity detector and a flow-through NaI detector. Radio-gas chromatograms were corrected for decay to compensate for differences in retention time.

6 PEP Detector

6.1 Hardware

A schematic cross section of the detector is shown in figure 2.10, and figure 5.4 gives an overview of the dimensions of the detector. A full description of the detector has already been given by Mangnus et al. [3,4] therefore, only a brief description is given here. The detector can be divided into the following main components: the detection elements, two movable racks which carry the elements, a bracket to position the oven in the center of the detector, and electronics to analyze the response from the elements.

The detection element is comprised of a BGO crystal and a photomultiplier tube. The crystal has the following dimensions: width 5.1 mm, height 20 mm, and length 100 mm. The smallest dimension (width) is along the direction of the reactor/oven. Every crystal is wrapped in Teflon followed by a layer of black tape to prevent detection of stray light. Teflon is used as a reflector to enhance light collection. The crystals are connected to the photomultipliers through a thin layer of light conducting grease (Scionix) to obtain a good optical contact. The photomultipliers are powered by high voltage power supply (Ortec) operating at 1200 V.

The individual elements can be mounted on the rack via two guides. The housing of a neighboring element was situated on the opposite side of the guides with respect to its neighbor (figure 2.10). This was necessary in order to place all crystals next to each other since the width of the housing of the photomultiplier is larger than the width of the crystal. Each rack holds nine elements (detection bank) and can be moved in a vertical direction. The racks are moved simultaneously in opposite direction by a spindle with a bi-directional thread (see figure 2.10). This spindle is connected to a crank which can
Figure 2.10. Cross section of the PEP detector.

rotate the spindle. This ensures that the reactor/oven is always placed in the center of the detector when the banks are moved. The distance between the banks can be varied between 72 mm and 500 mm. A movable bracket allows the reactor/oven or line source to be positioned in between the two detection banks.
6.2 Signal processing

Figure 2.11 shows a simplified scheme of how the signals of the photomultipliers of the two banks are processed. The photomultiplier signal of each detection element is first shaped by a preamplifiers (PA). The preamplifier generates two signals, a timing, and an energy pulse. The timing pulse serves as a trigger for coincident detection. The energy signal is equal to the total energy absorbed by the BGO crystal.

If an annihilation photon (511 keV) is absorbed by a crystal the timing signal passes a certain threshold thereby generating a logical pulse. The logical pulses of one bank are all processed by a logical unit in the 'OR' mode. This means that a logical pulse is generated only if one or more of the crystals detected a 511 keV photon. These logical pulses (one from each bank) are processed by a logical unit in the 'AND' mode, and a pulse is generated only when both inputs are activated coincidentally. In this case, coincident means that both inputs should become activated within a certain time window, the width of this window is 50 ns. The logical pulse generated by the coincident detection triggers the BITBOX to send its contents to a memory bank.

The BITBOX consists of two bytes (16 bits long), one for each bank, and every bit in this byte corresponds to a detection element. The bits in these bytes are set by the energy signal processing circuit. The energy circuit integrates the energy signal of the preamplifier. The resulting voltage pulse is equal to the total energy deposited in the crystal by a photon. If the height of this pulse lies between an adjustable lower and upper level (window) a bit in the BITBOX is set. This means that if the energy of the detected photon lies within this window the element detected a 511 keV photon and the corresponding bit is set. A value of 370 keV was used for the lower level and a value of 750 keV for the upper level. This large window is needed because of the poor energy resolution of BGO (27%). The energy resolution is related to the range of energies produced when a 511 keV photon is absorbed in the crystal. Using an energy window also allows scattered photons to be discarded because scattering causes the photon to lose energy.
6.3 Data processing and detector calibration

Data are collected at intervals of 0.5 seconds, in this mode a profile with a length of 1000 seconds could be recorded. The recorded profile was corrected for decay and was normalized. A calibration procedure was carried out to correct the profile for differences in sensitivity of the individual elements due to non-idealities of the hardware. These non-idealities are caused by differences in light output of the crystals and variances in the amplification by the photomultiplier tubes.

The detector was calibrated with a line source containing a solution of $^{22}\text{NaCl}$ to correct for differences in response of the individual detection elements. The calibration was carried out as follows: the line source was placed in the center of the detector and the response was recorded during 500 seconds at intervals of 1 second. The average response at each reconstruction position was normalized with the calculated theoretical response as determined with EGS4 (see chapter 5). The resulting response factors were used to correct the measured profile. This correction procedure results in a profile which can be compared with the simulation results. If the profile was to be used for plotting, a different procedure was followed. In this case the measured calibration response was only normalized and these values were used to correct the measured profile.

The mathematical treatment of a PEP profile is outlined in chapters 4 and 5. In short, chapter 4 deals with the extraction of mechanistic and kinetic information from PEP profiles. This entails combination of parameter estimation and numerical solution of the partial differential equations describing the reactions taking place. The partial differential equations were solved with the numerical method of lines. The principle of this method is to reduce the partial differential equations to a set of ordinary differential equations which can be solved with LSODES or RKF45. Since PEP experiments are performed under steady-state conditions the mathematical method also has to solve these equations. This involves solving a combined system of differential and algebraic equations. The differential equations describe convection and reaction of the gas phase, and the algebraic equations specify the surface concentration (occupancies) of the reacting species. The algebraic equations arise because there is no movement of species over the catalyst surface in the axial direction. The combined system of differential and algebraic equations was solved with DASSL.

The influence of positron range and photon scattering on the response is treated in chapter 5. The mathematical procedure results in a profile describing the change of the concentration through the reactor with infinite precision. However, the concentration profile determined with the PEP detector is measured with finite precision. The accuracy of the position detection process is influenced by the two effects mentioned above. Depending on the positron emitter and the density of the catalyst the position resolution can vary between 3 and 6 mm. The calculated result is corrected for this effect by convolution with a detector response matrix. The response matrix has been determined by Monte Carlo simulations with the EGS4 code. The EGS4 code describes transport of photons and positrons through matter allowing the effects of positron range and photon scattering on the detector response to be assessed.
7 REFERENCES


14. McCarthy, T.J., Dence, C.S., Holmberg, S.W., Markham, J., Schuster, D.P. and
EXPERIMENTAL PROCEDURES


PRODUCTION OF $[^{15}\text{O}]-\text{N}_2\text{O}$ BY DEUTERON IRRADIATION OF NITROGEN

ABSTRACT

A new in target method for the production of $\text{N}_2\,^{15}\text{O}$ has been developed which is based on the deuteron irradiation of high-purity nitrogen. $\text{N}_2\,^{15}\text{O}$ is a known byproduct of the $^{14}\text{N}(d,n)^{15}\text{O}$ nuclear reaction used for the production of $[^{15}\text{O}]-\text{O}_2$. This nitrous oxide is selectively removed from the target effluent by adsorption on mordenite. This yields a product with a high specific activity ($10^2$-$10^3$ fold increase over the current method [1]), and of high radiochemical purity ($>99.95\%$) which is present in a small gas volume (pulse). As such it can be used to study catalytic reactions of nitrous oxide with positron emission profiling (PEP). Substantial knowledge about the trace products $\text{N}_2\,^{15}\text{O}$ and $\text{N}^{15}\text{O}_2$ has been obtained using this selective adsorption method and this contributed to the further understanding of the target chemistry of the $^{14}\text{N}(d,n)^{15}\text{O}$ reaction.
CHAPTER 3

1 INTRODUCTION

Recently, the interest in nitrous oxide (N\textsubscript{2}O) has increased since it is known to play an important role in the earth's atmosphere, being responsible for ozone depletion and acting as a greenhouse gas. Molecule for molecule N\textsubscript{2}O is nearly 270 times more potent in greenhouse warming than CO\textsubscript{2} [2], therefore, a decrease in its emission is very beneficial. A method to reduce its emission is by catalytic decomposition, hereby converting it into nitrogen and oxygen [3]. Nitrous oxide is also used as a reactant for selective catalytic oxidation. For example, benzene is selectively oxidized to phenol when N\textsubscript{2}O is used [4,5]. The catalytic behavior of these decomposition catalysts and other catalytic reactions involving N\textsubscript{2}O can be studied with positron emission profiling (PEP) [6]. With the aid of positron emitting molecules, PEP allows in-situ monitoring of gas and surface concentrations in both time and space. This information can be used to deduce the elementary reactions taking place and their rate constants [7-9].

Suitable positron emitters for decomposition reaction are N\textsubscript{2}\textsuperscript{15}O or \textsuperscript{15}NNO. The oxygen labeled form is preferred since it is known that oxygen has a more profound interaction with the catalyst surface than nitrogen [3]. If \textsuperscript{15}O-N\textsubscript{2}O is to be used with PEP it has to satisfy several requirements such as high specific activity and being available in a small gas volume (pulse). Ideally, the N\textsubscript{2}\textsuperscript{15}O should be carrier free, since introduction of non-labeled nitrous oxide could influence the reaction taking place.

A known method for the preparation of \textsuperscript{15}O-N\textsubscript{2}O is by oxidation of ammonia over a platinum catalyst with a mixture of \textsuperscript{15}OO/O\textsubscript{2} [1], using the \textsuperscript{14}N(d,n)\textsuperscript{15}O reaction as a source for \textsuperscript{15}OO [10,11]. This method introduces an undesired large amount of non-labeled nitrous oxide and the tracer is not present in small gas volume. In addition, the yield and purity of \textsuperscript{15}O-N\textsubscript{2}O are difficult to control [1]. Therefore, an in target production route was sought for.

It is known that N\textsubscript{2}\textsuperscript{15}O is formed in small quantities (2.5%) during the preparation of \textsuperscript{15}O-O\textsubscript{2} by deuteron irradiation of high-purity nitrogen (99.99%) [1,10,12]. N\textsubscript{2}O is also formed in small amounts when mixtures of N\textsubscript{2}/O\textsubscript{2} (24% O\textsubscript{2}) are used [10,13], however, it is unclear whether this also occurs when very high-purity nitrogen (99.999%) is used. The present method is based on the selective adsorption of \textsuperscript{15}O\textsubscript{2}N-O\textsubscript{2} from the target gas using zeolitic adsorbents at low temperature (173 K). The tracer is regained by desorption at elevated temperatures. The labeled pulse obtained can be used with PEP to study the decomposition of N\textsubscript{2}O over platinum containing catalysts. In addition, a detailed discussion on the formation of \textsuperscript{15}O-N\textsubscript{2}O during deuteron irradiation is presented.

2 EXPERIMENTAL

Oxygen-15 labeled products were produced by the \textsuperscript{14}N(d,n)\textsuperscript{15}O nuclear reaction [10]. A 9.2 MeV deuterons beam was used to irradiate nitrogen (Hoekloos 99.999%, 4 ppm O\textsubscript{2}) at a pressure of 8 bar in a double foil cylindrical gas target, similar to the one used by Strijckmans et al. [14]. The two 25 \textmu m thick foils (Duratherm 600) reduced the beam energy to 7 MeV, at this energy the production of other radionuclides is severely
Production of oxygen-15 labeled nitrous oxide

Figure 3.1. Experimental setup for the production of [\(^{15}\text{O}\)]-N\(_2\)O.

Selection valve 1 (V1) can direct the target effluent to the adsorber or to the vent, in the latter case the adsorber is flushed with He which is used to control the adsorption time. Selection valve 2 (V2) is used as sampling valve for the GC. The radioactivity is monitored with collimated NaI detectors (NaI).

suppressed [10]. A beam current of 500 nA was used, unless mentioned otherwise. The target had an internal volume of 0.76 dm\(^3\) (diameter 44 mm, length 500 mm) and was water-cooled. Due to the high gas pressure, \(^{15}\text{O}\) labeled products were only produced in the first 45 mm of the target. The target exit was therefore placed near the beam entrance. Products were removed by continuously sweeping the target with fresh nitrogen at a rate of 2.5 liter/min.

Radiochemical impurities such as \([^{15}\text{O}]\)-O\(_3\) and \([^{15}\text{O}]\)-NO\(_2\) were removed by passing the effluent over soda lime (NaOH/Ca(OH)\(_2\), Merck, d\(_p\)=2.5 mm). The trap was replaced with fresh soda lime after 30 hours of use to prevent slip of \([^{15}\text{O}]\)-NO\(_2\) or \([^{15}\text{O}]\)-O\(_3\). Only \([^{15}\text{O}]\)-O\(_2\) and \([^{15}\text{O}]\)-N\(_2\)O were present after this treatment. These products were transported through a 50 m long Teflon tubing (i.d. 1.6 mm) to the adsorption equipment (figure 3.1). The radioactivity arriving at the adsorber was monitored with a collimated NaI detector.

The adsorber consisted of a U-shaped stainless steel tubing (length 150 mm, i.d. 2 mm) containing 0.05 g zeolite (13X, 5A, mordenite or ZSM-5) situated in the bend. The tubing was cooled by immersing it in an ethanol/N\(_2\)(l) bath (173 K) using a pneumatically controlled container. \([^{15}\text{O}]\)-N\(_2\)O was separated from the other gases by passage through this trap. The adsorption time, typically 150 s, was controlled with a four-way valve (V1). With this valve, the target effluent could be directed to the adsorber or directly to the vent (figure 3.1). Traces of \([^{15}\text{O}]\)-O\(_2\) present in the tubing and on the adsorbent were removed by flushing with helium (30 s, 500 ml/min). After removal of the coolant, the adsorbed \([^{15}\text{O}]\)N\(_2\)O was regained by quickly heating the adsorber in a stream of helium with a smaller gas flow rate (20 ml/min). Heating occurred by passing a high electrical current (15 A, 2 V) through the tubing of the adsorber. The amount of tracer in the adsorber during the adsorption-desorption process, and the amount present in the gas stream coming from the adsorber were monitored with a collimated NaI detector.
Products that desorbed during electrical heating of the adsorber were analyzed by gas chromatography using a Chrompack CP9001 chromatograph fitted with Haysep N/molsieve 13X (Chrompack) columns. The columns were maintained at 120°C. The desorbed products were led through the 1 ml sample loop of the GC which was monitored by a NaI detector. At maximum activity, the sample was injected (V2) on the Haysep column. It was also possible to separate the products on both the Haysep N and molsieve in series. With this setup N₂O, O₂, NO, N₂, CO, and CO₂ could be separated. Non-labeled and labeled products were analyzed by a thermal conductivity detector and a flow through NaI detector respectively. Radio-gas chromatograms were corrected for decay to compensate for differences in retention time. Typically, 40-60% of the total activity coming from the adsorber could be analyzed using this procedure. Consequently, when comparing different analyses only the N₂¹⁵O/N₂O ratio could be determined quantitatively. In addition, direct samples of the target effluent could also be taken, giving quantitative information about the ratio of ¹⁵OO and N₂¹⁵O.

3 RESULTS

A typical adsorption-desorption cycle of [¹⁵O]-N₂O using mordenite as an adsorbent is shown in figure 3.2. A cycle is divided into three stages and starts with the adsorption of [¹⁵O]-N₂O for 150 s at 173 K. As can be seen, the accumulation of tracer on the adsorbent is not constant with time but shows an exponential behavior. A mathematical description for such an exponential growth has been given by Clark and Buckingham [10]:

\[ A_{ads} = R(1 - e^{-\lambda_o t}) \]  

(3.1)

Where \( A_{ads} \) is the amount of adsorbed activity, \( t \) is the adsorption time, and \( \lambda_o \) is the decay constant for ¹⁵O. This equation describes the two processes which simultaneously occur on the adsorbent, namely, the accumulation of labeled N₂¹⁵O due to adsorption and the loss of activity due to decay. The maximal amount which can be adsorbed is therefore limited by the decay of labeled nitrous oxide. This equation only holds if the adsorption rate of nitrous oxide is constant. This assumption is justified here because the amount of nitrous in the target effluent is small, such that saturation of the adsorbent will only be reached after long adsorption times (> 30 min). The factor R is related to the amount of tracer present in the gas stream and the adsorption properties of the zeolite. This factor determines the maximal amount of activity which can be recovered from the adsorbent. The solid line shows the predicted trend, given by equation (3.1). Other zeolitic materials such as 13X, 5A, and ZSM-5 give similar results (R-values), however, the adsorption capacity of these zeolites decreased after several adsorption-desorption cycles. This is especially the case with 13X which shows a decrease of 50% after several cycles. In contrast, the adsorption capacity of mordenite is still constant after more than 200 cycles. Although the adsorption on mordenite is most efficient at 173 K, adsorption also occurs at room temperature; a 30% reduction is observed at room temperature. Similar reductions have been obtained for the other zeolites studied. During the second
**Figure 3.2.** Adsorption-desorption cycle of $[^{15}\text{O}]-\text{N}_2\text{O}$ on mordenite.

I Adsorption at 173 K, II Flushing with He, III Desorption as a result of electrical heating. The signals shown were recorded with different NaI detectors. The line annotated with NaI\text{ads} records the amount of radioactivity in the adsorber. The label NaI\text{loop} indicates the signal recorded in the sample loop (see figure 3.1). This detector measures the amount of radioactivity in the adsorber effluent.

Stage, the adsorber is flushed with helium. The decrease in activity is caused by the rapid decay of $\text{N}_2{^{15}}\text{O}$. In the last stage the activity is removed by rapidly heating the adsorbent, causing all the $[^{15}\text{O}]-\text{N}_2\text{O}$ to desorb. This procedure yields a pulse of $[^{15}\text{O}]-\text{N}_2\text{O}$ having a width (FWHM) of 3.5 seconds as determined from the pulse in figure 3.2.

The composition of the target effluent after the soda lime trap has been determined by

**Table 3.1.** Target effluent and desorption pulse composition after 150 s adsorption at a beam current of 500 nA.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Non-labeled components</th>
<th>Labeled components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{N}_2\text{O}$</td>
<td>$\text{O}_2$</td>
</tr>
<tr>
<td><strong>Target gas ($\text{N}_2$)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amount</td>
<td>-</td>
<td>4 ppm</td>
</tr>
<tr>
<td><strong>Target effluent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amount</td>
<td>0.4 ppm</td>
<td>4 ppm</td>
</tr>
<tr>
<td>product distribution ratio</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>specific activity ($10^{13}$ Bq/mol)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Desorption pulse</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>specific activity ($10^{13}$ Bq/mol)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>product distribution ratio</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Not present or below detection limit
= Not determined
radio-GC analysis. Only $^{15}\text{O}_2$ and $\text{N}_2^{15}\text{O}$ can be detected, $\text{N}_2$ is the only non-labeled product which is observed. Analysis shows a product distribution of 90% $^{15}\text{O}_2$ and 10% $\text{N}_2^{15}\text{O}$. The composition did not change upon removal of the soda lime trap. However, $[^{15}\text{O}]-\text{O}_3$ and $[^{15}\text{O}]-\text{NO}_2$ which are known byproducts of the irradiation procedure [10,12] cannot be analyzed with this system. Adsorption of the raw target effluent indeed showed the presence of an additional product, probably $[^{15}\text{O}]-\text{O}_3$ or $[^{15}\text{O}]-\text{NO}_2$. To discriminate between these products the soda lime trap was replaced with a MnO$_2$ trap, which selectively decomposes $[^{15}\text{O}]-\text{O}_3$ [15]. No change in the adsorption is found, therefore, it can be concluded that $[^{15}\text{O}]-\text{NO}_2$ is the byproduct formed during the irradiation. The ratio of the labeled products present in the raw target effluent is given in Table 3.1.

The presence of radionuclidic impurities (e.g. $^{11}\text{C}$ and $^{13}\text{N}$) has been checked by decay-curve analysis of the adsorbed products. This yielded a half-life of 2.07 min which is in good agreement with literature values (2.03-2.07 min) for the half-life of $^{15}\text{O}$ [10,11,16,17]. In addition, no significant contribution of the longer living radioisotopes can be observed. The (radio)-chemical purity of the adsorbed product was determined by GC analysis. Figure 3.3 shows the GC analysis of the labeled and non-labeled products present in the desorption pulse. As can be seen, all the radioactivity is in the form of nitrous oxide, no $^{15}\text{O}_2$ (or $\text{O}_2$) can be detected, even after increasing the amount of activity injected on the column (longer adsorption times). Given the detection limit of the system, the radiochemical purity is higher than 99.95%. However, the analysis also shows that non-labeled $\text{N}_2\text{O}$ is present, next to a small amount of nitrogen. This indicates that $\text{N}_2\text{O}$ is probably formed during the irradiation of nitrogen, this is possible because high-purity nitrogen always contains some oxygen (4 ppm). To exclude the possibility that $\text{N}_2\text{O}$ is an impurity in the target gas, the target gas was purified by passage through an

Figure 3.3. GC analysis of $[^{15}\text{O}]-\text{N}_2\text{O}$.

Desorbed products (stage III in figure 3.2) were analyzed by gas chromatography over a Haysep (Chrompack) and molsieve (Chrompack) column. Radioactive products were detected with a Nal detector, and non-labeled products were detected with a thermal conductivity detector (TCD).
activated charcoal trap [10,14]. After this purification N₂O is still present in the desorption pulse. The efficiency of the trap has been checked by also passing the target effluent through a used trap. In that case, no [¹⁵O]N₂O is detected in the effluent. As a result the specific activity of [¹⁵O]N₂O after 150 s adsorption is 4.5·10¹³ Bq/mol using a beam current of 0.5 µA. The specific activity of [¹⁵O]O₂ has been deduced from the amount of N₂¹⁵O adsorbed and the ratio between ¹⁵OO and N₂¹⁵O (Table 3.1). Since the exact amount of O₂ in the target gas is not known the content according to specifications of the manufacturer has been used.

In an attempt to lower the non-labeled N₂O concentration in the target effluent the oxygen content of the target gas was lowered by passage through a Cu trap. This trap is known to reduce the oxygen content to 0.1-0.5 ppm [1]. Lowering the oxygen concentration reduced the ¹⁵O recovery with 35% and the concentration of N₂¹⁵O and N₂O is also reduced. This indicates that N₂¹⁵O is not formed by a hot-atom reaction but is produced by some oxygen dependent intermediate species. The term hot-atom is used here to indicate a direct reaction between the ¹⁵O atom, formed by the nuclear reaction, and another molecule to yield N₂¹⁵O. It should be mentioned that the formation of N₂O is also observed when nitrogen is irradiated with 12 MeV protons, thus the formation is not an exclusive property of the deuteron irradiation procedure.

The influence of the adsorption time on the specific activity has been evaluated and is shown in figure 3.4. The specific activity decreases with increasing adsorption time, due to the decay of N₂¹⁵O. This decay limits the amount of radioactivity which can be adsorbed, whereas the adsorption of non-labeled N₂O is not limited. A high specific activity is therefore obtained at short adsorption times.

It is known from literature that radiolysis of nitrous oxide can occur in the target, but these results were obtained with a target gas containing 4% oxygen [10]. Figure 3.5 shows the influence of the beam current on the production of N₂¹⁵O and N₂O for a target filled with high-purity nitrogen. As can be seen, the amount of N₂¹⁵O increases linearly with
Figure 3.5. Influence of the beam current on the production of $\text{N}_2^{15}\text{O}$ (○) and $\text{N}_2\text{O}$ (□).

The production of $\text{N}_2^{15}\text{O}$ is determined by the amount of radioactivity adsorbed on mordenite (R-value)
All the values are normalized to the amount adsorbed at 5 µA. GC analysis has been used to determine
the $\text{N}_2\text{O}$ production. The maximal production is used as a normalization factor in this case. The
absolute amount of produced $\text{N}_2\text{O}$ is much higher than that of $\text{N}_2^{15}\text{O}$.

increasing current. There is no evidence of radiolysis for beam currents up to 5 µA under
these conditions. The production of $\text{N}_2\text{O}$ is completely different, the amount of $\text{N}_2\text{O}$ in
the target effluent quickly reaches a plateau with increasing beam current. A decrease in
the amount of $\text{N}_2\text{O}$ can only be observed at very low currents (<100 nA).

4 DISCUSSION

Deuteron irradiation of high-purity nitrogen gas produces mainly $^{15}\text{O}O$ and smaller
amounts of $[^{15}\text{O}]{\text{N}}_2\text{O}$ and $[^{15}\text{O}]{\text{N}}_2\text{O}_2$. The amount of $[^{15}\text{O}]{\text{N}}_2\text{O}_2$, found in this study, is
much lower than the value (65%) given by Clark and Buckingham [10]. This discrepancy
is probably due to the adsorption properties of $[^{15}\text{O}]{\text{N}}_2\text{O}_2$ which caused the amount of
$[^{15}\text{O}]{\text{N}}_2\text{O}_2$ to be overestimated in the experiments of Clark and Buckingham [10]. In
those experiments, the amount of $[^{15}\text{O}]{\text{N}}_2\text{O}_2$ was derived from the difference in activity of
the target effluent which was and which was not passed through a soda lime trap.
Adsorption of $[^{15}\text{O}]{\text{N}}_2\text{O}_2$ on the walls of the flow through detector could have caused an
overestimation of the activity in the case that the target effluent was not passed over soda lime.
The adsorption of $[^{15}\text{O}]{\text{N}}_2\text{O}_2$ also affected the present results, therefore, the value
given (20%) is only an upper limit, the actual value will be lower.

The formation of $^{15}\text{O}O$ as the main product can be explained by the following rapid
exchange reaction between $^{15}\text{O}$ and oxygen molecules [12,18,19].

$$^{15}\text{O} + \text{O} \rightarrow \text{O} + ^{15}\text{O}O$$  \hspace{1cm} (3.2)

This reaction causes quenching of most of the $^{15}\text{O}$ atoms when oxygen is added to the
target gas since 96% of the $^{15}$O atoms are then recovered as $^{15}$OO. In the presence of very small quantities of O$_2$ the main product is still $^{15}$OO, indicating that the exchange reaction prevails over other reactions of $^{15}$O atoms. It can be expected that this exchange is less efficient when the oxygen concentration is low, and that the $^{15}$O atoms are lost on the walls of the target to some extent. This is in agreement with the very low rate of $^{15}$O recovery when pure nitrogen is used as a target gas [10] and the observed loss in recovery when the oxygen concentration is lowered.

These observations indirectly imply that the other products formed during the irradiation (i.e. $[^{15}$O]-N$_2$O, $[^{15}$O]-NO$_2$) are not formed through hot-atom reactions. The focus will be placed on the formation of N$_2$O since no information was obtained on the production of NO$_2$. The following reactions (3.3:3.6) have all been shown to be possible pathways for the formation of N$_2$O during the irradiation of nitrogen-oxygen mixtures.

\[
N_2(A^3\Sigma) + O_2 \rightarrow N_2O + O(2P) \quad (3.3)
\]
\[
N + NO_2 \rightarrow N_2O + O \quad (3.4)
\]
\[
O(^1D) + N_2 \rightarrow N_2O \quad (3.5)
\]
\[
O_3^{N=O} + N_2 \rightarrow N_2O + O_2 \quad (3.6)
\]

The first reaction (3.3) was proposed by Zipf [20] as a direct route for the formation of N$_2$O. The lowest electronically excited state (A$^3\Sigma$) of nitrogen carries enough energy to react with oxygen to produce N$_2$O [21-24]. According to Zipf this reaction is very efficient, whereas Iannuzzi et al. [22] found that the yield of this reaction was very low. The reason for this discrepancy still remains unresolved [25]. The present results show that the N$_2$O yield is almost independent of the beam current indicating that something else is limiting the formation of N$_2$O. Increasing the beam current would also increase the amount of radiation induced particles like N$_2(A^3\Sigma)$. It is therefore highly unlikely that N$_2$O is produced via reaction (3.3).

The same argument rules out reaction (3.4) as a major source of N$_2$O [26-28], in addition this would require the presence of considerable amounts of NO$_2$. Results obtained with $^{13}$N recoil atoms [29] show that $^{13}$NN plays an important role in the formation of $^{13}$NNO and that NO$_2$ does not. The recoil $^{13}$N atoms used in this study were generated by the $^{12}$C(d,n)$^{13}$N reaction in mixtures containing CO$_2$, N$_2$, and O$_2$. The main products were $^{13}$NN and $^{13}$NNO. Through variation of the N$_2$ and O$_2$ concentration it was found that as the $^{13}$NN production decreased the amount of $^{13}$NNO also decreased. Hence, it was concluded that $^{13}$NNO could only be formed after formation of $^{13}$NN, and that direct formation by a hot-atom reaction did not occur. To explain these results the authors proposed a pathway similar to reaction (3.3), however, as mentioned, this does not seem to explain the present results.

A possible limiting factor in the N$_2$O formation is the oxygen concentration. Both reaction (3.5) and (3.6) show an oxygen dependency making them potential candidates for the formation of N$_2$O. The oxygen atoms in the latter reaction are either produced by radiolysis of oxygen or by the nuclear reaction. The production of N$_2$O can not be due to
the reaction (3.5) of O(1D) [30,31] because the rate of removal (return to the ground state) of O(1D) due to N₂ is very high [32]. It is also known that this reaction is an extremely inefficient process in the gas phase [2,32] which makes this reaction a very improbable source for N₂O. Reaction (3.5) is also a direct route for the production of N₂¹⁵O by a hot-atom reaction. If N₂¹⁵O would be formed by this reaction it can be expected that the specific activity of [¹⁵O]-N₂O would be higher than that of [¹⁵O]-O₂. Since similar specific activities have been found for these molecules it is more likely that both N₂O and N₂¹⁵O emanate from the same precursor, in this case [¹⁵O]-O₂. Furthermore, the combined decrease in N₂¹⁵O and ¹⁵OO upon reduction of the O₂ content also shows that ¹⁵O probably first reacts with O₂ (oxygen exchange) whereafter an intermediate is formed which reacts with N₂ to form N₂¹⁵O. A possible intermediate which could be produced from O₂ and which is also dependent on the oxygen concentration is ozone (O₃).

Recently, a new source for N₂O has been proposed by Prasad [2,32] based on the reaction of excited ozone with nitrogen, given by reaction (3.6). Ozone is a known product which is formed efficiently by radiolysis of oxygen [13,33-35] through the reaction of oxygen atoms (O(1D)) with oxygen. The symbol O₃°° in reaction (3.6) has been used to denote that only a specific excited state of ozone may react with nitrogen to give N₂O. This metastable precursor of ozone carries enough energy to react with nitrogen to form nitrous oxide and the existence of these metastable species during radiation has been shown by several authors [36,37]. Recently, some experimental evidence for this reaction has been given [38]. Reaction (3.6) exhibits all the characteristics to explain the present results. Excited O₃°° species are formed by the reaction of oxygen atoms with the oxygen pool containing O₂ and ¹⁵OO. This explains the mentioned oxygen dependency of the [¹⁵O]-N₂O yield, since the oxygen pool is reduced which in turn reduces oxygen atom formation or the amount of O₃ which can be formed from O₂. The oxygen atoms needed for the formation of O₃°° are produced by the radiolysis of O₂. The direct reaction of hot-atoms with O₂ to form O₃°° probably does not occur because of the high thermal energy of such atoms. The N₂O formation depends on the amount of radiolytic oxygen atoms which can be produced by the amount of O₂ which can react to O₃°°. These two factors are both dependent on the oxygen concentration in the target gas. Since the oxygen concentration is very low it limits the formation of N₂O, explaining the plateau in N₂O formation as shown in figure 3.5. The linear rise in the yield of N₂¹⁵O with increasing beam current, shown in figure 3.5, occurs because the amount of ¹⁵OO in the oxygen pool increases. The present results are thus a further indication that reaction (3.6) is a major pathway for the production of N₂O. These results are not restricted to the irradiation with deuterons but rather display the reactions taking place during radiation, since N₂O was also produced when protons were used.

The specific activity (Sₐ) has been shown to be dependent on the adsorption time. The decrease of the specific activity with increasing adsorption time is due to the decay of N₂¹⁵O. This decay causes the adsorbed amount of N₂¹⁵O to follow the trend given by equation (3.1) and as shown in figure 3.2. As a result the increase in the adsorbed
amount of \( N_2^{15}O \) reduces with increasing adsorption time, whereas the amount of non-labeled adsorbed \( N_2O \) which is adsorbed is expected to increase linearly with time. A linear increase is expected because all the \( N_2O \) in the target effluent is adsorbed and this amount is constant. The influence of the adsorption time on the specific activity can be described by the following equation:

\[
S_a = \left[ \frac{N_2^{15}O}{N_2O} \right] = \frac{R(1 - e^{-\lambda t})}{C_{N_2O}t}
\]

(3.7)

Where \( C_{N_2O} \) is the concentration of \( N_2O \) in the target effluent. The data from figure 3.4 were fitted with equation (3.7) using the ratio between \( R \) and \( C_{N_2O} \) as a fitting parameter. As can be seen, the solid line in figure 3.4 describes the found decrease in specific activity.

The specific activity \( S_{a,\text{effluent}} \) of \( N_2^{15}O \) in the target effluent can be found from the limit of equation (3.7) as the adsorption time \( t \) reaches zero, which is equal to:

\[
\lim_{t \to 0} S_a = \frac{\lambda R}{C_{N_2O}} = S_{a,\text{effluent}}
\]

(3.8)

Equation (3.8) is only valid when all the \( [^{15}O]-N_2O \) present in the target effluent is adsorbed, which is most likely when mordenite is used as adsorbent. In this case the value for \( R \) gives the adsorbed amount of \( N_2^{15}O \). The value for \( S_{a,\text{effluent}} \) can be used to compare the current method with literature values. The present production method yields a 50-fold increase in the specific activity of \( [^{15}O]-N_2O \) as compared to that of Diksic et al. [1]. This is a very large difference because the value given by these authors has probably been obtained at much larger beam current, viz. 50 versus 0.5 \( \mu \)A. For a reliable comparison the adsorption time experiments should be performed at higher beam currents, however, this is not possible with the current setup. Given the linear increase of the \( N_2^{15}O \) activity with increasing current it is expected that a much higher (\( 10^4 \) times) specific activity can be reached. The specified value (6.7\( \times 10^{13} \) Bq/mol) for the specific activity of \( [^{15}O]-N_2O \) in the target effluent is of course only a theoretical value and can not be realized experimentally. However, since the current method obtains \( [^{15}O]-N_2O \) in a small gas volume there is no need for further collection. Collection will also reduce the specific activity when using the preparation method given by Diksic et al..

The linear increase of the \( N_2^{15}O \) activity with increasing current was not expected, since Clark and Buckingham [10] reported a decrease with increasing beam current. This discrepancy may be caused by an higher \( N_2O \) radiolysis rate due to the higher oxygen concentration (4%) used in their experiments. It is known that excited oxygen and ozone are possible sinks for \( N_2O \) [2,32,39] and an increased amount of these species is expected at higher oxygen concentrations. For example \( N_2O \) may react with excited \( O_2 \) to give \( NO_2 \). This route might be a possible explanation for the formation of \( NO_2 \) in the target during deuteron irradiation. Other pathways for \( NO_2 \) formation usually involve \( NO \) and require higher concentrations of oxygen and ozone. The \( NO \) needed for this reaction is formed by the reaction of nitrogen atoms with oxygen. Since neither \( NO \) nor
N$^{15}$O were observed, which both could be detected and adsorbed on zeolites, it is not likely that NO$_2$ is formed via this reaction sequence. The precursor NO can be observed when the oxygen and ozone concentrations are low [13,25,34].

5 CONCLUSION

The selective adsorption of [$^{15}$O]-N$_2$O on zeolitic adsorbents allows much higher specific activity (10$^2$-10$^4$ fold increase) and radiochemical purity (>99.95%) to be obtained than with the methods used at present. The adsorption method presented here also concentrates the tracer so that it is available as a pulse, which is an ultimate requirement in PEP studies. Such a method has not been previously reported. The formation of N$_2^{15}$O and N$_2$O seems to occur via an identical pathway which does not involve any $^{15}$O hot-atom reactions with nitrogen to give N$_2^{15}$O. Upon irradiation an $^{15}$O containing oxygen (O$_2$) pool is formed in the target. This pool can react with oxygen atoms, produced by radiolysis of oxygen, to form an excited form of ozone. This ozone can further react with nitrogen to yield either N$_2^{15}$O or N$_2$O depending on the presence of a labeled oxygen atom in the oxygen precursor. The very low concentration of O$_2$ in the target gas limits the formation of N$_2$O. This occurs because the O$_2$ concentration influences both the amount of radiolytic oxygen atoms produced and the amount of O$_2$ which can react to O$_3^{15}$O.

6 SYMBOLS AND ABBREVIATIONS

- $A_{ads}$ amount of adsorbed activity
- Bq Becquerel (amount of radioactive material that undergoes exactly one disintegration per second)
- $C_{N_2O}$ amount of adsorbed N$_2$O
- d deuteron
- $d_p$ particle diameter
- GC gas chromatography
- n neutron
- Nal sodium iodine scintillation detector
- Nal$_{ads}$ Nal detector monitoring the adsorber (see figure 3.1)
- Nal$_{loop}$ Nal detector monitoring the sample loop (see figure 3.1)
- $^{14}$N(d,n)$^{15}$O $^{14}$N + d $\rightarrow$ $^{15}$O + n
- O$_3^{15}$O excited form of O$_3$ which reacts with N$_2$ to yield N$_2$O
- [$^{15}$O]-N$_2$O mixture of N$_2$O and N$_2^{15}$O
- p proton
- $S_a$ specific activity of N$_2^{15}$O
- $S_{a,effluent}$ specific activity of N$_2^{15}$O in the target effluent
- soda lime NaOH/Ca(OH)$_2$
- R amount of [$^{15}$O]-N$_2$O which can be adsorbed
- t adsorption time
**PRODUCTION OF OXYGEN-15 LABELED NITROUS OXIDE**

TCD  thermal conductivity detector  
V1, V2  valves  
\( \alpha \)  helium nucleus  
\( \lambda_0 \)  decay constant for \(^{15}\)O (0.34 min)

7 **REFERENCES**


MATHEMATICAL TREATMENT OF TRANSIENT KINETIC DATA

COMBINATION OF PARAMETER ESTIMATION WITH SOLVING THE RELATED PARTIAL DIFFERENTIAL EQUATIONS

ABSTRACT

To exploit the full potential of transient techniques modeling is required such that reaction rate constants of elementary reaction steps may be obtained. Such a model is characterized by a set of coupled partial differential equations (PDEs). The numerical method of lines has been employed here to solve the PDEs. The principle of this method is approximation of spatial derivatives reducing the PDEs to a set of coupled ordinary differential equations (ODEs). Several robust numerical methods for solving coupled ODEs are discussed. The unknown reaction parameters are estimated by coupling the PDE solving method to a method which minimizes the difference between the model and the experimental data. Several numerical minimization methods are discussed. The mathematical treatment of PEP profiles also involves solving the steady-state equations, which are given by a system of differential and algebraic equations (DAE). The general applicable DAE solver DASSL is described.
CHAPTER 4

1 INTRODUCTION

In the last decades the use of transient techniques to obtain mechanistic and kinetic information about reactions has become increasingly popular. In kinetic studies the reactor is usually operated under steady-state conditions. In that case the catalyst is considered to be a black box, and only the entrance and exit concentrations are examined. Data obtained in this way only contain averaged information about the overall process. Although the kinetic behavior of the overall reaction reflects the mechanism of the reaction, it can not be used to unambiguously deduce the elementary reaction steps, since different sequences of elementary steps may give the same kinetic behavior [1-3]. In contrast to steady-state experiments the application of transient techniques does give the opportunity to obtain such information.

The concept of transient technique in heterogeneous catalysis has been laid down by Tamaru [4], and numerous reviews [1,5,6] have been devoted to the subject since. The technique consists of introducing a perturbation of one or more experimental variables such as gas concentration, reaction temperature, or pressure. The system responds to this perturbation by relaxing into a new steady-state. This dynamic response of the system allows the determination of time constants of surface processes and hence the concentration of intermediate species can be measured.

A relatively new transient technique which can be used to study catalytic reactions is positron emission profiling (PEP). PEP [7-10] allows monitoring of surface and gas phase concentrations in both time and space. The technique consists of the following. A small amount of a positron emitting species (\(^{11}\)CO, \(N_2^{15}O,^{18}NO\)) is injected into the gas stream to the catalyst which is operating under steady-state conditions. The isotope used decays by emitting a positron which is the anti-matter counterpart of an electron. After its emission the positron annihilates with an electron, thereby producing two photons with an energy of 511 keV. The photons are emitted under an angle of nearly 180° with respect to each other. The energy of the two photons is high enough to penetrate the reactor tube and the surrounding oven to reach the two detector banks on opposite sides of the oven. Both detector banks contain nine independent scintillation crystals (BGO) each connected to a photomultiplier tube allowing detection of the 511 keV photons. Because the photons are detected coincidentally and energy sensitive, the position of the annihilation event can be reconstructed. The position can be deduced from the intersection of the line between the two crystals that detected a photon and the central axial axis of the reactor. The nine detection crystals make it possible to record the response at 17 unique reconstruction positions along the catalyst bed.

Transient techniques can be used to acquire both qualitative and quantitative information about the reaction. Qualitative information is used to obtain mechanistic information about the reaction. For example [11,12] with the temporal analysis of products (TAP) reactor [13] or Multitrack [14] it is possible to detect short-lived reaction intermediates that desorb from the catalyst surface into the gas phase. With this information the various elementary steps of the reaction may be determined. Another possibility to determine the characteristics of the reaction mechanism has been put
forward by Kobayashi and Kobayashi [6]. This method consists of introducing a concentration step to the system and analyzing the response curve. The authors showed that the shape of the response curve is related to the reaction mechanism.

Two types of quantitative information can be obtained from transient experiments. The first is quantifying the adsorbed amount of a certain species on the catalyst surface [6,11,12,15]. Such information can be easily obtained by integration of the response signals. In the case of PEP, if a species is retained by the catalyst then the adsorbed amount of this species can be determined from integration of the response at all the reconstruction positions.

The second type of quantitative information is more challenging and involves the determination of reaction rate constants for the elementary reaction steps, and the number of active sites. This requires setting up a model which describes the transient response of a system. In the simplest case the model only accounts for the time dependency. The model describes the concentration at the outlet of the reactor as a function of time. Thus, in the mass balance the time dependent term (accumulation term) is not disregarded as is the case in the steady-state approach. The latter leads to a system of ordinary differential equations (ODEs) [16,17], in which the number of ODEs is determined by the number of species. Such a system can easily be solved by existing ODE solving software packages.

With PEP information about the reactant can be obtained at several positions in the catalyst bed. It is not possible to describe such a system with ODEs. In contrast, partial differential equations (PDEs) can describe the concentration profile over the reactor as a function of time [18-23]. Several factors can be taken into account in this case such as convection, dispersion, and catalytic conversion. As with steady-state analysis different criteria have to be met to assure the absence of extra- and intraparticle and heat transport since they are usually not considered in the model. Dekker [20] has developed these criteria for transient experiments. The transient criteria have been related to the steady-state criteria since these are easily examined.

An additional issue which has to be dealt with when describing the results of PEP experiments is that the catalyst is operated under steady-state conditions when the transient is introduced. This requires solving the steady-state equations which describe the reaction taking place. These equations are related to the change in the concentration of gas phase and surface species. The gas phase equations contain a convection term to account for the movement of species in the axial direction, thereby introducing a differential term. In contrast, the equations describing the surface reactions do not contain this term. The overall system therefore contains both differential and algebraic equations which need to be solved.

This overview will focus on the extraction of kinetic parameters from a PDE model which describes the reactions taking place. This involves solving the PDE followed by estimation of the kinetic parameters such that the model describes the course of the experimental data. Therefore, a method will be outlined with which the PDE may be solved. The method of lines [24] has been applied here to give a numerical solution of the PDE. The various kinetic parameters in the model may be estimated by minimizing
the difference (sum of squares) between the model and the experimental data through variation of the parameters. Several techniques have been developed to accomplish this, but only the most frequently used methods will be discussed here. At the end, an example will be given showing the adequacy of the described numerical procedure by a numerical simulation experiment.

In addition, the mathematical treatment of PEP data will be described. As mentioned this involves solving a system of differential and algebraic equations (DAE) in combination with the PDE. These DAEs can not be solved with standard ODE solvers, therefore, the numerical method for solving such a system will be given. The overall process of solving the DAE/PDE model combined with parameter estimation, essential for describing PEP experiments, will also be presented.

2 SOLVING PARTIAL DIFFERENTIAL EQUATION

2.1 Partial differential equations and the numerical method of lines

As mentioned in the introduction, transient experiments are best expressed by a model that describes the problem at hand in both time and space. The mathematical expression of such a problem is given by one or more PDEs, depending on the number of components which are followed. The general notation of a spatially one dimensional PDE which is first order in time, is given by:

$$\frac{\partial C_i}{\partial t} = f_i(z,t) \frac{\partial^2 C_i}{\partial z^2} + f_2(z,t) \frac{\partial C_i}{\partial z} + f_3(z,t)f(C_i) + f_4(z,t) \tag{4.1}$$

where,

- $C_i$ concentration of component $i$
- $f(C_i)$ function describing the behavior of $C_i$
- $t$ variable in time
- $z$ variable in space
- $f_i(z,t)$ constants or functions of time and/or position

Usually, more than one component is included in the model. In that case a PDE is defined for every component $i$, leading to a system of PDEs which needs to be solved simultaneously. Equation (4.1) is the basic PDE model for the problem of finding the concentration as a function of time and position, however, it is not a complete mathematical model. In addition to the PDE, auxiliary conditions need to be specified to complete the model. These conditions are required for each independent variable. The number of conditions for each independent variable equals the order of the highest-order derivative for this variable. The auxiliary condition for time ($t$) is usually specified at $t=0$, the initial condition. For the other independent variables these conditions are specified at the first and/or the last position of the spatial direction, the boundary conditions.

Boundary conditions of various types are available. If the value of the dependent
variable, $C$ in this case, is predetermined at the boundary, the condition is called a Dirichlet boundary condition. The other type is known as a Neumann boundary condition. In this case the derivative of the dependent variable has a specified value at the boundary, for example:

$$\frac{\partial C_i(0,t)}{\partial t} = 0$$  \hspace{1cm} (4.2)

It is also possible to have a combination of Dirichlet and Neumann boundary conditions. The PDE and the initial and boundary conditions form the complete PDE model of the problem. A simple PDE model may be solved analytically, but most systems are too complex to be solved by that approach. Therefore, numerical methods are needed to solve these systems.

Several methods [23-25] have been developed for numerically solving systems of PDEs. All these methods are based on some kind of numerical approximation of the partial derivatives. Basically, there are two types of methods for the solution of PDEs. The first type, also known as global methods [25], consists of approximating both the spatial and time derivatives. The other method is known as the method of lines, the origin of this name will be explained below. The method of lines (MOL) is a relatively simple numerical technique to convert PDEs into a system of ordinary differential equations (ODEs). This is done by approximating all the (partial) derivatives but one. Usually, the derivative with respect to time remains.

A well-known method to approximate derivatives is by finite differences. In this method the spatial direction, for example, is divided into a set of grid points where the derivatives are to be approximated. This reduces the right hand side of equation (4.1) to a function without derivatives, which specifies the change of the concentration in time at every grid point.

Thus, by approximating the spatial derivatives of (4.1) by finite differences, equation (4.1) is reduced to a system of ODEs given by:

$$\frac{dC_{i,j}}{dt} = f_j(C_{i1},...,C_{i,N},t), \hspace{1cm} j = 1,...,N$$  \hspace{1cm} (4.3)

where,

$C_{i,j}$ concentration of component $i$ at grid point $j$

$j$ grid point number

$N$ total number of grid points

The resulting system of coupled ODEs can then be integrated simultaneously with a numerical ODE solver. Since there are several robust ODE solvers readily available the user is only concerned with the approximation of the spatial derivatives. Thus, in the MOL the spatial derivatives are approximated reducing the PDE to a system of initial value ODEs at every grid point. These ODEs are then solved simultaneously in time which results in solution 'lines' at every grid point, as shown in figure 4.1, this immediately explains the origin of the name.
2.2 Finite difference approximations

As mentioned, one of the essential steps in the numerical MOL integration of PDEs is the calculation of the spatial derivatives. There are two methods to approximate the spatial derivatives, the first is by finite difference, as mentioned above, and the other is by finite elements. In the latter method an approximation of the derivatives is given in terms of trial solutions, which are a linear combination of basis functions. The basis functions are piecewise continuous and linearly independent. Many examples of this method have been given by Hinton and Owen [26]. The finite difference method which is very easy to implement will be discussed here.

Consider a grid of equally spaced points in z where the value of the concentration of a component, \( c(z) \), is known at every grid point. The first derivative of \( c(z) \) at grid point \( z_j \) can be approximated as follows. A Taylor series for the value \( c(z_{j+1}) \) can be given by:

\[
c(z_{j+1}) = c(z_j) + \frac{dc(z_j)}{dz} \Delta z + \frac{1}{2!} \frac{d^2c(z_j)}{dz^2} (\Delta z)^2 + \ldots
\]  

(4.4)

Where, \( \Delta z \) is the grid point spacing defined as \( \Delta z = z_{j+1} - z_j \). Similarly a Taylor series for \( c(z_{j-1}) \) can be given by:

\[
c(z_{j-1}) = c(z_j) + \frac{dc(z_j)}{dz} (-\Delta z) + \frac{1}{2!} \frac{d^2c(z_j)}{dz^2} (-\Delta z)^2 + \ldots
\]  

(4.5)

with \( -\Delta z = z_{j-1} - z_j \). Since the first derivative of \( c(z) \) with respect to \( z \) is present in both equations, an expression for this derivative can be obtained by subtracting (4.4) and (4.5) and rewriting:
\[ \frac{dc(z_j)}{dz} = \frac{c(z_{j+1}) - c(z_{j-1})}{2\Delta z} \]  \hspace{1cm} (4.6)

Equation (4.6) gives the well-known second-order central difference approximation for the first derivative of \( c(z) \) at \( z_j \). It is called central since the dependent variable is evaluated at points \( z_{j1} \) and \( z_{j+1} \) located at equal distances on either side of point \( z_j \) where the first order derivative is to be evaluated. However, at the boundaries \( (j=1 \) and \( j=N) \) the values of \( c(z) \) at fictitious points \( (j=0 \) and \( j=N+1) \) have to be known. To avoid this problem in an application independent way it is necessary to derive different approximations for the boundaries, that only use real points. This is done in a similar way as above by writing a Taylor series for \( c(z_j) \) and \( c(z_{j+1}) \). This results in the following equations for the derivatives at the boundaries:

at \( j=1 \)
\[ \frac{dc(z_1)}{dz} = \frac{-3c(z_1) + 4c(z_2) - c(z_3)}{2\Delta z} \]  \hspace{1cm} (4.7)

at \( j=N \)
\[ \frac{dc(z_N)}{dz} = \frac{3c(z_N) - 4c(z_{N-1}) + c(z_{N-2})}{2\Delta z} \]  \hspace{1cm} (4.8)

Equation (4.8) is obtained by writing a Taylor series for \( c(z_{N+1}) \) and \( c(z_{N-2}) \). Equations (4.6), (4.7) and (4.8) form a set of equations with which the first derivative at all the grid points can be computed. Although this set has limited accuracy it is usually sufficient as a starting point since it does not require a lot of computation. There are however more accurate differentiation formulas available. These formulas use more points in the approximation, e.g., five points instead of three, a vast amount of these formulas have been reported by Fomberg [27]. Second order differentials can be approximated by sequential use of the above mentioned methods for the first derivative. The following finite difference approximation for the second derivative is obtained for an inner grid point when equation (4.6) is applied sequentially:

\[ \frac{d^2c(z_j)}{dz^2} = \frac{dc(z_{j+1})}{dz} - \frac{dc(z_{j-1})}{dz} = \frac{c(z_{j+2}) - c(z_j) - c(z_j) + c(z_{j-2})}{2\Delta z} = \]  \hspace{1cm} (4.9)

\[ \frac{c(z_{j+2}) - 2c(z_j) + c(z_{j+2})}{(2\Delta z)^2} \]

The spatial derivatives in the PDE (4.1) can be replaced by the finite difference approximations developed above. This leads to the following equation for the concentration of component \( i \) at an inner grid point \( z_j \):

\[ \frac{dc_{i,j}}{dt} = \alpha c(z_{j+2}) - \beta c(z_{j-1}) + \gamma c(z_j) + \beta c(z_{j+1}) + 2\alpha c(z_{j+2}) + f_i(z_j, t) \]

\[ j = 1 \ldots N \]  \hspace{1cm} (4.10)
where,

\[
\alpha = \frac{f_1(z_j, t)}{(2\Delta z)^2}, \quad \beta = \frac{f_2(z_j, t)}{2\Delta z}, \quad \gamma = \frac{f_3(z_j, t)}{(2\Delta z)^2} + f_3(z_j, t)
\]

Equation (4.10) shows that the PDE is reduced to a system of N ODEs only containing the concentration at various grid points. It is also evident that the solution at every grid point can only be obtained by simultaneously solving the attained system of ODEs, since a single ODE depends on the concentration at several other grid points.

It should be mentioned that there are also finite difference solutions for problems which contain a steep front that propagates through a tube. This is often the case when dealing with transient experiments in heterogeneous catalysis since the response of a system to a pulse or step is evaluated in a flow reactor. It has been shown [24,28] that the convection term can be best approximated by a biased up- or downwind approximation depending on the direction of the flow in the system (upwind for a positive direction of the flow). These approximations use a different number of grid points to the left and right of the evaluated grid point.

The finite difference formulas given above only hold for equispaced grids (i.e. grids with a constant \(\Delta z\)). There are two main situations for which the use of non-equispaced grids may be desirable. The first arises when the solution changes rapidly in space (e.g. moving front). In this case more grid points are needed to resolve the rapidly changing solution. Grid refinement throughout the complete solution domain increases the computational effort, therefore, the grid density should only be high where it is needed. The second reason for refinement is at the boundaries to compensate for the fact that one-sided approximations are less accurate than centered ones. Fornberg [27] has devised an algorithm for the generation of finite difference formulas for any user defined non-equispaced grid.

2.3 Solving initial value ODEs

The second step in solving the PDE is the integration of the ODE system. Since the initial state \((t=0)\) is assumed to be known, only ODE solvers for initial value problems will be discussed here. As mentioned, there are several methods available [29]. Before referring to a couple of these methods the different Euler methods will be explained, since all of the methods are based on these methods.

The simplest numerical method is the Euler method. The method is based on a truncated Taylor series:

\[
\frac{dy_n}{dt} = \frac{y_{n+1} - y_n}{h}
\]

(4.11)

Where, \(y_n = C(t), \ y_{n+1} = C(t+h), \) and \(h\) is the step in \(t\) (step size). Using this approximation for the derivative, the left-hand side of (4.3) can be replaced by the right-hand side of (4.11) when only a single ODE is considered (an ODE at a grid point for one component). Although the formulas derived here are based on a single ODE, they can
also be used for a system of ODEs. For a system of ODEs the scalars (e.g. $y_n, y_{n+1}$) in the formulas are replaced by matrices. When evaluating the right-hand side of (4.3) at the start of the step the explicit Euler method is obtained:

$$y_{n+1} = y_n + hf(y_n)$$  \hspace{1cm} (4.12)

The method is explicit because $y_{n+1}$ is computed directly knowing only the value of $y$ at the start of the step. A FORTRAN code which implements this method is EULEX [30].

On the other hand, the right-hand side of (4.3) can also be evaluated at the end of the step, at $y_{n+1}$, which gives the implicit Euler method:

$$y_{n+1} = y_n + hf(y_{n+1})$$  \hspace{1cm} (4.13)

For this method an (in general non-linear) equation has to be solved for each solution step. Therefore, there has to be an important reason when opting for an implicit method. This reason will be given in a moment.

A well-known family of explicit one step methods are the Runge-Kutta methods [31] which are based on the explicit Euler method. The method explained here (4.14) is known as the classical fourth-order Runge-Kutta formula:

$$\begin{align*}
  k_1 &= hf(t_n, y_n) \\
  k_2 &= hf(t_n + \frac{h}{2}, y_n + \frac{k_1}{2}) \\
  k_3 &= hf(t_n + \frac{h}{2}, y_n + \frac{k_2}{2}) \\
  k_4 &= hf(t_n + h, y_n + k_3) \\
  y_{n+1} &= y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + O(h^5)
\end{align*}$$  \hspace{1cm} (4.14)

Where, $O(h^5)$ is the truncation error of this method.

The Runge-Kutta methods constitute a clever and sensible idea. The unique solution of a well-posed initial value problem can be thought of as a single integral curve, however, due to truncation ($O(h^2)$) and round-off error the numerical solution is going to wander off that integral curve. The numerical solution is going to be affected by the behavior of these neighboring curves. Runge-Kutta methods try to gather information about these curves by evaluating the derivative, using Euler steps, at trial midpoints ($h/2$). The final step is yet another Euler step (last equation of (4.14)) which uses the weighed mean of the samples $k_1...k_4$. Thus, a Runge-Kutta method sends out feelers into the solution space to gather samples of the derivative, before deciding in which direction to take an Euler step.

There are several other methods which are based on these formulas. The most popular method used is RKF45 (FORTRAN code), a method developed by Fehlberg [32]. This method belongs to the class of embedded Runge-Kutta methods. The idea behind these methods is to derive Runge-Kutta methods of orders $p$ and $p+1$ (here $p=4$), which share the same set of vectors $(k_i)$. It should be mentioned that only one extra function

[61]
evaluation is needed for the calculation of the \( p+1 \) order. The difference between the values for \( y_{n+1} \) generated by these two methods is then used as an estimate of the local truncation error. In turn, this information is used to control the step size \((h)\) since the error term is determined by the step size. Thus, by adaptive step size control a combination of high accuracy of the solution and calculation speed can be maintained. Another explicit method which produces high accuracy solutions with minimal computational effort is the Bulirsch-Stoer method [33]. The basic idea behind this method is that several values for \( y_{n+1} \) are determined using different step sizes. Hence, a different number of steps are taken to calculate the different solutions for \( y_{n+1} \). These solutions are extrapolated to an answer that is supposed to correspond to infinitely fine sub steps (zero step size). A drawback of this method is that it can not be used for differential equations containing non-smooth functions. For example, a differential equation whose right-hand side is evaluated by table look-up and interpolation (see example 1).

A major drawback of methods based on the explicit Euler method is that they are not capable of solving stiff systems. A system of ODEs is called stiff if some components of the solution decay much more rapidly than others. For a linear system it can be shown that the separation in the eigenvalues of the coefficient matrix of the system determines the stiffness. However, for non-linear systems there is no simple relationship, since the components of the coefficient matrix depend on \((y_n,t)\). Therefore the system can vary between stiff and non-stiff. A more detailed description of stiffness is given by Lambert [31]. If the stiffness of the system is not known beforehand it can be determined with the FORTRAN program STIFFTEST [31].

A class of implicit linear \( k \)-step methods capable of solving stiff systems are the backward differentiation formulas (BDF) [31,34-36]. The simplest one step BDF method is the implicit Euler method (4.13) which consists of replacing the derivative by a backward difference. The resulting non-linear equation for \( y_{n+1} \) at each time step is usually solved by Newton’s method. The \( k \)-step (constant step size) BDF consists of replacing the right hand side of (4.11) by the derivative of the polynomial which interpolates the computed solution at \( k+1 \) points \( y_{n+1}, y_n, \ldots, y_{n-k+1} \), evaluated at \( y_{n+1} \). This yields:

\[
\frac{dy_{n+1}}{dt} = \frac{\rho y_{n+1}}{h}
\]

(4.15)

where,

\[
\rho y_{n+1} = \sum_{i=0}^{k} \alpha_i y_{n-i+1}
\]

polynomial

\[
\alpha_i, i = 0,1,\ldots,k
\]

coefficients of the BDF method

The values of \( y_n,\ldots,y_{n-k+1} \), are known and the value at \( y_{n+1} \) is to be determined. The preceding equation can be generalized to give an equation which gives the value at \( y_{n+1} \):
\[ y_{n+1} = \sum_{i=0}^{k-1} \alpha_i y_{n-i} + h\beta_k f(y_{n+1}) \]  \hspace{1cm} (4.16)

Where, \( \alpha_i \) and \( \beta_k \) are the BDF coefficients. The \( k \)-step BDF method is stable for ODEs for \( k<7 \). It turns out that \( k \) is also the order of the method. The BDF coefficients which give a stable method have been given by Gear [35,37] and Knöckler [34]. This results in the following formulas for \( k=1, \ldots, 6 \):

\[
\begin{align*}
  k=1: & \quad y_{n+1} = y_n + h f(y_{n+1}) \quad \text{(implicit Euler)} \\
  k=2: & \quad y_{n+1} = \frac{4}{3} y_n - \frac{1}{3} y_{n-1} + \frac{2}{3} h f(y_{n+1}) \\
  k=3: & \quad y_{n+1} = \frac{18}{11} y_n - \frac{9}{11} y_{n-1} + \frac{6}{11} y_{n-2} + \frac{6}{11} h f(y_{n+1}) \\
  k=4: & \quad y_{n+1} = \frac{48}{25} y_n - \frac{36}{25} y_{n-1} + \frac{16}{25} y_{n-2} - \frac{3}{25} y_{n-3} + \frac{12}{25} h f(y_{n+1}) \\
  k=5: & \quad y_{n+1} = \frac{300}{137} y_n - \frac{300}{137} y_{n-1} + \frac{200}{137} y_{n-2} - \frac{75}{137} y_{n-3} + \frac{12}{137} y_{n-4} + \frac{60}{137} h f(y_{n+1}) \\
  k=6: & \quad y_{n+1} = \frac{360}{147} y_n - \frac{450}{147} y_{n-1} + \frac{400}{147} y_{n-2} - \frac{225}{147} y_{n-3} + \frac{72}{147} y_{n-4} - \frac{10}{147} y_{n-5} + \frac{60}{147} h f(y_{n+1})
\end{align*}
\]

The sixth order BDF is an accurate and stable method capable of solving stiff systems. These properties are achieved by approximating the past values of \( y_n, y_{n-1}, \ldots, y_{n-5} \), by a sixth order polynomial and using an implicit derivative term. However, at the beginning of the solution only the initial condition is available so the computation must be started with the first order formula. Then, as the calculation progresses, the higher order BDFs can be used. Thus, the BDF method can be used for both stiff and non-stiff systems.

FORTRAN codes which use an implementation of the BDF method are LSODE [38,39], LSODES [40], and DASSL [41].

As mentioned, every step also involves the solution of a non-linear equation. When more than one ODE is evaluated a system of non-linear equations needs to be solved. This is done by using a modified Newton iteration. Newton’s method requires the calculation of a Jacobian matrix:

\[
J = \begin{bmatrix}
\frac{\partial f_1}{\partial y_1} & \cdots & \frac{\partial f_1}{\partial y_n} \\
\vdots & \ddots & \vdots \\
\frac{\partial f_n}{\partial y_1} & \cdots & \frac{\partial f_n}{\partial y_n}
\end{bmatrix}
\]  \hspace{1cm} (4.18)
The Jacobian is a matrix containing the partial derivative of each function on the right-hand side of equation (4.3) with respect to every variable in the system (e.g. the concentration of all components in all grid points). In the MOL the Jacobian is determined by the ODEs at every grid point, more specific, the entries in the Jacobian depend on the spatial approximation method used. The Jacobian can be specified by the user in the above mentioned codes, but it is a lot easier to let the code approximate the Jacobian numerically. Usually the Jacobian contains a large amount of zero elements and in that case the matrix is called sparse. A code which takes the sparsity into account is LSODES. This means that not every entry in the Jacobian needs to be determined, and it also facilitates the Newton solution. As a result, the Jacobian matrix is smaller (requires less memory) and less computation time is needed to solve the system.

It would seem from the previous discussion that the BDF method (LSODE(S), DASSL) is the best choice for every ODE system and that there is no need for explicit Runge-Kutta codes. However, problems containing a large amount of ODEs have a large Jacobian which needs to be evaluated. Since the Jacobian is usually evaluated numerically many function evaluations are needed for its calculation. In this case, Runge-Kutta codes which do not require a Jacobian matrix are a possible solution as long as non-stiff systems are considered. In addition, Runge-Kutta methods do not have high memory requirements.

This section is ended with some practical information for the reader who wishes to implement the above mentioned technique to solve PDEs. Most of the routines are readily available in the public domain. Well-known libraries which contain most of the FORTRAN routines (EULEX, RKF45, LSODE(S), DASSL) are maintained by Netlib and Elib. Netlib and Elib have a web site on Internet which can be reached with a web browser at URL: www.netlib.org or elib.zib-berlin.de respectively. A commercial FORTRAN package is DSS/2, differential system simulator, version 2, which contains most of the above mentioned routines, and is an easy to use implementation of the method of lines.

3 Parameter estimation

3.1 Non-linear least squares

A model which is supposed to describe the behavior of a certain reaction usually contains a number of parameters of which the values are not known beforehand. In transient experiments the model describes the behavior of the concentration of one or more components in time and space. Such a PDE model may be solved with the techniques described above, but determination of the unknown parameters (e.g. reaction rate constants, number of active sites) still remains. There exist several techniques with which these unknown parameters may be determined, such as the method of moments, and the method of maximum likelihood [42]. The most widely used estimation technique is the method of least squares which is a special case of the maximum likelihood method. This method will be discussed here.
The non-linear least squares method consists of minimizing the difference (residual) between the data predicted by the model \(C^{\text{cal}}\) and the experimental data \(C^{\text{obs}}\). This difference is called the sum of squares of residuals \(\text{SSR}\) and is given by:

\[
\text{SSR} = \sum_{n=1}^{N_c} \sum_{m=1}^{N_d} w_{n,m} (C_{n,m}^{\text{obs}} - C_{n,m}^{\text{cal}})^2
\]

(4.19)

where,

- \(n\) component number
- \(m\) observation number
- \(N_c\) total number of components
- \(N_d\) total number of observations
- \(w_{n,m}\) weighing factor of the \(m\)th observation of component \(n\)

Here, the \(\text{SSR}\) is determined for all the components which need to be analyzed simultaneously, and it is assumed that the behavior of the concentration needs to be described. The weighing factor may be used when not all data have the same significance. Since this is usually not the case or unknown the weighing factor is normally taken as one for every observation. The least squares method [43,44] is based on the following assumptions for the error \(\epsilon\) of the observations [42]: (1) the mean of \(\epsilon\) is zero, (2) the probability distribution of \(\epsilon\) is normal, (3) the variance of the probability distribution of \(\epsilon\) is constant, and (4) the errors of any two observations are independent. There are also methods that take an error for the independent variable into account, such a method is Orthogonal Distance Regression (ODRPACK) [45,46].

3.2 Minimization methods

Minimization of the \(\text{SSR}\) is achieved by varying the different parameters until a minimum is encountered. Figure 4.2 shows a flowchart of the scheme used to minimize the \(\text{SSR}\) when a PDE model is concerned. The heart of the minimization is a minimization routine. Again, there are several methods for finding the minimum of a function (\(\text{SSR}\)) [43,47-49]. All these methods are iterative in nature. The procedure is started with a given point \(\phi_i\), the initial guess, where \(\phi_i\) is a vector that contains the initial values of the parameters to be estimated. The procedure proceeds to generate a sequence of points \(\phi_2, \phi_3, \ldots\) which is supposed to converge to the point \(\phi^*\) at which the \(\text{SSR}\) is at its minimum value (\(\text{SSR}^*\)). In practice, the sequence is terminated after a finite number \(N\) of iterations and the value of \(\phi_N\) is then accepted as an approximation for \(\phi^*\). A criterion is needed to determine at which point the minimization sequence may be terminated and convergence has been reached. The available convergence criteria all assume that the change in some quantity is less than a predetermined tolerance. The four most used quantities are: (1) the maximum number of iterations, (2) change in the parameter vector \((\phi)\), (3) change in the \(\text{SSR}\), and (4) the norm of the gradient vector. The minimization methods can be divided into two categories, the direct search methods, and indirect search methods. An example of both categories will be given here.
The direct search methods only use the function value in determining the search direction. The most well-known algorithm of this class is the Simplex method implemented by Nelder and Mead [50]. This method, first proposed by Spendly et al. [51], consists of using a geometric figure (a simplex) to select points at the vertices of the simplex at which the function is to be evaluated. In two dimensions the figure is an equilateral triangle, in three dimensions a tetrahedron, and so on.

In the method of Nelder and Mead the function value at each of the vertices is determined at each iteration. The direction of search is oriented away from the point with the highest function value through the centroid of the simplex. A new point is selected in this reflected direction such that the geometric shape of the original simplex is maintained and the point with the highest function value is deleted. The function value is evaluated at the new point and a new search direction is calculated. If this new search direction is equal to the former a large step is taken in that direction, thereby expanding...
the original simplex. Finally the size of the simplex may also be reduced when a new search direction can not be determined or in order to enclose the minimum. This process of generating new simplexes is repeated until a convergence criterion is satisfied. Another method which should be mentioned here is Powell’s method [52]. Powell’s method has specifically been designed for finding the minimum of a least squares problem. The method locates the minimum by sequential unidimensional searches from the initial point along a set of conjugate directions generated by the method. New search directions are introduced as the search progresses. See Himmelblau [47] for a more detailed description of Powell’s method.

In contrast to the direct search methods given above the indirect search methods use information obtained from the derivative of the SSR to find the minimum. Actually, this class can be subdivided into methods that use the first order derivative, and those that also use the second order derivative. An example of a first order method is the steepest descent method. This method uses the negative of the gradient (first derivative) with a given step size as the search direction. The gradient vector of $SSR(\phi)$ is given by:

$$q_i = \frac{\partial SSR}{\partial \phi_i} \quad (4.20)$$

Where, $q_i$ is the gradient evaluated at $i^{th}$ iterate of $\phi$.

Unfortunately, this method is often very inefficient close to the minimum therefore, requiring a large number of steps before reaching the minimum.

Newton’s method uses the second order Taylor series expansion (quadratic approximation) to approximate the SSR in the vicinity of the minimum where it converges fast. The second order derivative of the SSR, given by the Hessian matrix, yields the correct step size to reach the minimum for parabolic functions. In the least squares case the Hessian may be approximated by the following relation:

$$H = J^T J \quad (4.21)$$

where,

- $J$ Jacobian matrix as defined by equation (4.18)
- $J^T$ transpose of the Jacobian matrix

For the determination of the Jacobian, the functions in (4.9) are represented by the residuals and the derivatives need to be determined for every element of $\phi$. Since the minimum needs to be determined the quadratic approximation is differentiated with respect to each of the parameters of $\phi$ and equated to zero to give:

$$\phi_{i+1} = \phi_i - H_i^{-1} q_i \quad (4.22)$$

where,

- $H_i^{-1}$ inverse of the Hessian matrix
- $\phi_i$ parameter estimates at iteration $i$
- $\phi_{i+1}$ new parameter estimates

Equation (4.22) defines the $i^{th}$ iteration of the Newton method. Note that both the
direction \((q_i)\) and the step size \((H_i^{-1})\) are specified in Newton’s method. A problem with Newton’s method is that it is only efficient close to the minimum. Levenberg [53] and Marquardt [54] devised a method for determining a search direction that lies between the steepest descent \((q_i)\) and the Newton \((-H_i^{-1}q_i)\) direction. The common idea behind these methods is that the Hessian matrix in equation (4.22) is replaced by \(H + \lambda P\). Usually, the identity matrix \((I)\) is used for \(P\) which gives the following expression for \(\phi_{i+1}\):

\[
\phi_{i+1} = \phi_i - (H_i + \lambda I)^{-1}q_i
\]

(4.23)

where,

\[\lambda\] Levenberg and Marquardt scalar

\[I\] identity matrix

For large \(\lambda\) the term \(\lambda I\) dominates \(H\) and the minimization approaches the steepest descent method. On the other hand, when \(\lambda\) is small the method approaches the Newton direction. The difference between the methods of Levenberg and Marquardt lies in the procedure for determining suitable values for \(\lambda\). The method given by Marquardt is the algorithm which is mostly used in computer codes (see Himmelblau [47] for a detailed description of this algorithm).

### 3.3 Interpretation of the estimates

It is not enough to compute the vector \(\phi^*\) and to state that this is the estimated value of the unknown parameters \(\phi\). The reliability and precision of the estimates need to be determined. A parameter is ill-determined if its estimated value is strongly affected by seemingly insignificant variations in the experimental data. Such a situation is characterized by the estimate having a large variance. A useful quantity in this case is the covariance matrix. This matrix can be used to construct the confidence regions and intervals [43,44,46,55].

The covariance matrix contains the covariance of the estimated parameters with respect to each other. The primary diagonal therefore contains the variance of the estimated parameters. From these values the confidence interval may be determined. In the least squares case the covariance matrix can be approximated by the following equation [44]:

\[
V = \sigma^2(J^TJ)^{-1}
\]

(4.24)

where,

\[\sigma^2\] population variance

The Jacobian matrix is evaluated at the estimated value \(\phi^*\). Since the real value of \(\sigma^2\) is usually not known it is estimated by the SSR at its minimum \((\text{SSR}^*)\) divided by its degrees of freedom:
\[ \sigma^2 = s^2 = \frac{SSR^*}{m - p} \] (4.25)

where,
- \( m \) number of observations
- \( p \) number of parameters
- \( s^2 \) variance

Thus, when replacing \( \sigma^2 \) with \( s^2 \) an estimate of \( V \) is obtained:

\[ V = s^2 (J^T J)^{-1} \] (4.26)

The confidence interval can be constructed from the covariance matrix. These intervals for every element \( k \) of the estimated parameter vector \( \phi^* \) are readily determined for a given probability level \( 1 - \alpha \) with the Student's t-distribution [42,43]:

\[ \phi^*(k) - t_{\frac{\alpha}{2}} \sqrt{V_{kk}} \leq \phi^*(k) \leq \phi^*(k) + t_{\frac{\alpha}{2}} \sqrt{V_{kk}} \] (4.27)

where,
- \( \phi^*(k) \) \( k \)th element of \( \phi^* \) (estimated parameter vector)
- \( t_{\frac{\alpha}{2}} \) \( \% \) percentage point of the Student's t-distribution with \( m-p \) degrees of freedom
- \( V_{kk} \) \( k \)th element of the primary diagonal of \( V \)

This section is also ended with some practical information concerning the use of the above mentioned minimization routines. Most of the routines have been implemented in FORTRAN, and can be found at Netlib (Simplex, Levenberg-Marquardt, ODRPACK), and in Numerical Recipes [44] (Powell).

4 Mathematical treatment of positron emission profiles

4.1 Differential algebraic equations and DASSL

PEP belongs to a specific class of transient techniques which are performed under steady-state conditions (steady-state isotopic transient kinetic analysis, SSITKA). This is made possible by the use of radioactive tracers, which are chemically identical to one of the reactants used. In contrast to other transient techniques which introduce some kind of perturbation to evoke a transient response, the isotopic technique does not influence the reaction taking place because the amount of added tracer is very small. In this case, the response of the isotope contains both kinetic and mechanistic information. Since the technique is performed under steady-state conditions, the mathematical model should also evaluate these reactions. The change in the concentration of reactants and products in the axial direction as a result of the steady-state reaction is described by a system of differential and algebraic equations. The notation of such a differential algebraic set of equations (DAE) is given by (4.28):
Chapter 4

\[
0 = -\frac{\partial C_i}{\partial z} + f_i(z)f(C_i) + \ell_2(z) \\
0 = \ell_2(z)f(C_i) + \ell_5(z)
\]  

(4.28)

where,

- \(f(C_i)\) function describing the behavior of \(C_i\)
- \(C_i\) concentration of component \(i\)
- \(z\) variable in space
- \(\ell_i(z)\) constants or functions of position

The differential equations in equation (4.28) describe the convection and reaction of the gas phase in the axial direction. The algebraic equations specify the occupancies of the reacting species on the catalyst surface. The algebraic equations arise because there is no movement of species over the catalyst surface in the axial direction.

Two basic methods can be applied to numerically solve DAEs. The first method is based on rewriting DAEs to a system of ODEs. This is easily applied to a system of equations which defines the steady-state by returning to the non-steady-state description. This means that the zeros in equation (4.28) are replaced by time derivatives. The resulting system of ODEs may be solved with one of the ODE solvers mentioned previously. In this case, the ODEs are evaluated in time until steady-state is reached using the gas phase concentrations of the reactants as the initial conditions. The steady-state is reached when there is no net change in the concentration for a given step in time. The time needed to reach steady-state depends on the system. This is the main disadvantage of this solution method, since it may require long computation times to reach this state. In addition, no change in the concentration in time is no guarantee for a steady-state, since the system may be evolving very slowly. The second method is therefore based on solving equation (4.28) directly.

The first direct numerical method for solving DAEs has been proposed by Gear in 1971 [37] utilizing the BDF method. The basic idea for solving DAEs using numerical ODE methods is to replace the derivative in equation (4.28) by a difference approximation. In the simplest case, the derivative is replaced by a backward difference (Euler). The resulting system of non-linear equations can be solved using Newton's method. This scheme is also applied in the general applicable code DASSL. However, instead of always using the simple backward difference, DASSL approximates the derivative using the \(k^{th}\) order BDF, where \(k\) ranges from one to five. A thorough description of DASSL is given by Brenan et al. [56].

A problem with this method is that a consistent set of initial conditions is needed to get started. The gas phase concentrations are known because they are defined by the experimental conditions. However, the surface concentration (occupancies) of the reactants and products are not known. This problem is easily tackled by assuming that the spatial derivatives and the gas phase product concentrations in equation (4.28) are equal to zero. The resulting system of non-linear equations is solved to obtain the surface occupancies. This solution is used as a set of consistent initial values.
4.2 Mathematical treatment of PEP data

The evaluation of PEP data is depicted in figure 4.3. The fitting procedure is similar to the one discussed previously; therefore, the emphasis will be placed on the treatment of PEP data in this sequence. A major difference with the previously described minimization procedure is that a combined DAE/PDE model needs to be solved. The DAE describes the steady-state concentrations on the catalyst surface and in the gas phase. These concentrations are determined by the reaction mechanism (elementary steps) and the rate constants, which are also in the PDE. The rate constants are usually used as parameters in the fitting procedure. The surface occupancies, determined by the DAE model, are used in the model (PDE mode) describing the response of the isotopic tracer. These surface occupancies are constant because it is assumed that they do not change upon introduction of the very small amount of tracer. The PDE model only needs to include the reactions of the tracer because the concentration of the other components
does not change. The PDE is solved by spatial approximation followed by solution of the resulting system of ODEs with either LSODE(S) or RKF45. An upwind approximation is used to describe the convection of the tracer through the reactor. This procedure results in the determination of the tracer concentration on the surface and in the gas phase at several positions \( (N) \) in the reactor. The total response at a certain position is determined by the sum of the surface and gas phase concentrations of all the isotope containing species. This results in a concentration profile \( (CP_{\text{calc}}) \) that is compared to the experimental data. A problem with this approach is that the mathematical procedure yields a solution with infinite position resolution, which is not the case for the PEP profile. The accuracy of the position detection process of the PEP detector lies between 3 and 6 mm depending on the isotope and the density of the catalyst. The limited accuracy has an averaging effect on the real concentration profile. This averaging of the concentration at several axial positions is described by the sensitivity profile for that position. A sensitivity profile for each reconstruction position has been determined with the Monte-Carlo code EGS4, as described in chapter 5. This results in a sensitivity matrix \( (S_{\text{PEP}}) \) describing the position sensitivity of the 17 reconstruction positions \( (RP) \). The sensitivity matrix is given by:

\[
S_{\text{PEP}} = \begin{bmatrix}
S_{U} & \cdots & S_{RP,1} \\
\vdots & \ddots & \vdots \\
S_{U,N} & \cdots & S_{RP,N}
\end{bmatrix}
\]

(4.29)

The columns of the matrix contain the sensitivity profiles for each reconstruction position. The length of the column is equal to the number of positions at which the isotope concentration has been calculated. Thus, the factor \( S_{m,n} \) determines the contribution of the concentration (activity) at position \( n \) to the total response at reconstruction position \( m \). The mathematical profile is convoluted with the sensitivity matrix to obtain a concentration profile, \( CP_{\text{conv}} \), which includes the non-idealities of the detection process. The convolution consists of multiplying the response matrix with the calculated isotope concentration profile, according to equation (4.30):

\[
CP_{\text{conv}} = S_{\text{PEP}} CP_{\text{calc}}
\]

(4.30)

The SSR is calculated from the convoluted profile \( CP_{\text{conv}} \) and the experimental data. The minimization routine generates new parameters based on this SSR. When the convergence criteria have been met, the routine returns the parameters which give the smallest SSR. The steady-state gas concentrations at the end of the catalyst are also compared to the experimentally determined conversion during the minimization.

5 EXAMPLE: NUMERICAL SIMULATION

The adequacy of the procedure described above will be shown with a numerical simulation experiment applied to 3D data. The dispersion model \([57,58]\) for flow through
Figure 4.4. Plot of simulated data (ν=2 and Pe=100) used in the minimization procedure.
A. Simulated data without noise, B. Simulated data with 10% Gaussian noise.

A packed bed of catalyst particles has been used:

\[
\begin{align*}
\frac{\partial C}{\partial t} &= \frac{\nu L}{Pe} \frac{\partial^2 C}{\partial z^2} - \nu \frac{\partial C}{\partial z} \\
Pe &= \frac{\nu L}{D_a}
\end{align*}
\]

(4.31)

The initial and boundary conditions are:

**initial conditions:** \( C(z,0) = 0 \)

**boundary conditions:** \( C(0,t) = f(t) \)
\[
\left. \frac{\partial C}{\partial z} \right|_{z=L} = 0
\]

where,

- \( C \) concentration
- \( D_a \) axial dispersion
- \( L \) reactor length
- \( Pe \) Peclet number
- \( t \) time
- \( \nu \) superficial velocity
- \( z \) position in reactor
- \( f(t) \) input function

- m² s⁻¹
- m
- m
- s
- m s⁻¹
- m

-
Table 4.1. Effect of Gaussian noise (% of peak maximum, $P_{\text{max}}$) on parameter estimates and their 95% confidence intervals.

<table>
<thead>
<tr>
<th>Noise [%]</th>
<th>Superficial velocity $v$ [-]</th>
<th>$Pe$ [-]</th>
<th>$\frac{s}{P_{\text{max}}} \times 100$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.00 \pm 5.3 \cdot 10^{10}$</td>
<td>$100 \pm 3.8 \cdot 10^{7}$</td>
<td>$7.6 \cdot 10^{7}$</td>
</tr>
<tr>
<td>5</td>
<td>$2.00 \pm 3.6 \cdot 10^{3}$</td>
<td>$98 \pm 4.1$</td>
<td>4.9</td>
</tr>
<tr>
<td>10</td>
<td>$1.99 \pm 7.0 \cdot 10^{3}$</td>
<td>$102 \pm 4.1$</td>
<td>10.0</td>
</tr>
<tr>
<td>20</td>
<td>$2.00 \pm 1.4 \cdot 10^{2}$</td>
<td>$97 \pm 9.2$</td>
<td>20.0</td>
</tr>
</tbody>
</table>

The model includes both the effects of axial dispersion and convection on a pulse injected into a gas stream. The PDE was solved by approximating the first derivative (convection term) by a five point biased upwind finite difference. A five point centered approximation was used for the second derivative. The resulting system of ODEs was solved with LSODES using 51 grid points and a Gaussian shaped pulse as the input function ($f(t)$). Figure 4.4A shows a typical numerical result of the model. Data for the minimization procedure were generated by adding different quantities of Gaussian noise [44] to this result. Figure 4.4B shows the result after adding 10% (of the peak maximum) Gaussian noise. Table 4.1 shows the parameter estimates produced by the minimization procedure according to the Levenberg-Marquardt method. The initial surface was produced with $v=2$ and $Pe=100$. It can be seen that the estimates closely correspond to the initial values of $v$ and $Pe$, and are within their 95% confidence interval (4.27). As expected, the confidence interval increases with increasing noise. Furthermore, the estimated standard deviation (4.25) correctly returns the amount of noise added to the data. The minimization procedures given by Powell, and Nelder and Mead (Simplex) gave similar results.

6 CONCLUSION

Correct mathematical treatment of transient experiments involves solving a set of PDEs. The PDEs describe the behavior of the concentration in both time and space. Existing software packages can only solve a system of ODEs. An easy to implement method has been presented with which PDEs can be solved with existing FORTRAN code. The method applied is the numerical method of lines. It consists of approximating the spatial derivatives by finite differences, although other approximation methods like finite elements are also possible. The approximation reduces the PDEs to a set of coupled ODEs. Several existing FORTRAN codes are available which can solve these ODEs. Therefore, the user is only concerned with the approximation of spatial derivatives and the ODEs are ideally solved by robust ODE solvers.

Parameter estimation is the next step in the mathematical treatment. The PDE solving FORTRAN code can easily be coupled to existing minimization routines. These routines vary the parameters which need to be estimated in such a way that the difference
between the calculated model and experimental data is minimized. This permits the
determination of reaction constants of elementary reaction steps or validation of a
model.
The presented procedure allows much more useful information to be obtained from
transient experiments than from qualitative or quantitative analysis which only take the
time dependency into account. Using FORTRAN procedures to solve the PDEs creates a
large amount of flexibility which existing software packages usually do not offer.
However, the flexibility comes at small cost since the user is required to learn the basics
of FORTRAN.

7 SYMBOLS AND ABBREVIATIONS

_**Solving partial differential equations**_

\( c(z) \)  concentration of a component in the spatial direction \( z \)
\( C_i \)  concentration of component \( i \)
\( C_{ij} \)  concentration of component \( i \) at grid point \( j \)
\( f(C_i) \)  function describing the behavior of \( C_i \)
\( f_i(z, t) \)  constants or functions of time and/or position
\( h \)  time step
\( i \)  component number
\( j \)  grid point number
\( J \)  Jacobian matrix
\( k \)  BDF order
\( N \)  total number of grid points
\( t \)  variable in time
\( \text{URL} \)  Uniform Resource Locator (www address)
\( y_n \)  value of the concentration in time
\( y_{n+1} \)  value of the concentration in time at the next time step
\( z \)  variable in space
\( z_j \)  grid point \( j \) in the spatial direction \( z \)
\( \alpha_k, \beta_k \)  BDF coefficients

_**Parameter estimation**_

\( C^{\text{cal}} \)  calculated data
\( C^{\text{obs}} \)  experimental data
\( H \)  Hessian matrix
\( H^{-1} \)  inverse Hessian matrix
\( i \)  iteration number
\( I \)  identity matrix
\( J \)  Jacobian matrix
\( J^T \)  transpose of the Jacobian matrix
\( k \)  (parameter) vector element number
CHAPTER 4

\( m \)  
observation number

\( n \)  
component number

\( N \)  
total number of iterations

\( N_c \)  
total number of components

\( N_d \)  
total number of observations

\( P \)  
arbitrary matrix

\( p \)  
number of parameters

\( q_i \)  
gradient vector at iteration \( i \)

\( s^2 \)  
variance

\( SSR \)  
sum of squares

\( SSR^* \)  
minimum of SSR

\( t_{\gamma/2} \)  
\( \gamma/2 \)-percentage point of the Student's \( t \)-distribution with \( m-p \) degrees of freedom

\( V \)  
covariance matrix

\( V_{kk} \)  
\( k^{th} \) element of the primary diagonal of \( V \)

\( \omega_{ij} \)  
weighing factor of the \( j^{th} \) observation of component \( i \)

\( \varepsilon \)  
observation error

\( \lambda \)  
Levenberg and Marquardt scalar

\( \phi^* \)  
parameter estimates at \( SSR^* \)

\( \phi_i \)  
parameter estimates at iteration \( i \)

\( \phi^{*(k)} \)  
\( k^{th} \) element of \( \phi^* \)

\( \phi_i^* \)  
initial guess vector

\( \sigma^2 \)  
population variance

\( \Phi_N \)  
parameter estimates after \( N \) iterations

**Mathematical treatment of positron emission profiles**

\( C_i \)  
concentration of component \( i \)

\( CP_{isotope} \)  
calculated isotope concentration profile

\( CP_{PEP} \)  
calculated PEP concentration profile

\( \kappa(C_i) \)  
function describing the behavior of \( C_i \)

\( f_i(z) \)  
constants or functions of position

\( m \)  
reconstruction position index

\( N \)  
number of positions

\( n \)  
position index

\( RP \)  
reconstruction position

\( S_{mn} \)  
sensitivity coefficient for reconstruction position \( m \) at axial position \( n \)

\( S_{PEP} \)  
detector sensitivity matrix

\( z \)  
variable in space

76
Abbreviations

BDF   backward differentiation formulas
BGO   bismuth germanium oxide
DAE   differential and algebraic equations
MOL   method of lines
Multitrack multiple time resolved analysis of catalytic kinetics
ODE   ordinary differential equations
PDE   partial differential equations
SSITKA steady-state isotopic transient kinetic analysis
SSR   sum of squares of residuals
TAP   temporal analysis of products

8 REFERENCES


and their application to some heat transfer problems. Report No. 315, NASA TR.
Properties of the PEP Detector
Prediction of the detector response by Monte Carlo simulations to aid the data interpretation

Abstract
Positron emission profiling is a transient technique capable of measuring gas and surface concentrations of a radioactive compound in a catalytic reactor as a function of position and time. Reaction kinetic data are extracted from these profiles with the aid of a mathematical model. This model, however, does not include the position resolution of the detector, which is given by the sensitivity profile for each detection position. The mathematical model was corrected by convolution with these profiles. Sensitivity profiles were simulated with the EGS4 Monte Carlo code, which describes the transport of positrons and photons through matter. The adequacy of the code was checked by comparing the simulations with experimental data of $^{11}$C and $^{22}$Na point sources. The influence of source characteristics, catalyst density, and detector properties were studied. The EGS4 code was able to predict the experimental data in each case. The effect of the convolution procedure on the mathematical solution is discussed.
CHAPTER 5

1 INTRODUCTION

Positron emission profiling is an in-situ isotopic transient technique that enables monitoring of gas and surface concentrations in a catalytic reactor operating at steady-state [1-6]. The technique is made possible due to the special properties of the radioisotope (positron emitter) used. Common positron emitters which are used to label molecules are $^{11}$C, $^{13}$N, and $^{15}$O. These radioactive atoms can be used to prepare the positron emitting counterparts of reactants used in exhaust gas catalysis. The various properties of these emitters are given in Table 5.1. Upon decay, these radioactive atoms emit a positron (antiparticle of an electron) that can annihilate on encounter with an electron in the surrounding matter. This annihilation event produces two high energy photons (511 keV) capable of permeating through the reactor and the surrounding oven. The high energy photons can be detected with a special detector allowing deduction of the position of the annihilation event. This principle is based on the medical technique positron emission tomography (PET) used in nuclear medicine to follow minute amounts of a radioactive tracer in a living organism [7,8].

The PEP detector consists of two arrays of nine independent detection elements, which are placed on opposite sides of the reactor/oven [3,4]. Each detection element contains a bismuth germanium oxide (BGO) scintillation crystal coupled to a photomultiplier tube. The position of the annihilation event is deduced as follows. During annihilation two 511 keV photons are formed which are emitted under an angle of 180 degrees. The photons are detected coincidentally by two elements, one from each array. In this case, coincidental means that both photons have to be detected within a specified time window of 50 ns [9,10]. The position is reconstructed from the intersection of the line connecting the two elements that have detected a photon, and the central axial axis of the reactor. Consequently, the activity (concentration) can be measured at 17 unique equidistant positions (reconstruction positions) along the axial axis of the reactor.

As mentioned, PEP allows the concentration of a radioactive tracer to be determined as a function of position and time. The tracer used is the isotopic analog of one of the reactants taking part in the catalytic reaction. Minute amounts (fmol) of this tracer are added to the gas stream fed to the catalyst operating under steady-state conditions. Since the concentration of the tracer is very low it does not influence the steady-state, and

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{22}$Na</td>
<td>545</td>
<td>215</td>
<td>2.7</td>
<td>0.3</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>960</td>
<td>385</td>
<td>6.5</td>
<td>1.0</td>
</tr>
<tr>
<td>$^{13}$N</td>
<td>1190</td>
<td>487</td>
<td>8.6</td>
<td>1.4</td>
</tr>
<tr>
<td>$^{15}$O</td>
<td>1720</td>
<td>729</td>
<td>13.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>
therefore, the behavior of the tracer can reveal information (e.g. reaction rates, elementary steps) about the reactions taking place under these conditions. A mathematical model is needed to extract the reaction kinetic information from a PEP profile.

The mathematical model needs to describe the concentration of the tracer as a function of time and position. This automatically leads to a system of partial differential equations (PDEs) describing the behavior of the tracer based on the elementary reactions and their reaction rates. The solution of this system describes the evolution of the concentration in time at any given position in the catalyst bed [11]. This is compared with the trend measured with the PEP detector. Ultimately, the model can be fitted to the PEP profile to obtain values for the reaction rates which are usually used as parameters during the fitting process. A problem with this approach is that the model calculates the concentration at a specific position, with an almost infinite accuracy, however, the detection process of the PEP detector does not determine the position of the tracer with such an accuracy.

The accuracy of the detection process in the spatial direction (position resolution) is limited by several factors. First, the crystal width determines the upper bound of the position resolution. Hence, thin crystals would give a high position resolution. A high position resolution means that the position of the decaying tracer can be determined very accurately. A second factor that influences the position resolution is the positron range. When a positron is emitted it travels a certain distance before annihilation takes place, depending on the kinetic energy of the positron and the density of the surrounding medium. Therefore, the annihilation position is not identical to the position of the decaying tracer, causing a further decrease of the position resolution. The last factor is the effect of photon scattering in the scintillation crystals and the reactor/oven. For example, a photon may get scattered in a BGO crystal causing it to be detected in a neighboring crystal, leading to an invalid reconstruction of the annihilation position. Most of the photons lose energy due to scattering, so this effect can be used to discriminate between scattered and non-scattered 511 keV photons. This scheme is also incorporated in the detection process. However, the energy resolution of BGO is poor [9,10] and therefore this energy selection process is not very efficient. A fraction of the scattered photons is therefore also used during reconstruction, leading to mis-positioning and loss of position resolution. The result of the limited position resolution is that the detector does not measure the concentration at a single position, but rather the average concentration of a range (3 - 6 mm) of positions. The contribution of the activity at other positions than the reconstruction position is determined by the sensitivity profile for that reconstruction position. The shape of this sensitivity profile depends on the factors mentioned above.

The averaging effect of the detector on the real activity profile only needs to be considered if the activity gradient over the catalyst is very steep. This is usually the case during PEP experiments, because the activity is introduced as a discrete pulse. Also, during the reaction the tracer may be specifically adsorbed at the beginning of the catalyst as shown by Jonkers et al. [5]. There are two possible solutions to compensate
for the averaging effect (sensitivity profile) of the detector. The first method is based on correcting the measured profile for the detector sensitivity. A problem with this deconvolution method is that the activity is only known at a limited amount of positions (17 reconstruction positions), reducing the effectiveness of the procedure [12]. For example, deconvolution can lead to negative activities at positions where the activity is low. The second method is correcting the calculated profile for the averaging effect (convolution). The concentration can be calculated at every position in the reactor giving enough information to perform the convolution procedure. This method requires that the detector sensitivity profile is also known at enough positions to make the convolution accurate. The sensitivity profile can be determined experimentally by monitoring the response of the detector to a point source placed at various axial positions between the detector arrays. This is applicable for the relatively long living positron emitters $^{11}$C and $^{22}$Na, but not for the short lived emitters $^{15}$O and $^{15}$N. An additional problem is that it is difficult to prepare point sources that are contained in the same medium as used during the PEP experiments. This is an important requirement because both the positron range and photon scattering are dependent on the density of this medium. The sensitivity profile can also be obtained by Monte Carlo simulations that address the transport of photons and positrons through matter. The simulations can be used to predict the sensitivity profiles for the short lived emitters, and can also include the actual experimental composition of the catalyst bed.

The Monte Carlo simulations were carried out with the general purpose EGS4 code [13-17]. The EGS4 (electron gamma shower, version 4) code describes the transport of positrons/electrons and photons through matter and allows incorporation of the geometry of the PEP setup. The basis of the EGS4 code will be described in the next section. To prove the adequacy of the Monte Carlo simulations they were compared with point source measurements of $^{22}$Na and $^{11}$C. The influence of various experimental conditions like the oven/reactor system, catalyst density, and mis-configurations of the detector will be discussed. This chapter will be ended with the effect of the convolution method on the calculated profile.

2 PEP DETECTION PRINCIPLES

The PEP detector consists of two arrays, each holding nine independent detection elements. The detection elements are mounted horizontally next to each other with the oven/reactor placed in-between the two arrays. Each detection element consists of a bismuth germanium oxide (BGO, Bi$_4$Ge$_3$O$_{12}$) crystal connected to a photomultiplier tube. The BGO crystal absorbs the high energy photons, producing a number of less energetic photons (photoelectric effect) which are then amplified by the photomultiplier. The amount of photons produced by this process depends on the energy of the incoming photon. The two 511 keV photons produced by annihilation of the positron have a fair chance to be absorbed by the two arrays. If the photons are detected coincidentally by a crystal in each array, the annihilation position can be reconstructed. The photons are considered to be detected coincidentally when they are both detected within a specified
Figure 5.1. Reconstruction principle.
A schematic of the two detector banks, each containing nine BGO crystals, is shown. The reconstruction position is deduced from the line between two crystals that detected a photon (reconstruction line) and the central axial axis. The maximum number of reconstructions is defined by the number of possible reconstruction combinations, as shown for reconstruction positions 1 to 3.

time window, 50 ns in this study. The paths of the two photons, which are emitted in opposite direction, can be reconstructed from the line (reconstruction line) connecting the two crystals that detected a photon (detection pair) and the central axial axis of the detector. These reconstruction lines can be formed between every crystal from one array with crystal from the second array resulting in 81 (9 x 9) reconstruction lines, as shown in figure 5.1. Due to redundancy these reconstruction lines form 17 unique equidistant reconstruction positions along the axial axis (see figure 5.1). When all the detection elements are placed next to each other ('close-packed' form) the average distance between these reconstruction positions is 3.25 mm.
The number of possible reconstructions for each position is determined by the number of reconstruction lines that cross that position. For example, reconstruction position 1 and 17 can only be formed by a single reconstruction line (the line between the outermost opposing crystals, see figure 5.1). The maximum number of reconstructions for each position is mentioned in figure 5.1. These maximums hold when all possible reconstructions are considered. It is also possible to only consider the reconstructions between opposite and opposite-adjacent detection elements. and other combinations are also possible. All the results mentioned in this chapter result from considering all
possible reconstructions, unless mentioned otherwise. The annihilation photons do not always travel in a straight line before being absorbed in a detection crystal, but also get scattered in the reactor/oven and in the BGO crystals. Scattering results in a direction change of the photon and most of the scattered photons (Compton scattering) lose energy during this process. Scattering can lead to mis-positioning of the annihilation event because the photon is detected in a faulty detection crystal, as is shown in figure 5.2. To reduce such mis-positioning errors the energy of the incoming photon is also taken into account during coincident detection. Photons falling outside of the energy window, centered around 511 keV, are rejected. Due to the poor energy resolution ($\pm$ 140 keV) of the BGO crystal-photomultiplier combination this window is large and is set between 370 keV and 750 keV. This large window hampers the energy selection process such that a significant part of the scattered photons are still included in the reconstruction procedure.

3 Monte Carlo simulation of Positron and Photon transport with EGS4

3.1 Introduction

The EGS4 (electron gamma shower, version 4) Monte Carlo system has been developed to study coupled electron/positron and photon radiation problems that occur in high energy physics applications [13]. The PEP technique is also a combination of positron and photon transport, which can be described with this code. Figure 5.2 shows an overview of the processes taking place after a positron emitter decays in the catalytic reactor system. Positron emitters are unstable nuclei because they carry an insufficient amount of neutrons, this situation is corrected by conversion of a proton into a neutron and a positron. The positron is emitted by the atom with a certain kinetic energy. The energy of these positrons varies from zero to a maximum value, depending on the decaying nucleus. Table 5.1 lists the values of the maximum and the average positron energy of the positron emitters used in this study. Before annihilation with an electron, the positron must reduce its energy to near thermal values by inelastic scattering with electrons in the surrounding matter. This positron thermalization causes the positron to travel a certain range in matter before annihilation occurs. Most of the positrons (98%) annihilate via this process, and only a small fraction (2%) annihilates in flight. Annihilation with an electron results in the formation of two photons, which are emitted in opposite direction. These photons can interact with the surrounding matter by either Compton/Rayleigh scattering or photoelectric absorption. Scattering changes the energy and direction of the photon, as shown in figure 5.2. The physical processes considered and the models used to simulate the transport of positrons and photons will be described here, a more thorough description is given by Nelson et al. [13].
MONTE CARLO SIMULATIONS OF THE PEP DETECTOR

Figure 5.2. Diagram of the processes taking place during positron/photon transport which are incorporated in the Monte Carlo code EGS4.

The process starts with the decay of a positron emitting atom, producing a positron and a neutron. The positron travels through the surrounding matter losing energy (thermalization) and changing direction on its course. When its energy is low enough it can annihilate with an electron. Annihilation produces two photons traveling in opposite direction with the same energy (511 keV). The photons can penetrate the surrounding reactor to reach the BGO crystals of the detector which results in the detection of the photon (photoelectric effect). During its flight the photon can change direction due to scattering.

3.2 Compton/Rayleigh photon scattering

During transport the photons interact with matter as a result they change direction and their energy may be reduced. This process is known as scattering of which there are two types: Compton and Rayleigh. Compton scattering is the result of an inelastic collision between a photon and an electron in the atomic shell of a nucleus. After this interaction, the photon has transferred a certain amount of its energy to the electron. The cross section (interaction probability) of this interaction is taken from the Klein-Nishina
Figure 5.3. Cross sections of the various photon interactions as a function of photon energy.
A. Cross sections (interaction chance) for aluminum, the major component of the oven. B. Cross sections for BGO used for the detection of the annihilation photons. Note the scale difference (10-fold) between aluminum and BGO.

formula which applies to free electrons. Binding effects are not taken into account, which is a good approximation for photon energies higher than 10 keV.
Rayleigh scattering is a less important low energy process. This interaction is the result of elastic collision of a photon with an atom. This process only deflects the photon and no energy is lost. The cross sections of both the Compton and Rayleigh interaction for different photon energies are shown in figure 5.3 for aluminum and BGO. As can be seen, Compton scattering dominates Rayleigh scattering at higher energies.

3.3 Photoelectric effect
The dominant low energy photon process is the photoelectric effect. In this case, the photon is absorbed by an electron of an atom, resulting in escape of the electron from the atom. The rapidly formed excited atom falls back to its ground state accompanied by the emission of low energy photons (wavelength in the visual spectrum). The energy of the electron equals the photon energy less the electron binding energy. The cross sections for the photoelectric effect are taken directly form Storm and Israel’s tables [18]. These cross sections increase for lower photon energies and higher atomic numbers, as can be seen in figure 5.3.

3.4 Positron scattering and energy loss
As a positron slows down in material, it undergoes thousands of elastic scatterings with electrons and nuclei which change its angle but have little effect on its energy. To make this problem applicable for Monte Carlo techniques it is not possible to consider all these interactions. Therefore, the positron is transported through a small distance and then the
angle of deflection due to the multiple scattering is determined using the theory of Moliere, as formulated by Bethe [19]. The most accurate theory is that of Goudsmit and Saunderson [20,21]. It is however difficult to implement and requires longer calculation times. Because of its accuracy, it has been the method of choice for the ETRAN [22,23] based codes. Recently, the PRESTA algorithm [14] has been added to the EGS4 code increasing the accuracy of the scattering angle and energy loss calculations. The inelastic scattering of positrons by an electron is taken into account using the cross sections of Bhabha [24,25] as formulated by Messel and Crawford [26]. The electron is assumed to be free in this formulation. The Bhabha cross section contains a term related to the possibility of positron annihilation and includes spin and relativistic effects.

To account for the energy loss of the positrons (stopping power) it is assumed that this energy is lost continuously along its path. Energy loss occurs by collisions which cause ionization and excitation of atomic electrons and Bremsstrahlung radiation, the latter contribution is negligible for positron energies lower than 4 MeV. The continuous energy loss for positrons is given by the Bethe–Bloch theory as expressed by Berger and Seltzer [27]. The theory incorporates the Bhabha cross sections for positrons [28].

3.5 Positron annihilation

The predominant mode of annihilation by a thermalized positron is via production of two 511 keV photons. This is taken into account by producing two photons when the energy of a positron reaches value lower than 10 keV. The photons are emitted under an angle of 180 ± 0.5° at the position of the positron. In flight positron annihilation is also employed by using the cross section of Heitler [29]. These two processes make up 99% of the annihilation events, only a small amount (1%) results in the production of three photons. The three photon process is ignored in EGS4.

3.6 PEP simulations

Simulation with EGS4 requires that the user writes a code describing the geometry of the problem, and a code which keeps track of the quantities of interest [3,4,13]. The latter involves recording the energy deposited in the BGO crystals. The geometry describes the material boundaries of the problem. The path of photons and positrons depends on the properties of the material in which they are transported. The main factor, influencing this transport, is the density of the material. The transport logic of EGS4 is based on sampling the distance to a new interaction, transport of the particle over this distance, followed by sampling of the interaction distribution. If a material boundary needs to be crossed during transport, the particle is first transported to the boundary along the path it was traveling. At the boundary a new mean free path is calculated for the new material. In principle, EGS4 is not limited to simple geometries, however, complex geometries usually increase the computational burden. Complex geometries increase the difficulty with which the intersection of particle path and boundary is calculated. In addition, modeling of positron transport also requires the shortest distance to the boundary to be known which is also elaborate for complex geometries.
Figure 5.4. Cross sections of the simulated PEP setup.
A. Axial cross section showing the configuration of the catalyst bed with respect to the detection banks.
B. The vertical cross section gives details about the structure of the oven and the surroundings. All dimensions are given in millimeters.

The geometry used in these simulations is shown in the cross sections depicted in figure 5.4. The configuration of the PEP detector is the ‘close-packed’ form (all the crystals are placed next to each other). The space between the crystals is filled with PVC because the real crystals are wrapped in PVC tape to prevent detection of stray light. The PVC also increases the gap between the crystals; an average gap width of 1.4 mm is used here. As can be seen from figure 5.4, the complex structure of the oven is modeled with simple cylindrical boundaries. The housing of the photomultiplier is also not taken into account in the simulations because this would also increase the complexity of the geometry. This is allowed because the scatter contribution is expected to be small due to the low overall density of the housing.

The decay of the positron emitter followed by the detection of the 511 keV annihilation photons by the BGO crystals was simulated as follows. The geometry of the positron source was considered to have the shape of a cylindrical slab. Random selection determines the position of the positron emitter in the source volume. The positron is then emitted isotropically with a random energy sampled from the energy spectrum of the positron emitter used [30]. The positron is then allowed to be transported through the
surrounding media using the EGS4 code. Annihilation occurs when the energy of the positron falls below 10 keV, or when the EGS4 code samples an in-flight annihilation. The annihilation photons are created at the current positron position. The positron is disregarded and the photons are emitted isotropically with an angle of $180 \pm 0.5^\circ$ between the photons. The photons are then transported with EGS4 and their energy deposited in the BGO crystals is recorded. Energy is deposited either by the photoelectric effect or by Compton scattering. Which of the two processes occur in the BGO crystal is determined by EGS4. The selection relies on the specific cross section for each interaction. The energy loss of the photon, as a result of the processes mentioned above, is considered to be totally deposited in the crystal. The creation of secondary electrons is disregarded. A positive reconstruction occurs when the photons have deposited an energy quantity between 370 keV and 750 keV in a crystal in the upper and the lower array. The energy resolution of BGO is also taken into account in this process. The detection position is then determined from the intersection of the line that connects the two elements that detected a photon and the central axial axis. When the response of the whole detector is determined every possible reconstruction is taken into account.

4 RESULTS AND DISCUSSION

4.1 Positron transport

Simulating the response of the PEP detector to a positron emitting source involves description of the transport of positrons and photons. The EGS4 Monte Carlo code is capable of simulating both processes in any material. The adequacy of EGS4 in predicting positron transport has not been reported yet. The transport of electrons with EGS4 has frequently been addressed showing that the results of these calculations are in close agreement with the ETRAN Monte Carlo code and experimental data [31]. The ETRAN code has been tested extensively against experimental data showing good agreement, it is therefore considered as benchmark for other codes. To examine the adequacy of EGS4 in predicting positron transport, the transmission of positrons through thin aluminum foils was determined. Figure 5.5 shows the transmitted fraction of 960 keV positrons incident on aluminum foils. The results of these calculations are compared with ETRAN and the only existing experimental data from Seliger [32]. Aluminum is chosen here since its density is similar to that of catalytic material. The results were obtained from samples of 1 million Monte Carlo histories of positrons. The particle histories were followed until their energy fell below 10 keV. The number of histories was sufficiently large such that the statistical errors in the transmitted fraction were in the order of 1% or smaller. The transmission predicted by EGS4 is much lower than the experimental data, and also lower than the ETRAN results. Berger [23] also addressed the difference between ETRAN and Seliger's [32] results and concluded that this is likely caused by experimental error. Comparison between ETRAN and Seliger's results for the transmission of electrons through the same aluminum foils also showed large discrepancies. In contrast, comparison with other experimental data obtained for
electrons passing through aluminum has shown to be in rather good agreement. Other Monte Carlo calculations [33,34] which have been devoted to describe Seliger's results also failed to give a satisfactory description. The difference between EGS4 and ETRAN is probably caused by the different treatment of scattering (Goudsmit-Saunderson) and energy loss (Landau) [23]. A similar difference between EGS4 and ETRAN has also been found for the transmission of electrons through aluminum foils [16]. Although the transmission calculated by EGS4 is somewhat less than that of ETRAN, it is considered sufficient because the response of the PEP detector is also affected by photon transport.

Figure 5.6 shows the calculated range of positrons emanating from a source containing either $^{15}$O, $^{13}$N, or $^{11}$C in catalytic material (Pt/Al$_2$O$_3$). A density of 0.45 g/cm$^3$ has been used for the catalytic material which is common for $\gamma$-alumina (high surface area) supported catalysts. The results were obtained by following the histories of 2 million positrons emanating from an isotropic source until annihilation occurred (thermalization and in flight). The $z$-position (axial) of each annihilation event is recorded and the histogram (bin width 0.02 mm) of these results is shown. The initial kinetic energy of the positron was sampled from the positron energy spectrum of the isotope. The range of the emitted positrons depends on the average kinetic energy with which they are emitted, these energies are shown in Table 5.1 for the isotopes used. The average and maximum range calculated from the positron ranges shown in figure 5.6 are also given in Table 5.1. The range of positrons influences the accuracy with which the position of the emitting atom can be determined. The position resolution of an $^{15}$O containing molecule will therefore always be lower than that of an $^{11}$C molecule, this can be a criterion when selecting a positron emitter.

4.2 Photon transport

Annihilation of the positron produces two 511 keV photons which are emitted in
Figure 5.6. Positron range in catalytic material (Pt/AI₂O₃, 0.45 g/cm³).

opposite direction. The photons travel through space before reaching a BGO crystal by which they are absorbed. The simplest configuration of the detector consists of two detection elements (BGO crystals) placed on opposite sides of the source, which is shown in figure 5.7. The response of this configuration to a source placed at different axial positions (z-position) between the detectors is determined by the detection angle. In this case, it is assumed that the positron is emitted without kinetic energy, and the annihilation position is therefore equal to the source position. The detection angle is defined by the angle between the two lines determining the outermost possibilities which result in coincident detection, see figure 5.7. When the source is situated at the center, the response is maximal because the detection angle is the largest. As the source moves to the edge, of the crystal the angle and accordingly the response becomes smaller. This situation is depicted in figure 5.7, here z determines the position of the source with respect to the center of the crystal. The detection angle (response) for the entire crystal is given by the following mathematical function:

\[
\alpha = 2 \sqrt{2} \arctan \left( \frac{b - z}{\sqrt{x^2 + h^2}} \right) dx \tag{5.1}
\]

where,
- \( \alpha \) detection angle
- \( b \) crystal width (5.1 mm)
- \( h \) source distance
- \( l \) crystal length (100 mm)
- \( x \) axis along the length of the crystal
- \( z \) source position

The integral in this equation arises because the detection crystal is not infinitely thin as depicted in figure 5.7, therefore, the response needs to be integrated along the length of
the crystal. For an infinitely thin (zero length) detection crystal, as shown in figure 5.7, equation (5.1) reduces to:

\[ \alpha = 2\arctan \left( \frac{\frac{1}{2}b - z}{h} \right) \]  

(5.2)

The simplified form of (5.2) shows that a triangular response is expected, because the detector response is proportional to the detection angle. The solution of equation (5.1) is shown in figure 5.8. The theoretical response indeed has a triangular shape with its maximum at the center and zero response at the edges of the crystal. The response to a moving source for the simple detector configuration has also been simulated with EGS4. The source was placed at several positions (interval 0.1 mm) between the two detection elements and the number of coincidently detected photons was recorded. At each position 5 million positrons were emitted with zero kinetic energy resulting in annihilation at the source position. Only photons that deposited an energy between 370 and 750 keV in the BGO crystal were used for reconstruction. The simulated profile is also shown in figure 5.8. As can be seen, the shape of this profile is similar to the theoretical response. The main differences are that the number of reconstructions is much lower, and that the top is less pronounced. The number of reconstructions is lower because not all the photons that reach the BGO crystal are totally absorbed (detected). Only 28% of the photons are stopped in the BGO crystals in this detector configuration.

Figure 5.7. Determination of the theoretical response for opposing crystals.
The response of a single detection pair is defined by the detection angle (\( \alpha \)). This angle is determined by the position of the source in relation to the center of the crystals (\( z \)).
Figure 5.8. Comparison of the theoretical response for opposing crystals with simulations by EGS4 for a moving point source.

(©) Number of reconstructions as determined with EGS4. The setup of the moving point source is shown in figure 5.7. (—) Theoretical number of reconstructions (see equation 5.1).

Since similar values were obtained for opposite-adjacent detection pairs, the detection efficiency of the PEP detector will therefore be around 28%. Flattening at the center of the simulated profile occurs because photons that reach the crystal surface at small incidence angles near the edges of the crystal have a smaller chance of being stopped in the crystal. The length the photon has to travel before it can escape from the crystal is smaller in this case. The relative contribution of such photons is larger when the source is situated at the center than at the edges of the crystal, see figure 5.8. The simulated response of a single detection pair allows determination of the position resolution based on the properties of the detection elements. With the current setup a minimal position resolution of 2.55 mm can be obtained. The position resolution is defined by the full width at half maximum (FWHM) of the profile. The position resolution can be increased by decreasing the crystal width, however, the crystal width is restricted by the dimensions of the photomultiplier [3,4].

The previous results were obtained for a simple detector configuration and do not include the influence of scattering of photons in neighboring BGO crystals. The simulated response for the whole detector configuration, nine crystals in each array, is shown in figure 5.9. This detector setup is similar to the one shown in figure 5.4, but the influence of the reactor/oven is not taken into account. The results were obtained for a source placed at regular intervals (0.65 mm) between the detectors. The origin of the source was placed at the center of the detector. The source emitted 1 million positrons without kinetic energy. The annihilation photon tracks were followed and the deposited energy in each BGO crystal was scored, only events with an energy between 370 and 750 keV were selected for reconstruction. The profile shown is the response (sensitivity profile) for reconstruction position 9 (see figure 5.1). The response for the whole detector geometry is compared with the previous results for the single detection pair. The
Figure 5.9. Simulated sensitivity profiles for a single crystal compared with the response curves for the whole detector geometry (9 crystals).

(—) Response curve for two opposing single crystals to a moving source emitting positrons without kinetic energy. This curve is identical to the response curve (○) shown in figure 5.8. (—) Response curve for reconstruction position 9 when the whole detector configuration is included. (—) Response curve when both the positron range and the detector geometry are considered.

simulation shows that the position resolution has decreased when neighboring crystals are present. This decrease can only be attributed to scattering of photons in a BGO crystal, causing the photon to be detected in an adjacent crystal. Scattering of the photons is mainly due to Compton scattering because the Rayleigh contribution is very small for a photon energy of 511 keV in BGO. Hence, the photons lose energy upon scattering but are still detected because the energy resolution of the BGO scintillation crystal is poor. This mis-positioning decreases the position resolution to 3.4 mm.

When the effects of photon scattering in the crystals and the positron range are both considered, the position resolution decreases even further, as shown in figure 5.8. The medium in which the positrons were emitted had a density of 0.7 g/cm³. For more dense materials the effect would be less pronounced. The opposite is true for less dense materials like the catalytic material used previously. In the next sections the effects of the reactor/oven, detector misalignment, and source distance on the detector response will be analyzed. In addition, the Monte Carlo simulations will be compared with experimental data.

4.3 Results for ²²Na point sources

A point source allows experimental determination of the sensitivity profile for a reconstruction position. The sensitivity profile contains information about the contribution of the activity at other positions than the reconstruction position. This profile can be determined experimentally by measuring the number of reconstructions at a reconstruction position as a function of the source position. A point source has been used to eliminate effects of the source geometry on the sensitivity profile. The source
Figure 5.10. Sensitivity profile for a $^{22}$Na point source measured in air, and in the aluminum oven.

(O) Point source in air. (□) Point source in the aluminum oven.

consisted of a bead (1 mm) of ion-exchange material (polymer) sealed in a small rectangular perspex container (25x10x3 mm). The ion-exchange material had been exchanged with $^{22}$Na. The advantage of a $^{22}$Na point source is that the range of positrons is very limited (approximately 0.1 mm), due to the low kinetic energy of the emitted positrons, see Table 5.1. Therefore, the annihilation position is almost equal to the source position. A disadvantage of a $^{22}$Na point source is that besides a positron it also emits a prompt gamma, with an energy of 1274 keV. This photon is emitted at a random angle which is not correlated to the direction of the positron (separate processes). Measurements were performed by placing the source at several positions between the detector arrays and determining the total number of reconstructions after 55 seconds. The distance between the source and the detection arrays amounted to 10 cm.

Figure 5.10 shows the sensitivity curves for reconstruction position 9 of the $^{22}$Na point source measured in air and in the aluminum oven. The measured profiles were normalized to the maximum activity reached in each case. When the source is placed in the oven the maximum number of reconstructions decreases due to increased interaction (photon absorption, scattering) of photons with the aluminum oven. The profiles both have a Gaussian shape. The maximum number of reconstructions is recorded at the center of the crystal (the origin of figure 5.10). The number of reconstructions decreases when the source is positioned further away from the center. However, the response does not fall to zero at greater distances from the center. A small constant number of reconstructions is still recorded at distances larger than 5 mm. These nonspecific reconstructions (background reconstructions) must be due to photon scattering or detection of the prompt gamma. Scattering of photons can occur in the detection crystals or in the material surrounding the source. Both possibilities are shown in figure 5.11. The chance that a mis-reconstruction is due to scattering of a photon in a detection crystal is very low, because the photon has to pass a neighboring crystal
Figure 5.11. Possible types of photon scattering for the $^{22}$Na point source resulting in nonspecific reconstructions. 
(A) Scattering in a BGO crystal. (B) Scattering in the perspex container which holds the $^{22}$Na point source.

without being absorbed (see figure 5.11). In addition, the photon is scattered under a large angle, which will significantly reduce the energy of the photon. Hence, it is unlikely that the energy of the photon will be large enough to fall within the predetermined energy window (370-750 keV). A more probable explanation is that scattering occurs in the material in direct vicinity of the source. In this case, the scattering angle is smaller and the photon does not need to permeate through a BGO crystal before being detected. It is evident that photon scattering in the vicinity of the source is responsible for the observed nonspecific reconstructions. For the $^{22}$Na source measured in air scattering of the photons can only occur in the perspex container. This chance is not very high because the density of the perspex container is low. In this case, detection of the prompt gamma must be responsible for the nonspecific reconstructions observed. A rise in the amount of scattered photons may therefore be expected when the density and the amount of material surrounding the source increases. Both factors enhance the chance that a photon gets scattered before reaching the detector arrays. Placing the source in the oven indeed increases the amount of nonspecific reconstructions (background level), as shown in figure 5.10. The shape of the peak is hardly influenced by the aluminum oven because it is nearly identical to the one of the $^{22}$Na source measured in air.

The position resolution for both cases is 3.8 mm, this value is larger than the simulated value (3.4 mm) from figure 5.8. Although transport of positrons has not been included in this simulation, the influence of the positron range on the position resolution is expected to be very small for $^{22}$Na. Another explanation for the observed difference may be horizontal misalignment of the detection elements or vertical misalignment of the
Figure 5.12. Sensitivity profiles for a $^{22}$Na point source, measured with the outer crystal pairs only, showing the effect of crystal bank misalignment. 

(○) The detection pair formed by crystal 1 of the upper bank and crystal 9 of the lower bank. (□) The pair formed by crystal 1 of the lower bank and crystal 9 of the upper bank.

source. The latter misalignment may arise if the source is not positioned exactly in between the crystal banks, however, this deviation is expected to be small. The effect of crystal misalignment can be determined experimentally by only considering the reconstruction lines between the outermost crystals. Figure 5.12 shows the sensitivity profiles of the two pairs formed by the outermost crystals of the upper and lower detection bank. The measured profiles are shifted with respect to each other by 2.2 mm. Shifts between the sensitivity profiles have also been measured for more inner lying detection pairs. If the shift is due to mis-centering of the source, the misplacement will be around 5 mm which is too large for experimental error. Therefore, vertical misalignment of the detection elements is more likely, since it is hard to achieve exact alignment of the crystals in the current setup.

The sensitivity profile of the $^{22}$Na point source in the aluminum oven has been simulated with EGS4 to evaluate the influence of the simplified geometry. The results were obtained by emitting 2 million positrons at every source position in the geometry shown in figure 5.4, without the quartz reactor. The energy of the positron was sampled from the spectrum of $^{22}$Na. The positrons were allowed to travel in a geometry similar to that of the experimental point source. The average range of the positrons in this setup was 0.15 mm, therefore, the effect of the positron range is expected to be nihil. The observed detector misalignment was also taken into account by assuming a vertical shift in the source position (5 mm). Figure 5.13 shows the comparison of the EGS4 simulations with the experimental results. The agreement between the experimental results and the simulation is good. The simplifications used in the geometric model clearly do not influence the simulations. As mentioned, the influence of the positron range is very small in this case, therefore, in the next section the effect of positron range will be evaluated with an $^{11}$C point source.
4.4 Results for $^{11}$C point sources

It has been shown (figure 5.9) that the positron range has a large effect on the position resolution. This range varies with the energy of the emitted positron (see figure 5.6). Since the range of positrons emitted by $^{22}$Na is very small, point sources containing $^{11}$C have been used to evaluate this effect. The size and geometry of the previous $^{22}$Na point source module did not allow the effects of the catalyst and the quartz reactor to be included, therefore, the $^{11}$C source consists of small particles which can be embedded in the catalyst bed. The $^{11}$C point source was prepared in-situ because of the short half-life of $^{11}$C (chapter 2). It consisted of small, dried 13X molsieve particles (diameter 0.4 mm) with adsorbed $^{11}$CO$_2$. It is known that $^{11}$CO$_2$ adsorbs nearly irreversibly on 13X. Nevertheless, results with these particles showed that $^{11}$CO$_2$ desorbed during the measurements. To prevent desorption of $^{11}$CO$_2$ the particles were sealed with a quick hardening polymer coating after $^{11}$CO$_2$ adsorption. Figure 5.14 shows two sensitivity profiles measured with an interval of 45 minutes. As can be seen, the two profiles are identical, confirming that $^{11}$CO$_2$ desorption does not occur in this case.

The $^{11}$C point sources were embedded in the catalyst bed such that a small layer (thickness 0.5 mm) of activity was surrounded by the catalyst particles used during the PEP experiments. Two types of catalysts were used, alumina supported and coated glass bead catalysts. The alumina supported catalyst has a density of 0.45 g/cm$^3$, and the glass beads used for coating have a density of 1.77 g/cm$^3$. The mentioned densities take into account the void fraction resulting from packing of the particles in the reactor tube. The sensitivity profiles for both materials are shown in figure 5.15, the distance between the sources and the detection arrays is 17 cm. As expected, the profile obtained for the point source in glass beads is narrower than that of the less dense alumina catalyst. These results show that the position resolution of the reactor system is indeed influenced by the
density of the catalyst, although the influence is rather small.
The effect of the positron range is clearly illustrated by these results. Simulations have
been done with EGS4 to see whether the effects of the positron range can be predicted.
The simulations also included the properties of the $^{11}$C source. The source was simulated
as a small layer placed in between the surrounding material the diameter of the quartz
reactor. Positrons were generated randomly across the whole volume of the source layer.
The presence of the polymer coating was not taken into account, because its density is
low and the layer is thin. The density of the source material was assumed to be equal to
its overall bed density (0.7 g/cm$^3$). In section 4.6 it will be shown that this is a valid

---

**Figure 5.14.** Sensitivity profiles displaying the stability of the source.
(⊙) Initial sensitivity profile of an $^{11}$C point source made of small 13X particles with adsorbed $^{14}$CO$_2$.
(→) Sensitivity profile after 45 min using the same source.

---

**Figure 5.15.** Sensitivity profiles for an $^{11}$C point source surrounded by different media positioned inside the oven.
(⊙) Catalyst (0.45 g/cm$^3$), (⊙) glass beads (1.77 g/cm$^3$).
assumption. The results of these simulations are shown in figure 5.16. The agreement with the experimental results is not as good as in the results with the $^{22}$Na point source. At the base of the $^{11}$C profile the simulated values decrease more rapidly than the experimental values. A possible explanation is that the positron range is indeed underestimated by EGS4, as observed previously. However, the positron range is one of the factors that determines the width of the profile. The width is correctly described by the simulation and the width also varies according to the experimental results.

Another possibility is that the disagreement with the experimental $^{11}$C results is caused by the different properties of the sources used. The main difference is that the $^{11}$C sources are more active than the $^{22}$Na source. The higher activity manifested itself in two ways, a higher count rate, and the distance between the source and detector had to be increased to stay within the linear range of the detector. Another consequence of the higher activity may be an increased amount of nonspecific reconstructions due to incidental reconstructions. The time window used for coincident detection is not infinitely small, therefore photons from different annihilation events may be detected as if they originate from a single annihilation event. The chance of such an occurrence is higher when more annihilations take place (higher activity). To examine this possibility the source was placed out of the oven and outside the field of view of the detector (see insert of figure 5.17). Under these conditions, the detector still records residual activity at every reconstruction position. Subsequently, the source was shielded from the detector with lead slabs, causing a decrease in the number of reconstructions. The ratio of the number of reconstructions with and without shielding is shown in figure 5.17. This procedure eliminates any differences in sensitivity among the detection elements. The results show that the high activity source is responsible for the nonspecific reconstructions measured previously. Since the source was not present in the oven it is expected that the contribution of scattered photons is very small. Thus, the nonspecific reconstructions
Figure 5.17. The effect of a point source situated outside the field of view of the detector on the response at different reconstruction positions.

The response of the detector to an $^{14}$C point source in air was measured, afterwards, the source was shielded from the detector with lead slabs and the response was determined again. In both cases the source was placed outside the field of view of the detector (see insert). The ratio between these two responses is plotted in this figure.

must be due to detection of photons coming from different annihilation events from the high activity source. The increase in the amount of nonspecific reconstructions (background level) is the largest close to the source, resulting in an increase by at least a factor 2. The actual increase during the measurements is probably larger because the source was situated 5 cm from the detector arrays.

To evaluate that the elevated background level is not caused by the oven, a high activity source was also measured in air. The source consisted of a tri-sphere (see 4.6) with adsorbed $^{14}$CO$_2$ placed in a small quartz tube (diameter 6 mm). The amount of scattering in the quartz tube is expected to be low and it will be lower than in the aluminum oven. The sensitivity profile of this source is shown in figure 5.18. It has been compared with the previous results obtained for the $^{14}$C point source in the glass bead medium (figure 5.15). The results show that the background level is similar in both cases. This also indicates that scattering in the aluminum oven is not responsible for the high background level observed previously, but is more likely linked to the high activity of the source. The amount of invalid reconstructions can be decreased by using a smaller time window for coincident detection. However, a smaller time window will also decrease the sensitivity of the detector. The current value of 50 ns is a compromise between the sensitivity and the number of incidental reconstructions.

The simulations presented in figure 5.16 have been corrected for the extra background reconstructions due to the high activity source, these results are shown in figure 5.19. The correction consisted of adding the background level measured for the point source to the simulated values. This level is 2.5-fold higher than the value simulated with EGS4. The same background level has been used to correct the two profiles in figure 5.16. The
Figure 5.18. Comparison of the sensitivity profiles for a high activity $^{11}$C point source measured in air and in the oven.

(○) Point source in air. The $^{11}$C source consisted of a trisphere placed in a quartz tube with a diameter of 6 mm. The trisphere was held in place with quartz wool. The trisphere is made of three 13X spheres (0.8 mm diameter) stuck together in a triangular form with adsorbed $^{11}$CO$_2$. (□) Point source in the aluminum oven. Profile is taken from figure 5.16 B.

agreement between the corrected simulation and the experimental data is quite good. However, this correction method has as side effect that the sensitivity profile can not completely be simulated by EGS4. The amount of radioactivity used during PEP experiments is similar to the amount present in the point source, therefore, the current background level will be used to correct the profiles. Point sources with a low activity, like the $^{22}$Na source and the $^{11}$C source shown in figure 5.24, do not need to be corrected because the number of invalid reconstructions is low.

Figure 5.19. Simulated sensitivity profiles, with background correction, for an $^{11}$C point source embedded in different media compared with experimental data.

A. Catalyst (0.45 g/cm$^3$). B. Glass beads (1.77 g/cm$^3$). (○) Experimental, (—) EGS4 simulation.
Figure 5.20. Simulated influence of the source distance on the position resolution.

4.5 **Influence of source distance**

To accommodate for the varying amounts of radioactivity used during PEP experiments, the distance to the source can be varied to stay within the linear detection range of the detector. The influence of the source distance on the position resolution has been determined via simulations with EGS4. To this end, sensitivity profiles have been simulated at various detector distances, and the width (FWHM) of these profiles has been taken as criterion for the position resolution. The simulations were performed for an $^{11}$C source embedded in a bed of catalytic material similar to the system used to predict the profiles shown in figure 5.19. The results of these simulations are shown in figure 5.20. The position resolution of the detection process increases with increasing source distance. If only the reconstructions between opposing crystals are considered the distance does not influence the position resolution (results not shown). This indicates that the distance dependency of the position resolution must be related to reconstructions of detection pairs formed by crystals separated by one or more crystals. At smaller source distances the incidence angle of the photon with the detection crystal decreases, which can increase the number of mis-reconstructions. This effect is shown in figure 5.21A. At small incidence angles the photon can pass through the crystal without being absorbed (detected). The photon is then detected in a neighboring crystal causing mis-positioning of the annihilation position. Increasing the incidence angle also increases the path length of the photon before it can escape from the crystal without being detected. Hence, the chance of the photon being absorbed in the correct crystal also increases, as is shown in figure 5.21B. At greater source distances the chance of mis-positioning decreases and this in turn increases the position resolution.

A consequence of the distance dependency of the sensitivity profiles is that these profiles have to be simulated at every distance used during the PEP experiments. This is a tiresome process requiring long computation times. Depending on the positron emitter
Figure 5.21. Influence of distance on the degree of mis-positioning.
A. The small source distance allows photons to pass a BGO without being absorbed. The photon is then detected in a neighboring element. B. At larger source distances the incident angle increases which in turn increases the mean free path of the photon in the BGO, and hence the chance upon absorption.

used, the experiments have either been performed at large distances (180-220 mm) or at short distances (80-100 mm). At larger distances the effect on the sensitivity profiles is not so large, therefore, only a single profile will be simulated to accommodate this range. At smaller distances the dependency is more profound, and therefore, a profile will be calculated for each case.

Figure 5.22. Influence of source characteristics on the sensitivity profiles using glass beads as surrounding medium.
A. Comparison of small source particles (□) with a trisphere source (○). B. Comparison of EGS4 simulation (→) with experimental data obtained with the trisphere source (○). The trisphere is made of three 13X spheres (0.8 mm diameter) stuck together in a triangular form.
4.6 Influence of source and medium characteristics on the positron range

The source medium influences the positron range due to the preparation method of the source. The source has been prepared by adsorption of gaseous $^{11}$CO$_2$ throughout the particle which will generate positrons everywhere in the particle. Therefore, the range of these positrons will be influenced by the density and geometry of the source. In the simulations with EGS4, it was assumed that the source particles formed a uniform layer with a density equal to the packed density of these particles. To verify the accuracy of these assumptions, the effect of the source geometry and packing will be examined. Changing the source geometry also allows verification of the previous experimental results.

The same material (13X molsieve) was used to prepare an $^{14}$C point source by adsorption of $^{11}$CO$_2$. The source consisted of three identical 13X spheres with a diameter of 0.9 mm. The spheres were coated with a quick drying polymer and were stuck together in a triangular form before the coating had dried. The geometry of the tri-sphere can be easily included in the geometry used for the EGS4 simulations. Figure 5.22A shows the comparison between the tri-sphere source and the small particle previous source embedded in the glass beads medium. The sensitivity profiles are clearly influenced by the characteristics of the source. The width of the tri-sphere profile is slightly, though significantly, larger than that of the small particle source. Such a difference is not expected because the densities of the source and surrounding media are identical in both cases. In addition, the size of both sources is also similar. Simulations with EGS4 have been performed to examine the possibility that the geometry of the tri-sphere is the source of the wider profile. These simulations are shown in figure 5.22B. The simulations do not predict a wider profile, but rather a profile similar to the one obtained with the small particles. A possible explanation is that the density of the glass beads around the tri-
sphere source is not equal to the overall density of the packed bead. To rule out experimental error due to ill-packing of glass beads around the tri-sphere source the experiments were repeated in a medium with a smaller particle size. The density of this medium is also lower (0.74 g/cm$^3$) than that of the glass bead medium. The sensitivity profile obtained with this medium is shown in figure 5.23A. Comparison with the previous results clearly shows the influence of the particle size on the sensitivity profile. Placement of the point source in a bed with the smaller sized particles gives a narrower profile than when the denser glass beads are used, which is contrary to expectation. In contrast to the glass bead simulations, the results of the small particle medium can be predicted with EGS4, as shown in figure 5.23B. These results indicate that incorrect packing of the glass beads around the tri-sphere must have influenced the previous experimental results. The simulations with EGS4 also show that the density surrounding the tri-sphere must be lower than the expected packed density of the glass beads. Figure 5.24 shows the simulation using a density of 0.55 g/cm$^3$ (⅓ of the expected density) for the surrounding medium. The agreement with the experimental data is satisfactory now. The experimental results can be explained by poor packing of the particles around the tri-sphere, another possibility is that the range in a packed medium (non-homogeneous) is indeed different from a homogeneous medium. To verify this assumption the range of positrons in such a non-homogeneous medium has been simulated with EGS4. These simulations were performed as follows. A cylinder with a diameter of 10 mm was randomly packed with spheres with a diameter of 0.65 mm, similar to the diameter of the glass beads. The numerical rules used to create random packing of spheres were similar to those proposed by Visscher and Bolsterli [35]. Briefly, the spheres are dropped sequentially from a random point above the cylindrical bin. The floor of the cylinder is assumed to be flat. When the ball drops it hits sphere $k$ or the floor. If it contacted sphere $k$ it rolls down in a vertical plane along $k$ until it hits sphere $l$. If the sphere falls below
Figure 5.25. Simulated positron range in a packed bed and a homogeneous medium.

(—) Quartz tube (diameter 10 mm) filled with spheres. (—) Homogeneous medium having the same overall density as the packed bed.

sphere $k$ without hitting another sphere, it loses contact with sphere $k$ and the previous procedure is repeated. If it contacted sphere $l$ it then rolls downward in contact with both $k$, and $l$ until it contacts sphere $m$. If the contact with $k$, $l$, and $m$ is stable, it stops. Otherwise, it rolls on the double contact of the two lowest spheres, repeating the previous procedure. Any time a sphere hits the wall of the cylinder the wall is considered a contact point with the falling sphere. A stable position can therefore also be formed between the wall and two other spheres. The resulting packed bed had a height of 30 mm. The density of the spheres was equal to 3.0 g/cm$^3$ resulting in a packed density of 1.7 g/cm$^3$. To eliminate packing effects at the base of the cylinder the positrons were generated on a plane perpendicular to the cylinder at the center of the bed. Positrons were only generated in the void space between the spheres. The positrons were followed until their energy fell below 10 keV. Figure 5.25 shows the range of positrons in this packed bed. The results are compared with the range of positrons in a homogeneous medium with the same density as the packed bed. The range in the packed bed is almost identical to the homogeneous medium. The alternation of regions with high and low density (glass and air) can clearly be modeled by a medium with the same average density.

4.7 Correction of calculated PEP profiles

As mentioned in the introduction, if the mathematical model must correctly describe the results of PEP experiments, the model must include the influence of positron range and photon scattering. These effects are included in the sensitivity profiles for each reconstruction position, the sensitivity matrix ($S_{PEP}$). The mathematical solution can be corrected by convolution with this matrix. The results from the previous sections have
Figure 5.26. Simulated response curves for every detection position for $^{15}$O containing tracer molecules. Response curves are for a quartz reactor containing Pt/Al$_2$O$_3$ (bed length 35 mm) surrounded by glass beads inside the aluminum oven (see figure 5.4). The response of the whole detector (17 detection positions) is recorded for an $^{15}$O cylindrical source with a radius of 5 mm and zero width placed in this system at intervals of 0.25 mm.

shown that EGS4 can adequately simulate the response of the PEP detector for point sources. EGS4 will now be used to simulate the sensitivity profiles for the catalyst/reactor system to obtain a sensitivity matrix for this system. The geometry used for these simulations is identical to the geometry shown in figure 5.4. It includes the presence of a catalyst containing region, sandwiched between two regions containing a different medium (inert/glass beads). The different composition/density of these regions is included in the simulations. The sensitivity profiles were determined for a cylindrical source with an infinitely small length (a cylindrical slab). The radius of the cylinder was equal to the radius of the quartz reactor. The positrons were emitted randomly across the cylindrical source directly into the catalyst/inert material. This setup mimics the situation during PEP experiments where the gaseous radioactive molecules emit positrons throughout the filled reactor tube.

Figure 5.26 shows the simulated sensitivity profiles for every reconstruction position for $^{15}$O containing tracer molecules. The tracer $^{15}$O has been chosen to clearly demonstrate the effect of the positron range on the sensitivity profiles (this system is similar to the experimental setup in chapter 6). The most marked features of the profile will be discussed here. The position resolution for $^{15}$O molecules in the catalyst bed is very poor. The position resolution is the lowest at the center of the detector, and increases at the sides of the detector. The peak height of the sensitivity profiles also increases from the center towards both ends of the detector. These effects can all be explained by the difference in positron range in the catalyst and the beads. The density of the glass beads is four times higher than that of the catalyst. Figure 5.27 shows the difference in the number of annihilations at the catalyst-beads interface for an $^{15}$O line source. The results
Figure 5.27. Number of annihilations at the catalyst/glass beads interface.
A. Diagram showing the simulated setup used to determine the response shown in B. A quartz reactor containing the catalyst/glass beads interface has been filled homogeneously with $^{15}$O point sources. B. The $z$ value (axial direction) of the annihilation position of the emitted positrons is recorded. The $z$-axis is parallel to the reactor.

were obtained by recording the annihilation positions ($z$-values) of positrons emitted by $^{15}$O point sources randomly placed in the volume of the line source, as indicated in figure 5.27A. The catalyst-beads interface is placed at the origin of the axial direction. At the interface an increased amount of positrons are stopped on the side of the beads. The higher density of the beads stops the positrons from escaping from the lower density region (catalyst). The enhanced stopping in the glass beads medium causes the increase in position resolution and the increase in the peak height towards the sides of the detector. The sudden jump in the peak height of the profile in the glass beads medium can be explained by the enhanced positron stopping power of this medium. The positrons emitted at both sides of the $^{15}$O line source show the range of these positrons in the catalyst and glass beads (see figure 5.27). This range in the glass beads medium is much smaller than in the catalyst, due to the higher density of the beads. This means that positrons are stopped in a smaller volume and that therefore the activity per unit volume increases. This effect leads to the larger peaks observed in the beads medium.

The sensitivity profiles show a large degree of variation around the catalyst/beads interface. This variation might impose a problem if these profiles are to be used for correction of the mathematical model. During PEP experiments, the exact position of this
interface in relation to the detector is not known. Hence, it will be difficult to construct a correct sensitivity matrix for this setup. There are two possible solutions to this problem. The first is that the experimental data around the interface are not used for modeling. The second more elegant solution is that the density of the inert is chosen to be the same as the catalyst, thereby removing the distortion around the interface. The latter solution may not be applicable in every case. Both methods will be used in this study, the latter method is applied by coating the inert (glass beads) with the catalyst.

Figure 5.28 shows the results of the convolution correction on the mathematical results of a gas pulse flowing through a packed bed. The mathematical description of this system is given by equation (4.31). The profiles shown are for reconstruction positions 1, 5, 9, 13, and 17. The sensitivity profile shown in figure 5.19B (glass beads medium) has been used to correct the responses at every reconstruction position. For simplicity, it is assumed that the bed is packed with glass beads and that the sensitivity profiles for each position are equal. The main effect of this correction is the addition of a substantial background at all positions when the pulse comes within the field of view of the detector. A second effect, is that the shape of the pulse also changes due to the correction. The pulse gets wider and the relative height of the pulse increases at the end of the reactor. Thus, the limited position resolution of the detector will cause an overestimation of the dispersion coefficient if the correction is not applied. To examine this effect, the corrected profile (including the detector sensitivity) has been fitted to the model given by equation (4.31). The fitting procedure applied is given in chapter 4. This resulted in a decrease of the dispersion coefficient by almost 50%.

4.8 Line source calibrations

The PEP detector needs to be calibrated to correct the activity profile for differences in

112
sensitivity of the individual elements due to non-idealities of the hardware. These non-idealities are caused by differences in light output of the crystals and variances in the amplification by the photomultiplier tubes. A $^{22}$Na line source is used for the calibration procedure. It is also possible to perform the calibration with the moving $^{22}$Na point source, however, use of a line source simplifies the measurement procedure. The line source produces a homogeneous activity profile along the length of the detector. In principle, every reconstruction position should give an identical response, and deviations can be ascribed to differences in sensitivity of the detection elements. Correction consists of dividing the measured experimental tracer concentration at a certain reconstruction position by the response to the line source at this position followed by normalization, according to:

$$CP_{ip,\text{corr}} = R_{\text{max}} \frac{CP_{ip,\text{exp}}}{R_{ip,\text{line}}}$$  \hspace{1cm} (5.3)

where,

- $ip$ reconstruction position
- $CP_{\text{corr}}$ corrected concentration profile
- $CP_{\text{exp}}$ experimental concentration profile
- $R_{\text{line}}$ line source response
- $R_{\text{max}}$ maximum line source response (normalization factor)

The different detection pairs do not all measure the same amount of activity (detection volume). For example, direct opposite detection pairs detect a smaller region of the line source than an opposite-adjacent pair because part of the side faces of the crystals also contributes to the reconstruction process. In addition, the contribution of scattered photons is not equal for all the detection pairs. For instance, the outermost crystals can only receive scattered photons from one side. These effects are already included in the sensitivity profiles for every reconstruction position. Thus, application of equation (5.3) to an experimental PEP profile will result in an overcompensation.

Figure 5.29 shows the simulated response of the 17 reconstruction positions to a $^{22}$Na line source. The range of positrons does not influence the homogeneous distribution of activity in the line source, it was therefore omitted in these simulations. In addition to a positron, $^{22}$Na also emits a prompt gamma with an energy of 1274 keV. The effect of the prompt gamma was also included in the simulations. The response profile has a maximum at the center of the detector. The lower response at the sides of the detector is a result of the decreased contribution of scattered photons. The response profile shown in figure 5.29 was determined for a source distance of 80 mm. Simulations at other distances showed that the profile is rather insensitive to the distance. This is expected because the response only depends on the properties of the detector, and is independent of the positron range and properties of the line source. The line source only provides a homogeneous distribution of annihilation photons.

The line source clearly does not produce a linear response profile. Thus, when a PEP
profile is used for the fitting procedure (see previous section) the correction should include this non-linear response. The adapted overall correction is given by:

$$CP_{p,cor} = R_{\text{max}} \frac{CP_{p,exp}}{R_{p,\text{line}}} R_{p,\text{sim}}$$  \hspace{1cm} (5.4)

where,

$$R_{\text{sim}}$$ simulated response to a line source at \( r p \) (figure 5.29)

The line source calibrations have been performed at the distance used during the measurements. The distance independency of the simulated response profile requires that only a single profile needs to be simulated. Therefore, equation (5.4) can be used to correct each experimental profile with the measured line source response obtained at another distance. However, it is actually only necessary to determine the line source response at 80 mm and then apply equation (5.4).

4.9 Data treatment and interpretation

In the two previous sections the various steps have been described leading to the correction of the mathematical model and the experimental data. The mathematical model (DAE/PDE system, see chapter 4) is corrected by convolution with the sensitivity matrix \( S_{\text{PEP}} \). The convolution procedure is described in chapter 4 (equation 4.30). This matrix is obtained by simulation with EGS4. The matrix includes the influence of the positron emitter, source distance, densities of the catalyst and inert and the geometry of the aluminum oven and the PEP detector. Several matrices are shown in the Appendix which have been simulated to describe the various experimental conditions. The experimental results are corrected for differences in the sensitivity of the individual elements measured with the line source (equation 5.4).
The total procedure for the treatment of the experimental data and the results of the mathematical model is given below:

1. **Measurement of the reaction matrix** \((RM_{\text{exp}})\).
   This matrix displays the course of the positron emitter concentration as a function of position and time. Each row of the matrix describes the tracer concentration profile \((CP_{\text{exp}})\) along the axial axis of the reactor at a certain time. The matrix thus contains the tracer concentration profiles from \(t_0\) to \(t_{\text{end}}\).

2. **Measurement of the correction matrix** \((CM_{\text{exp}})\).
   The matrix contains the response of the detector to the \(^{22}\text{Na}\) line source at 80 mm as a function of time. If the calibration was performed at another distance then use this matrix. The values in each column (17 columns) of the matrix are summed to obtain \(R_{\text{line}}\).

3. **Simulate the line source response** \((R_{\text{sim}})\).
   The response of the PEP detector to a \(^{22}\text{Na}\) line source is simulated with EGS4 to obtain the response shown in figure 5.29.

4. **Simulate the reaction matrix** \((RM_{\text{calc}})\).
   Setup a combined DAE/PDE model describing the reactions taking place. The model contains the steady-state equations and the transient equations. Solve the model according to the procedure developed in chapter 4 to obtain \(RM_{\text{calc}}\). Each row of the matrix describes the simulated tracer concentration profile \((CP_{\text{calc}})\) along the axial axis of the reactor at a certain time. The matrix thus contains the simulated tracer concentration profiles from \(t_0\) to \(t_{\text{end}}\).

5. **Simulate the sensitivity matrix** \((S_{\text{PEP}})\).
   The sensitivity matrix is determined by simulations with EGS4. It describes the effects of the positron range and photon scattering in the experimental setup on the PEP detector response.

6. **Correct \(CP_{\text{exp}}\) to obtain \(CP_{\text{corr}}\)**.
   The measured tracer concentration at each reconstruction position is corrected according to equation (5.4) using the simulated \((R_{\text{sim}})\) and measured \((R_{\text{line}})\) \(^{22}\text{Na}\) line source response.

7. **Correct \(CP_{\text{calc}}\) with \(S_{\text{PEP}}\) to obtain \(CP_{\text{conv}}\)**.
   The simulated tracer concentration profile is corrected by convolution with the sensitivity matrix. This consists of multiplying the sensitivity matrix \((S_{\text{PEP}})\) with the simulated tracer concentration profile \((CP_{\text{PEP}})\) according to equation (4.30).

8. **Repeat steps 6 and 7 to construct the convoluted reaction matrix** \((RM_{\text{conv}})\).
   Steps 6 and 7 are repeated to fill the convoluted reaction matrix with the \(CP_{\text{conv}}\) at different times. These steps are repeated for all time points from \(t_0\) to \(t_{\text{end}}\).

9. \(RM_{\text{conv}}\) can be compared with \(RM_{\text{exp}}\).
CHAPTER 5

5 CONCLUSION

Reaction kinetic data can only be extracted from a PEP profile with the aid of a mathematical model. To give a correct interpretation of the experimental PEP profile, the limited position resolution (position accuracy) of the detector should be taken into account. This effect is added to the mathematical solution by convolution with the sensitivity profiles for each reconstruction position. The sensitivity profiles and the position resolution are influenced by the range of positrons and the scattering of photons. The Monte Carlo code EGS4 has been used to describe the transport of photons and positrons during PEP experiments.

Scattering of photons in the reactor/oven and in the detection elements causes the photons to deflect from their straight path. Consequently, the photon can be detected in a neighboring (faulty) detection element resulting in mis-positioning of the annihilation position. This has a negative effect on the position resolution of the detector. Scattering in the BGO crystals has the largest negative effect on the position resolution. Scattering in the oven only increases the amount of nonspecific reconstructions (background level) of the sensitivity profiles.

When a positron is emitted it travels a certain distance, the positron range, before it annihilates. The annihilation position is therefore not equivalent to the position of the decaying tracer, causing a further decrease of the position resolution. The range depends on the energy of the positron and the density of the catalyst and inert material used in the reactor. Denser materials decrease the positron range which in turn increases the position resolution.

The EGS4 simulation results have been compared with experimental data from $^{22}$Na and $^{11}$C point sources. The agreement with the experimental data for $^{22}$Na is very good, showing that photon transport in the PEP system is described accurately by EGS4. The response profiles of low activity $^{11}$C point sources are also described sufficiently well by EGS4, which is not true for high activity $^{11}$C point sources. EGS4 can predict the width of the profile but is unable to predict the number of nonspecific reconstructions. The large number of positrons emitted by this source substantially increases the amount of background noise at each reconstruction position. The high background is due to coincident detection of photons from two different annihilation events. Agreement with the experimental data for high activity sources can only be achieved when the increased background level is taken into account.

As mentioned, the experimental results with the point sources can all be predicted with the EGS4 code. Therefore, this code was used to predict the sensitivity profiles of gaseous positron emitters in the catalytic reactor. The difference in the densities of the inert (glass beads) and the catalyst has a large effect on the sensitivity profiles around the interface between these materials. This effect can hamper the convolution procedure for correction of the mathematical solution because the exact position of this interface is not known. Therefore, it is best to use an inert material with the same density as the catalyst being used.
The convolution procedure has two effects on the corrected profiles. The first is that it adds a substantial amount of background noise to the simulated profiles, which is also seen experimentally. The second effect is that the shape of the profile is also altered, influencing the parameters which are extracted from the PEP profiles with the mathematical model.

6 SYMBOLS AND ABBREVIATIONS

\( \alpha \) detection angle
\( b \) crystal width (5.1 mm)
BGO bismuth germanium oxide (Bi\(_4\)Ge\(_3\)O\(_{12}\))
\( CM_{\text{exp}} \) experimental correction matrix
\( CP_{\text{calc}} \) simulated tracer concentration profile
\( CP_{\text{conv}} \) convoluted concentration profile
\( CP_{\text{cor}} \) corrected concentration profile
\( CP_{\text{exp}} \) experimental concentration profile
DAE differential algebraic equations
EGS4 electron gamma shower, version 4
FWHM full width at half maximum
\( h \) source distance
\( l \) crystal length (100 mm)
PDE partial differential equation
PEP positron emission profiling
\( R_{\text{line}} \) line source response
\( R_{\text{max}} \) maximum response of the line source
\( R_{\text{m,calc}} \) simulated reaction matrix
\( R_{\text{M,conv}} \) convoluted reaction matrix
\( R_{\text{M,exp}} \) experimental reaction matrix
\( r_p \) reconstruction position
\( R_{\text{sim}} \) simulated response to a line source
\( S_{\text{PEP}} \) sensitivity matrix
\( t_0 \) start time
\( t_{\text{end}} \) end time
\( x \) axis along the length of the crystal
\( z \) source position
CHAPTER 5

7 REFERENCES


DECOMPOSITION OF $N_2^{15}O$ OVER Pt/Al$_2$O$_3$

1. Spill-over of $^{15}O$ formed during the decomposition

ABSTRACT

The decomposition of nitrous oxide over Pt/Al$_2$O$_3$ was studied with positron emission profiling. The behavior of oxygen formed by the decomposition was determined using $N_2^{15}O$ as a tracer. It was found that the formed $^{15}O$ atoms were retained on the catalyst. Removal of $^{15}O$ by associative desorption did not occur within the given analysis time (15 minutes). It was shown that migration (spill-over) of the $^{15}O$ to the support was the only possible explanation for the experimental results. Once on the support the $^{15}O$ atoms mix with the huge $^{16}O$ pool already present on and in the support, this reduces the chance that $^{15}O$ atoms return to the metal surface and desorb as $^{15}OO$. The spill-over of $^{15}O$ on this catalyst does not only occur during the decomposition of $N_2^{15}O$ but also during the oxidation of CO with $^{15}O_2$. This indicates that the precursor of the adsorbed $^{15}O$ does not influence the spill-over of oxygen. The results presented here are further evidence that spill-over of reactive species occurs under realistic conditions.
1 INTRODUCTION

Interest in nitrous oxide (N₂O) has increased since it is known to play an important role in the earth’s atmosphere, being responsible for ozone depletion and acting as a greenhouse gas. N₂O is 300 times more potent in greenhouse warming than CO₂ [1], therefore, a decrease in its emission is very beneficial. A method to reduce its emission is by catalytic decomposition, hereby converting it into nitrogen and oxygen [2]. The decomposition of N₂O over platinum metal has been the subject of various studies [3-4] [5-9] since the initial experiments by Hinshelwood and Prichard in 1925 [10]. The decomposition of N₂O on platinum consists of adsorption of N₂O on the metal surface followed by dissociation into nitrogen and an adsorbed oxygen. Oxygen is removed through the desorption of two adsorbed atoms as O₂. This mechanism is given by the following equations:

\[
N₂O + \star \xrightleftharpoons[\kappa_{-1}]{\kappa_{1}} N₂O\star \tag{6.1}
\]

\[
N₂O\star \xrightarrow{\kappa_{2}} N₂ + O\star \tag{6.2}
\]

\[
O\star + O\star \xrightleftharpoons[\kappa_{3}]^{\kappa_{4}} O₂ + 2\star \tag{6.3}
\]

It has been shown that the product O₂ has a retarding effect on the decomposition reaction. Early studies [9] even mentioned that O₂ formed in the reaction is more effective in inhibiting the reaction than is added oxygen.

The catalytic behavior of platinum as a decomposition catalyst can be studied with positron emission profiling (PEP) [11,12]. With the aid of positron emitting molecules, PEP allows in-situ monitoring of gas and surface concentrations in both time and space. This information can be used to deduct the elementary reactions taking place and their rate constants [13-15]. Suitable positron emitters to study this reaction are N₂¹⁵O or ¹⁵NNO. The oxygen labeled form is preferred in view of the previous mentioned effect of oxygen on the decomposition reaction. In addition, nitrogen is not expected to have a strong interaction with the catalyst surface since it is immediately released after dissociation has taken place.

The present study will focus on the decomposition of N₂O on supported platinum which has not been examined previously. Using labeled N₂¹⁵O as a tracer it is possible to follow the behavior of the oxygen atoms formed by the decomposition. This should allow examination of the retarding effect of oxygen after its desorption from the platinum surface. In addition, it has been reported that reactive species, like adsorbed oxygen atoms, can migrate to the support. This effect has been defined as spill-over and consists of the migration of dissociated species from the solid phase where they are formed to another solid phase where it does not directly adsorb. PEP has been used to determine the magnitude of these effects during the decomposition of N₂¹⁵O on Pt/Al₂O₃.
2 EXPERIMENTAL

2.1 Materials
The gases were obtained from Hoekloos, and were used without further purification. The \( \text{N}_2\text{O} \) was supplied from a cylinder containing a mixture of 5\% \( \text{N}_2\text{O} \) in helium. The helium had a purity of 99.999\%, and contains small amounts (2-4 ppm) of \( \text{O}_2 \) as an impurity. The 0.3 w\% Pt/Al\(_2\)O\(_3\) catalyst (density: 0.45 kg/m\(^3\)) was obtained from Johnson-Matthey. The catalyst was characterized by CO adsorption. The platinum surface area determined by CO adsorption was 284 m\(^2\)/g Pt. Assuming hemispherical platinum particles on the surface of Al\(_2\)O\(_3\), the particle size was determined from the ratio between the platinum metal volume and surface area. This resulted in particles with an average diameter of 2 nm. The dispersion is defined as the number of adsorbed CO molecules divided by the total number of Pt atoms. This resulted in a dispersion of 56\%.

2.2 \( \text{N}_2\text{O}^{15} \) production
The production of \( \text{N}_2\text{O}^{15} \) has been described in chapter 3. Since the procedure was slightly modified, a brief description of the method will be given. Nitrogen gas was irradiated with 7 MeV deuterons in a cylindrical target to produce \( \text{N}_2\text{O}^{15} \), \( \text{N}_2\text{O}^{15} \) and trace amounts of \( \text{N}_2\text{O} \). A beam current of 1 \( \mu \text{A} \) was used to produce the isotopes. The \( \text{N}_2\text{O}^{15} \) was selectively removed from the target effluent by adsorption on mordenite at 173 K. The adsorbed product (\( \text{N}_2\text{O}^{15} \) and \( \text{N}_2\text{O}^{15} \)) was removed by electrically heating the adsorbent in a stream of helium (38 ml/min). The resulting pulse was injected into the reaction feed mixture flowing over the catalyst. An adsorption time of 30 s was used to minimize the amount of non-labeled \( \text{N}_2\text{O} \) in the desorbed product. The higher beam current compensated the loss in activity due to the shorter adsorption time. In this way, a sufficient amount of \( \text{N}_2\text{O}^{15} \) (several fmol) was adsorbed to perform PEP experiments. The amount of non-labeled \( \text{N}_2\text{O} \) present in the desorbed product is 18 nmol. Assuming a pulse width of 3 seconds the average amount of non-labeled \( \text{N}_2\text{O} \) is still a factor 1000 lower than the steady-state concentration of \( \text{N}_2\text{O} \). It is therefore assumed that the injected pulse of \( \text{N}_2\text{O}/\text{N}_2\text{O}^{15} \) will not influence the steady-state reaction.

2.3 PEP experiments
A thorough description of the procedure to perform the PEP experiments is given in chapter 2, therefore, only a short description will be given here. The quartz reactor was loaded with 1.45 g of the 0.3\% Pt/Al\(_2\)O\(_3\) catalyst, resulting in a bed length of 4.1 cm, and was further filled up with glass beads (diameter 0.65 mm) on both sides of the catalyst bed. The catalyst was pretreated with a mixture of 2\% \( \text{O}_2/\text{He} \) at 775 K for 1 hour. When performing pulse experiments (without \( \text{N}_2\text{O} \) in the reaction mixture), the catalyst was pretreated with a mixture of 5\% \( \text{CO}/\text{He} \) at 475 K. Non-reacted CO was removed by heating the catalyst in helium for 1 hour at 775 K. The catalyst temperature was then allowed to reach the reaction temperature while flowing with helium (50 ml/min). Upon reaching the reaction temperature, 2500 ppm of \( \text{N}_2\text{O} \) was added to the reaction mixture.
and the flow was adjusted to 40 ml/min. The catalyst was allowed to reach steady-state for at least 10 hours. Upon subsequent changes (rise) in the temperature the catalyst reached steady-state in less than 30 minutes. The conversion of N$_2^{15}$O over Pt/Al$_2$O$_3$ was investigated in the temperature range from 675 K to 825 K.

PEP experiments were performed by injecting the adsorbed N$_2^{15}$O/N$_2$O in the reaction mixture to the catalyst. Because the amount of radioactivity in the injected pulse was not very high the distance between the detection banks was adjusted to 160 mm (distance to the center of the reactor is 80 mm). A sampling time of 1 second was used for recording the PEP profiles. The PEP profile contains the $^{15}$O activity measured at 17 equidistant positions in the reactor as a function of time. The profiles were corrected for the decay of $^{15}$O during the analysis time. The results from the profile can be displayed as a function of time at a specific position in the reactor (time profile). The other possibility is that the results are displayed as a function of position at a specific time point (position profile).

3 RESULTS

3.1 Decomposition of N$_2^{15}$O over Pt/Al$_2$O$_3$ and Al$_2$O$_3$

The PEP technique allows determination of the N$_2^{15}$O concentration in the reactor as a function of time and position. The section of the reactor being analyzed by the PEP detector contains the entire catalyst bed and part of the inert material. This situation is depicted by the schematic in figure 6.1. The decomposition of a pulse N$_2^{15}$O during steady-state decomposition of N$_2$O over Pt/Al$_2$O$_3$ at 725 K is shown in figure 6.1. Each panel shows the response as a function of time (time profile) at different positions in the reactor. Figure 6.1A shows the signal in the inert material, and as such displays the shape of the incoming N$_2^{15}$O pulse. Figures 6.1B, C, and D show the time profiles at different positions in the catalyst bed. As can be seen, the N$_2^{15}$O pulse passes through the catalyst bed. After passage, a residual amount of activity is still present on the catalyst which does not decrease with time. This indicates that an $^{15}$O containing molecule (e.g. N$_2^{15}$O or $^{16}$O) is retained on the catalyst. Figure 6.2 shows the time profiles at the beginning of the catalyst bed at different temperatures. Increasing the temperature from 675 K to 825 K increases the amount of $^{15}$O that is retained on the catalyst. The increase in temperature does not influence the residence time of the label on the catalyst. Within the analysis time, the label is not removed as this would result in a decrease in the amount of measured activity. The analysis time is limited because the half-life of $^{15}$O is short (2 minutes). After 3 half-lives the amount of residual activity before decay correction is very low which results in a high noise level after correction. Therefore, the results are only given for the first minutes after introduction of the pulse. Figure 6.3 shows the time profile at the beginning of the catalyst bed at the highest temperature (825 K) for a longer analysis time. At this temperature, a sufficient amount of radioactivity is retained allowing the analysis time to be increased. This time profile shows that the amount of label on the catalyst remains constant for at least 15 minutes and is therefore not removed.
Figure 6.1. PEP time profiles of the decomposition of $\text{N}_2^{15}\text{O}$ over Pt/Al$_2$O$_3$ operating under steady-state conditions at 725K.

The PEP response has been measured at different axial positions in the reactor as a function of time. The positions are shown in the schematic. The labels in the schematic correspond to the figure labels. BGO is a bismuth germanium oxide crystal used for the detection. The profiles were corrected for the decay of $^{15}\text{O}$ during the measurement.

The amount of activity present in the effluent is monitored with a sensitive NaI detector. The sensitivity of this detector is much higher than that of the PEP detector. The profiles measured at the reactor exit are shown in figure 6.4. The amount of label present in the...
Figure 6.2. PEP time profiles of the decomposition of $\text{N}_2^{15}\text{O}$ over Pt/Al$_2$O$_3$ measured at the beginning of the catalyst bed at different temperatures (675 K – 825 K).

The beginning of the catalyst bed corresponds to position B in the schematic in figure 6.1.

effluent strongly depends on the reaction temperature. At high temperatures, most of the radioactivity remains in the reactor and the opposite is true for low temperatures. The composition of the reactor effluent was determined by gas chromatography. The decomposition of N$_2$O produces both N$_2$ and O$_2$, and both products are present in the analysis of the non-labeled molecules. Analysis of the labeled fraction only shows the presence of N$_2^{15}$O. Extensive examination of the composition by taking GC samples at different time points of the labeled target effluent did not reveal the presence of $^{15}$O$_2$. The total amount of N$_2^{15}$O present in the target effluent was determined by integration of the outlet signals (figure 6.4). The N$_2^{15}$O conversion was determined with these values. A comparison between the labeled and non-labeled conversion is shown in figure 6.5. As can be seen, the conversions are nearly identical. Thus, the amount of N$_2^{15}$O present in the target effluent is a good measure for the decomposition activity of the catalyst.

The decomposition activity of the support (Al$_2$O$_3$) was determined by evaluating the decomposition of a labeled pulse (N$_2^{15}$O) only. The activity of the support is expected to be low. Therefore, evaluation of the conversion with N$_2^{15}$O is preferred because it is more sensitive than analysis of the N$_2$O conversion. The experiments were performed by injecting a pulse of N$_2^{15}$O in a stream of helium going to the catalyst. No N$_2$O was added to increase the sensitivity of the system. At temperatures above 650 K radioactivity starts being retained on the support. The retention of labeled molecules is probably not due to the adsorption of N$_2^{15}$O on Al$_2$O$_3$ because no radioactivity is present on the support at lower temperatures. The activity on the support displays the same behavior as seen with the platinum catalyst, hence, initially incorporated label is not removed from the support. The conversion was therefore determined from the fraction of N$_2^{15}$O which was present in the reactor effluent. Figure 6.6 shows the conversion of N$_2^{15}$O over Al$_2$O$_3$. The activity of Al$_2$O$_3$ is much lower (5-fold) than that of Pt/Al$_2$O$_3$. When the N$_2^{15}$O pulse is injected in
Figure 6.3. PEP time profile of the decomposition of N$_2^{15}$O at 825 K for an analysis time of 15 minutes.
The beginning of the catalyst bed corresponds to position B shown in the schematic in figure 6.1. A longer analysis time was used to show that the amount of radioactivity on the catalyst is constant with time.

a stream of He/N$_2$O (steady-state) the activity even decreases by an additional factor of 2. Thus, under the steady-state conditions used during the experiments with Pt/Al$_2$O$_3$ the activity of the support can be neglected.

3.2 Interaction of oxygen with Pt/Al$_2$O$_3$ and Al$_2$O$_3$

The interaction of O$_2$ molecules with the support and Pt/Al$_2$O$_3$ can be determined by examining the adsorption/exchange of $^{15}$OO molecules with these materials. To this end, the materials were subjected to a pulse of $^{15}$OO in helium at several temperatures. The amount of $^{15}$O that remained on the support or catalyst after passage of the pulse was recorded. Figure 6.7 shows the interaction of $^{15}$OO with the support as a function of the temperature. The support had been pretreated with helium for 30 minutes prior to addition of $^{15}$OO. The response of the PEP detector indicates the amount of $^{15}$O still present on the entire Al$_2$O$_3$ bed after 3 minutes. The amount of label retained on the support increases experimentally with increasing temperature. The radioactivity remaining on the support can originate from either $^{15}$OO or $^{15}$O. Since the label only starts being retained at higher temperatures this probably indicates that a reaction is responsible for this effect. Thus, the $^{15}$OO molecules exchange their labeled oxygen atom with the support. This exchange is absent when the support is pretreated with a mixture of helium and oxygen (steady-state conditions), as indicated in figure 6.7. The amount of exchange is relatively low at all temperatures because hardly any $^{15}$OO is consumed by the exchange. This is also indicated in figure 6.7 by the $^{15}$OO conversion level.
The interaction of $^{15}$OO with the catalyst (Pt/Al$_2$O$_3$) is completely different. The added $^{15}$OO pulse is completely consumed when the catalyst has been pretreated in helium. Figure 6.8 shows the distribution of $^{15}$O along the catalyst bed (position profile) after
addition of the $^{15}\text{O}_2$ pulse. As can be seen, the whole $^{15}\text{O}_2$ pulse is adsorbed directly at the beginning of the catalyst bed. These results are compared with the distribution of $^{15}\text{O}$ when only the support is used. The amount of radioactivity adsorbed on the support is very small compared to the catalyst. The $^{15}\text{O}$ is also distributed evenly along the support, indicating that the amount of $^{15}\text{O}_2$ present in the gas phase is not limiting in this case.

Figure 6.5. $\text{N}_2\text{O}$ and $\text{N}_2^{15}\text{O}$ conversion over Pt/Al$_2$O$_3$ as a function of temperature. (—) Conversion of $\text{N}_2\text{O}$. (○) Conversion of $\text{N}_2^{15}\text{O}$. The conversion of $\text{N}_2^{15}\text{O}$ was determined by dividing the integrated $^{15}\text{O}$ reactor effluent profile at a certain temperature by the integrated response at 0% conversion (650 K).
Figure 6.6. N$_2^{15}$O conversion over Al$_2$O$_3$ as a function of temperature.
The results were obtained by determining the conversion level of the N$_2^{15}$O pulse only (N$_2^{15}$O in He).
The point marked with "steady-state" was obtained by injecting the N$_2^{15}$O pulse into a gas stream
containing N$_2$O (N$_2^{15}$O in N$_2$O/He). The conversion of N$_2^{15}$O is determined as described previously in
figure 6.5.

4 DISCUSSION

The PEP technique allows reactions to be followed under steady-state conditions. It
consists of adding a minute amount of labeled molecules (i.e. N$_2^{15}$O) to the reaction
mixture. The interaction of the labeled molecules with the catalyst can be followed with
the PEP detector. Since the molecule is chemically identical to the reactant, it will
display the same behavior. The addition of N$_2^{15}$O molecules to the reaction mixture
therefore allows the decomposition of N$_2$O to be probed.
The decomposition of N$_2^{15}$O under steady-state conditions over the Pt/Al$_2$O$_3$ catalyst
displays an unusual behavior. The results show that an $^{15}$O containing compound is
retained on the catalyst. This $^{15}$O can originate from either $^{15}$O, a product of the
decomposition, or from adsorbed N$_2^{15}$O. It is not possible to distinguish between these
possibilities with the PEP technique. It is not likely that adsorbed N$_2^{15}$O is the retained
species, since this would mean that N$_2^{15}$O remains on the surface even at 100% N$_2$O
conversion. At low temperatures (<675 K) no labeled species are retained on the catalyst,
this only occurs at the onset temperature of the decomposition reaction. This indicates
that the decomposition reaction itself is the source of the retained species. In addition,
the fraction of label that remains on the catalyst matches the conversion level of N$_2$O
(figure 6.5). This also shows that exchange of oxygen from N$_2^{15}$O or N$_2$O is not
responsible for the retention of $^{15}$O. Hence, $^{15}$O must be responsible for the signal
observed on the catalyst. From these results only it is impossible to exclude the possibility
that some N$_2^{15}$O remains adsorbed. To examine this possibility PEP experiments
performed with $^{15}$N$_2$O instead of N$_2^{15}$O would be required. However, N$_2$O adsorbs weakly
on metal surfaces like Pt [16]. In addition, Schmidt et al. [17] reported that N$_2$O does not
Figure 6.7. The interaction of $^{15}$O with $\text{Al}_2\text{O}_3$ as a function of temperature.

(©) The exchange activity of $^{15}$O with $\text{Al}_2\text{O}_3$ was measured by determining the total PEP response after injection of an $^{15}$O pulse into a He stream going to the reactor containing $\gamma\text{Al}_2\text{O}_3$ ($^{15}$OO in He). The total PEP response is the summation of the amount of activity measured at every reconstruction position. The point marked with "steady-state" was obtained by injecting the $^{15}$O pulse into a gas stream containing $\text{O}_2$ ($^{15}$OO in $\text{O}_2$/He). (©) The amount of $^{15}$O still present in the reactor effluent after exchange with $\gamma\text{Al}_2\text{O}_3$. The response was normalized to the average concentration measured. The constant level of the $^{15}$OO amount indicates that it is hardly consumed.

appear to chemisorb on platinum in UHV experiments in the temperature range from 700 to 1600 K.

The previous results show that $^{15}$O produced during the decomposition of $\text{N}_2^{15}$O is deposited on the catalyst. The use of $^{15}$O with its short half-life limits the analysis time. If a sufficient amount of radioactivity is retained, the system can be analyzed for 15 minutes. Therefore, it is not possible to observe whether the $^{15}$O atoms are permanently bound to the catalyst. However, results at the highest temperature (825 K) indicate that the $^{15}$O atoms are not removed within 15 minutes. Five possible explanations can be given for the long retention of $^{15}$O on the catalyst:

1. $^{15}$O and $^{16}$O remain adsorbed on the platinum surface.
2. Bulk oxidation of platinum.
3. Decomposition of $\text{N}_2^{15}$O by the support or exchange of oxygen from $\text{N}_2^{15}$O with the support, followed by $^{15}$O bulk diffusion.
4. Exchange of $^{15}$O$_2$ with the support.
5. Migration of $^{15}$O atoms from platinum to the support (oxygen spill-over), followed by bulk diffusion.

These possibilities will be discussed in more detail now. The unusual behavior of $^{15}$O is not related to an abnormality of the technique preventing the desorption of $^{15}$O. Results on the decomposition of $\text{N}_2^{15}$O over ion-exchanged ZSM-5 catalysts (chapter 8) and Co-Rh hydrotalcites (results not shown) indicate that $^{15}$O$_2$ can be formed and reaches the reactor exit under reaction conditions.
Figure 6.8. Comparison between the $^{15}$O exchange activity of Pt/Al$_2$O$_3$ and Al$_2$O$_3$. The PEP position profiles were measured 100 s after an injection of an $^{15}$O pulse in He. (O) Adsorbed amount of $^{15}$O on the Pt/Al$_2$O$_3$ catalyst as a function of the axial position in the catalyst bed. (□) Adsorbed amount of $^{15}$O on Al$_2$O$_3$. Note that the measured amount was multiplied by a factor 10 to obtain the results shown.

Decomposition of N$_2$O over platinum produces N$_2$ and an adsorbed O atom (O$_{ads}$) [3,6,8-10,18]. The O$_{ads}$ is removed from the metal surface by associative desorption producing gas phase O$_2$ [19-24]. If $^{15}$O remains adsorbed on the platinum surface, the surface would be covered with $^{15}$O$_{ads}$ and $^{16}$O$_{ads}$ because the $^{16}$O atoms display the same behavior as the $^{15}$O atoms. It is known that O$_{ads}$ inhibits the decomposition of N$_2$O [4,9,10,20]. Under the steady-state conditions used here, the surface would be poisoned within 3 seconds by O$_{ads}$ at the highest temperature (complete N$_2$O conversion). This clearly does not occur, because decomposition continues to take place before and after injection of the N$_2$$^{15}$O pulse. This rules out the first possibility. The second possibility was shown not to occur for platinum [25]. Within the temperature range from 200 to 900 K no bulk oxide phases are formed on platinum.

The decomposition of N$_2$O over Al$_2$O$_3$ has been reported to start at a temperature of 650 K [26]. However, Al$_2$O$_3$ does not appear to be an active decomposition catalyst. The activity of the support was also determined by evaluating the decomposition of only N$_2$$^{15}$O. The results (figure 6.6) indicate that the support is active in this case. The label is also retained on the support just as on the Pt/Al$_2$O$_3$ catalyst. However, the decomposition activity is 5 times lower and decreases even further under steady-state conditions. The retention of $^{15}$O on the support might be due to the exchange of $^{15}$O from N$_2$$^{15}$O with $^{16}$O from the support. This is not likely because the amount of converted N$_2$$^{15}$O is similar to the amount of N$_2$O which is converted under steady-state conditions. Furthermore, the low amount of $^{15}$O retained on Al$_2$O$_3$ also indicates that exchange of $^{15}$O from N$_2$$^{15}$O with Al$_2$O$_3$ can not be solely responsible for the deposition of $^{15}$O on the catalyst. If oxygen exchange with the support by N$_2$O or N$_2$$^{15}$O would be very efficient it is expected that $^{15}$O
could be removed again by N$_2$O. These arguments rule out possibility 3. The results of the decomposition of N$_2^{15}$O on Al$_2$O$_3$ do show that $^{15}$O which is deposited on the surface of the support is also retained. This retention is probably due to the exchange of formed $^{15}$O with oxygen atoms in Al$_2$O$_3$. This exchange prevents the removal of $^{15}$O from the support. The exchange of $^{15}$OO with Al$_2$O$_3$ might also be responsible for the observed retention of $^{15}$O on the catalyst. However, this process should be very efficient, because otherwise $^{15}$OO would be observed at reactor exit. Oxygen exchange with the support does occur, but with a very low efficiency. Actually, exchange only takes place when the support is pretreated with He. Pretreatment and injection of the $^{15}$OO pulse in a He/O$_2$ mixture almost completely prevents this exchange. When only helium is present each O$_2$ molecule which participates in the exchange reaction contains $^{15}$O. Addition of oxygen to the reaction mixture has a rigorous effect on the $^{15}$OO/O$_2$ ratio. This decreases the chance that an $^{15}$O containing O$_2$ molecule can exchange with the support. This indicates that only a small amount of sites is available for exchange. The low activity of Al$_2$O$_3$ in the exchange with gaseous O$_2$ has also been shown in several other studies [27-29]. The previous discussion has shown that $^{15}$OO exchange with the support can not be responsible for the observed retention of $^{15}$O, rejecting possibility 4.

Comparing the amount of $^{15}$OO exchange with the catalyst and the support shows that adsorption of $^{15}$OO or exchange with the catalyst is very efficient. The added $^{15}$OO is completely adsorbed/exchanged at the beginning of the catalyst bed. The efficient adsorption of $^{15}$OO with the catalyst might also be the cause of the seemingly slow removal of $^{15}$O. In this case, $^{15}$OO which desorbs from the metal surface immediately adsorbs again in the vicinity of the desorption location. Hence, the removal of $^{15}$O is controlled by a continuous desorption-adsorption cycle. During each cycle, isotopic mixing on the metal surface further influences the removal of $^{15}$O by desorption. To exclude this possibility, a pulse of $^{15}$OO has also been added under steady-state reaction conditions. In this case, $^{15}$O is also retained, but $^{15}$OO is also found in the reactor effluent. Re-adsorption of $^{15}$OO under reaction conditions is not efficient enough to prevent $^{15}$OO from escaping the catalyst bed. Thus, a continuous desorption-adsorption cycle cannot be responsible for the retention of $^{15}$O.

This leaves the migration of $^{15}$O atoms from platinum to the support as the only explanation for the retention of $^{15}$O on the catalyst. This effect is known as spill-over. Spill-over of dissociated species such as hydrogen and oxygen on a carrier (e.g. Al$_2$O$_3$, SiO$_2$, and carbon) was first shown by Boudart et al. [30]. Since then the subject has received a great deal of attention [31,32]. The most direct evidence for the spill-over of oxygen was obtained in studies of the removal of coke from a deactivated platinum reforming catalyst [33]. The spill-over of oxygen atoms ($^{15}$O) seems to be the explanation for the results presented here. To ascertain that the $^{15}$O atoms are not present on the platinum surface, attempts were made to remove the atoms with CO. To this end, a pulse of N$_2^{15}$O was allowed to react with the catalyst under steady-state conditions, after which the reaction mixture was changed to CO/He. At temperatures above 525 K, adsorbed oxygen is converted to C$^{15}$OO which does not adsorb on the catalyst. The addition of CO did not remove $^{15}$O from the catalyst. Hence, the labeled atoms must reside on the support.
Figure 6.9. Schematic of the decomposition of N$_2^{15}$O over Pt/Al$_2$O$_3$.
A graphical representation of the decomposition mechanism of N$_2^{15}$O, as described in the discussion, is shown here. The schematic shows the fate of the labeled oxygen atom ($^{15}$O) formed during the decomposition of N$_2^{15}$O. The $^{15}$O atom is rapidly transferred to the support (Al$_2$O$_3$) where it mixes with $^{16}$O atoms present on the surface and in the bulk of Al$_2$O$_3$. As a result, desorption of labeled molecules hardly occurs. Deposition of $^{15}$O atoms due to direct exchange/exchange of N$_2^{15}$O with the support occurs with a low efficiency. Removal of $^{15}$O from the platinum surface or the support by exchange with N$_2^{16}$O does not take place.

The migration rate of $^{15}$O to the support is faster than the desorption rate of $^{15}$OO, as was shown by the absence of any $^{15}$OO in the target effluent. Martin and Duprez [29] have also analyzed the migration speed of oxygen atoms from a noble metal to the support and back. They deduced the oxygen mobility from the amount of isotopic exchange of $^{18}$O$_2$ with $^{16}$O from the support. Their results with Pt/Al$_2$O$_3$ only indicated that the slow desorption of oxygen from platinum was the rate controlling step in the exchange. Using other noble metals for which the desorption of oxygen was not rate controlling (e.g. Rh) they were still not able to determine the migration efficiency of oxygen atoms from the metal to the support. They assumed that isotopic exchange on Rh/Al$_2$O$_3$ was controlled by the migration of atomic oxygen across the support. As mentioned, the spill-over of $^{15}$O may be an efficient process due to the slow desorption of oxygen. To determine the efficiency of spill-over for the Pt/Al$_2$O$_3$ catalyst used here, the amount of spill-over was determined during the oxidation of CO with $^{18}$OO. The catalyst was allowed to reach steady-state in a stream of O$_2$ and CO at 550 K. Under these conditions (excess of CO) all the O$_2$ is converted to CO$_2$. A pulse of $^{18}$OO was then added to the reaction mixture and the PEP response was recorded. It is expected that $^{15}$OO would be converted to C$^{15}$OO in this case. The results showed that even at 100% O$_2$ conversion no C$^{15}$OO nor $^{15}$OO could be found in the reactor effluent. All the $^{15}$O is adsorbed at the beginning of the catalyst bed and remains bound to the catalyst. Thus, even under these conditions $^{15}$O is preferentially transported to the support. This indicates that spill-over is an efficient process on this Pt/Al$_2$O$_3$ catalyst, with a rate that exceeds the rate of oxygen removal by CO. The small Pt (diameter 2 nm) particles on Al$_2$O$_3$ are likely to be responsible for the fast exchange of oxygen atoms from the metal surface to the support. Abderrahim and Duprez [27,28] have shown that the rate of exchange is essentially a function of the dimension of the perimeter of the metal/support interface. Hence, small particles are more effective in the exchange than large particles.
The results obtained for the oxidation of CO by $^{15}$O$_2$ have two major implications. First, it shows that spill-over also occurs under reducing conditions, indicating that the formation of platinum oxides is not responsible for the retention of $^{15}$O. Secondly, spill-over is not dependent on the precursor from which adsorbed $^{15}$O atoms are formed, both N$_2$$^{15}$O and $^{15}$O$_2$ produce $^{15}$O which can spill-over.

The following mechanism is proposed for the decomposition of N$_2$$^{15}$O on a Pt/Al$_2$O$_3$ catalyst with small Pt particles. A schematic of this mechanism is shown in figure 6.9. The decomposition reaction starts with adsorption of N$_2$$^{15}$O on the platinum surface. The adsorbed N$_2$$^{15}$O is instantaneously dissociated into N$_2$ and an adsorbed $^{15}$O atom. The adsorbed $^{15}$O rapidly migrates to the metal/support interface. The migration rate of $^{15}$O is fast enough to prevent associative desorption of $^{15}$OO during its course to the interface. At the interface $^{15}$O atoms exchange with $^{16}$O atoms already present on the support (spill-over). Once on the support the $^{15}$O atoms mix with the $^{16}$O pool on the surface. The chance that an $^{15}$O exchanges back on the metal surface and is removed through desorption is small, because of the excessive amount of $^{16}$O atoms on the support. Furthermore, bulk diffusion of $^{15}$O can also occur. In this case, $^{15}$O atoms are exchanged with $^{16}$O atoms from Al$_2$O$_3$. Thus, the support acts as a huge tank containing mainly $^{16}$O and a very small amount of $^{15}$O, therefore, the chance that an $^{15}$O atom is removed from this tank is very small. This explains the long retention of $^{15}$O on the catalyst.

5 CONCLUSION

The decomposition of N$_2$$^{15}$O produces both gas phase N$_2$ and adsorbed $^{15}$O atoms. The $^{15}$O atoms migrate (spill-over) to the support where they remain retained. The support acts as a large $^{16}$O containing reservoir from which the added $^{15}$O atoms are very slowly released. The use of $^{15}$O as a label limits the analysis time, thus it is not possible to observe whether the oxygen atoms remain retained indefinitely. In principle, spill-over could also be observed with non-radioactive N$_2$$^{18}$O. In this case, only the reactor effluent can be monitored (i.e. by mass spectrometry). Since the removal of oxygen atoms is slow, this would probably lead to the vague conclusion that the label is retained somewhere in the reactor. The PEP technique offers the advantage that the position of the retained oxygen atoms can be monitored, showing that the labeled atoms are present on the catalyst, and that they are hardly removed.
6 REFERENCES


DECOMPOSITION OF $\text{N}_2^{15}\text{O}$ OVER

Pt/Al$_2$O$_3$

II. MODELING

ABSTRACT

The decomposition of $\text{N}_2^{15}\text{O}$ has been studied with positron emission profiling (PEP). In a previous study it was shown that oxygen formed by the decomposition is retained on the catalyst. The resulting $^{15}\text{O}$ catalyst bed profiles have been modeled. Reaction kinetic data are extracted from these profiles with the aid of a mathematical model and a model describing the detector sensitivity. This combined procedure was used to elucidate the reaction kinetics of the decomposition of $\text{N}_2\text{O}$ over Pt/Al$_2$O$_3$. The measured PEP profiles could be accurately described using this combined approach, which would have been impossible if the detector sensitivity was not included. Previous studies on the kinetics did not take the realistic coverages of oxygen and $\text{N}_2\text{O}$ into account. Using a complete model it was shown that the decomposition is impaired by high coverage of oxygen under the reaction conditions. The activation energy for the dissociative adsorption of $\text{N}_2\text{O}$ on Pt/Al$_2$O$_3$ was found to be 257 kJ/mol.
CHAPTER 7

1 INTRODUCTION

Positron emission profiling is an in-situ isotopic transient technique that enables monitoring of gas and surface concentrations in a catalytic reactor operating at steady-state [1-6]. The technique is made possible due to the special properties of the radioisotope (positron emitter) used. To study the decomposition of N\textsubscript{2}O on Pt/Al\textsubscript{2}O\textsubscript{3} the tracer N\textsubscript{2}\textsuperscript{15}O has been used. Upon decay, these radioactive atoms emit a positron (antiparticle of an electron) that can annihilate on encounter with an electron in the surrounding matter. This annihilation event produces two high energy photons (511 keV) capable of permeating through the reactor and the surrounding oven. The high energy photons can be detected with a special detector allowing deduction of the position of the annihilation event.

PEP can be used to obtain both qualitative and quantitative information about the catalytic reaction being observed. In a previous study (chapter 6) it was shown that PEP can reveal information about the behavior of oxygen atoms, formed by the decomposition of N\textsubscript{2}\textsuperscript{15}O, on the catalyst surface. This qualitative study indicated that adsorbed oxygen is efficiently transferred from the metal surface to the support. On the support labeled oxygen atoms exchange with non-labeled oxygen already present on the surface and in the oxidic support. This results in a permanent retention of the labeled oxygen atoms on the catalyst. The present study will focus on modeling the PEP profiles obtained with the \textsuperscript{15}O tracer. To obtain quantitative information the reactions taking place on the catalyst surface have to be described by a mathematical model.

The mathematical model describes the concentration of the tracer as a function of both time and position. This automatically leads to a system of partial differential equations (PDEs) describing the behavior of the tracer based on the elementary reactions and their reaction rates. The solution of this system describes the evolution of the concentration in time at any given position in the catalyst bed [7]. However, the accuracy of the detection process in the spatial direction (position resolution) is limited. The averaging effect of the detector on the real activity profile can be taken into account by including the detector sensitivity in the procedure. The detector sensitivity has been determined by Monte Carlo simulations (see chapter 5).

Utilization of the mathematical solution in combination with the detector sensitivity is used here to elucidate the kinetics of the decomposition of N\textsubscript{2}O over Pt/Al\textsubscript{2}O\textsubscript{3}. Previous studies on platinum metal revealed that produced oxygen has a retarding effect on the decomposition reaction. On a clean platinum surface dissociation already takes place at room temperature. However, under steady-state conditions high temperatures are needed (675 K) to remove the adsorbed oxygen from the metal surface. In a recent kinetic study on the decomposition of N\textsubscript{2}O on platinum by Takoudis and Schmidt [8], the inhibition of O\textsubscript{2} was not taken into account. A Langmuir-Hinshelwood rate expression was proposed to describe the decomposition. In their derivation they assumed that the decomposition of adsorbed N\textsubscript{2}O was rate limiting, while adsorption-desorption equilibrium was assumed for both N\textsubscript{2}O and O\textsubscript{2}. In the present study, the model is not confined by such assumptions, allowing the possible oxygen inhibition to
be considered. The results obtained in this way are more likely to reveal the kinetics under realistic conditions.

2 EXPERIMENTAL

2.1 Materials

The gases were obtained from Hoekloos, and were used without further purification. The N₂O was supplied from a cylinder containing a mixture of 5% N₂O in helium. The helium had a purity of 99.999%, and contains small amounts (2-4 ppm) of O₂ as an impurity. The 0.3 w% Pt/Al₂O₃ catalyst (density: 0.45 kg/m³) was obtained from Johnson-Matthey. The catalyst was characterized by CO adsorption. The platinum surface area determined by CO adsorption was 284 m²/g Pt. Assuming hemispherical platinum particles on the surface of Al₂O₃, the particle size was determined from the ratio between the platinum metal volume and surface area. This resulted in particles with an average diameter of 2 nm. The dispersion is defined as the number of adsorbed CO molecules divided by the total number of Pt atoms. This resulted in a dispersion of 56%.

2.2 N₂¹⁵O production

The production of N₂¹⁵O has been described in chapter 3. Since the procedure was slightly modified, a brief description of the method will be given. Nitrogen gas was irradiated with 7 MeV deuterons in a cylindrical target to produce¹⁵O₂, N₂¹⁵O and trace amounts of N₂O. A beam current of 1 μA was used to produce the isotopes. The N₂¹⁵O was selectively removed from the target effluent by adsorption on mordenite at 173 K. The adsorbed product (N₂¹⁵O and N₂O) was removed by electrically heating the adsorbent in a stream of helium (38 ml/min). The resulting pulse was injected into the reaction feed mixture flowing over the catalyst. An adsorption time of 30 s was used to minimize the amount of non-labeled N₂O in the desorbed product. The higher beam current compensated the loss in activity due to the shorter adsorption time. In this way, a sufficient amount of N₂¹⁵O (several fmol) was adsorbed to perform PEP experiments. The amount of non-labeled N₂O present in the desorbed product is 18 nmol. Assuming a pulse width of 3 seconds the average amount of non-labeled N₂O is still a factor 1000 lower than the steady-state concentration of N₂O. It is therefore assumed that the injected pulse of N₂O/N₂¹⁵O will not influence the steady-state reaction.

2.3 PEP experiments

A thorough description of the procedure to perform the PEP experiments is given in chapter 2, therefore, only a short description will be given here. The quartz reactor was loaded with 1.45 g of the 0.3% Pt/Al₂O₃ catalyst, resulting in a bed length of 4.1 cm, and was further filled up with glass beads (diameter 0.65 mm) on both sides of the catalyst bed. The catalyst was pretreated with a mixture of 2% O₂/He at 775 K for 1 hour. When performing pulse experiments (without N₂O in the reaction mixture), the catalyst was
pretreated with a mixture of 5% CO/He at 475 K. Non-reacted CO was removed by heating the catalyst in helium for 1 hour at 775 K. The catalyst temperature was then allowed to reach the reaction temperature while flowing with helium (50 ml/min). Upon reaching the reaction temperature, 2500 ppm of N₂O was added to the reaction mixture and the flow was adjusted to 40 ml/min. The catalyst was allowed to reach steady-state for at least 10 hours. Upon subsequent changes (rise) in the temperature the catalyst reached steady-state in less than 30 minutes. The conversion of N₂¹⁵O over Pt/Al₂O₃ was investigated in the temperature range from 675 K to 825 K.

PEP experiments were performed by injecting the adsorbed N₂¹⁵O/N₂O in the reaction mixture to the catalyst. Because the amount of radioactivity in the injected pulse was not very high the distance between the detection banks was adjusted to 160 mm (distance to the center of the reactor is 80 mm). A sampling time of 1 second was used for recording the PEP profiles. The PEP profile contains the ¹⁵O activity measured at 17 equidistant positions in the reactor as a function of time. The profiles were corrected for the decay of ¹⁵O during the analysis time. The results from the profile can be displayed as a function of time at a specific position in the reactor (time profile). The other possibility is that the results are displayed as a function of position at a specific time point (position profile).

3 Modelung

3.1 Decomposition mechanism

The decomposition of nitrous oxide over non-supported platinum has been described by several authors. The most extensive mechanism consists of the following steps. The reaction starts with the reversible adsorption of N₂O on the platinum surface. Adsorbed N₂O can decompose to give N₂(g) and a surface oxygen atom. The adsorbed oxygen can be removed by recombination with another surface oxygen followed by desorption. Naturally, the desorbed O₂ can readorsb dissociatively on the surface. Another mode of removal is the direct reaction of gas phase N₂O (Eley-Rideal step) with surface oxygen under formation of N₂ and O₂. These four steps are given by the following equations:

\[ \text{N}_2\text{O} + \ast \xrightleftharpoons[k_1]{k} \text{N}_2\text{O} \ast \]  \hspace{1cm} (7.1)

\[ \text{N}_2\text{O} \ast \xrightarrow{k_2} \text{N}_2 + \text{O} \ast \]  \hspace{1cm} (7.2)

\[ \text{O} \ast + \text{O} \ast \xrightleftharpoons[k_{\text{re}}]{k_{\text{ad}}} \text{O}_2 + 2\ast \]  \hspace{1cm} (7.3)

\[ \text{N}_2\text{O} + \text{O} \ast \xrightarrow{k_4} \text{N}_2 + \text{O}_2 + \ast \]  \hspace{1cm} (7.4)

The chemisorption of N₂O on platinum (step (7.1)) has been studied by Schmidt et al. [9]. They reported that N₂O does not appear to chemisorb on platinum in UHV.
experiments in the temperature range from 700 to 1600 K. Furthermore, a study by Alnot et al. [10] showed that N$_2$O adsorbs dissociatively on platinum between 300 K and 500 K. Also, no N$_2$O was found during temperature programmed desorption after adsorption of N$_2$O. Reversible adsorption does not seem to occur under the present conditions on this catalyst (Pt/Al$_2$O$_3$). Figure 7.1 shows the PEP response profiles, recorded at several positions in the catalyst bed, of a N$_2^{15}$O pulse flowing through the bed at 700 K. At this temperature a small fraction of N$_2$O is decomposed, showing the existence of some interaction with the surface. If significant adsorption and desorption on the catalyst take place, it is expected that the pulse becomes broader at the end of the bed. This clearly does not occur indicating that reversible adsorption or dispersion of N$_2^{15}$O do not take place. Therefore, adsorbed N$_2$O is probably not a precursor for the dissociative adsorption of N$_2$O. Accordingly steps (7.1) and (7.2) should be combined to one step, as indicated by equation (7.5).

Furthermore, the direct reaction of N$_2$O with surface oxygen does not seem to take place with this catalyst. After addition of a N$_2^{15}$O pulse to the catalyst operating under steady-state conditions, no $^{15}$O$_2$ is present in the target effluent. As shown in the previous chapter all the $^{16}$O formed by dissociation is retained on the catalyst. If reaction step (7.4) occurs, the labeled oxygen from N$_2^{15}$O would be directly transferred to $^{16}$O$_2$, which then has a fair chance to escape from the reactor. However, addition of $^{15}$O$_2$ to the reaction mixture under steady-state conditions showed the presence of $^{15}$O$_2$ in the reactor effluent. Excluding step (7.4) from the reaction sequence leads to the following simple description for the decomposition of N$_2$O on this catalyst:

$$\frac{N_2O + \ast}{k_{decom}} \rightarrow \frac{N_2 + O\ast}{(7.5)}$$

$$\frac{O\ast + O\ast}{k_{des} \leftrightarrow k_{ads}} \rightarrow \frac{O_2 + 2\ast}{(7.6)}$$

where,

- $k_{decom}$: N$_2$O decomposition rate constant
- $k_{ads}$: oxygen adsorption rate constant
- $k_{des}$: oxygen desorption rate constant

This reaction sequence consists of the irreversible dissociative adsorption of N$_2$O resulting in a surface oxygen and N$_2$. The decomposition rate constant therefore also contains the sticking probability of N$_2$O on the platinum surface. Surface oxygen is removed by recombination with another surface oxygen. Product inhibition can occur through the readsoption of O$_2$.

### 3.2 Model equations

The evaluation of PEP profiles consists of modeling both the steady-state and transient response. The steady-state leads to a system of differential and algebraic equations (DAE). The differential equations describe the concentration change in the gas phase
Figure 7.1. PEP response curves displaying the absence of measurable adsorption and dispersion at 675 K.
PEP response curves were recorded at the beginning (O), center (□), and at the end (○) of the catalyst bed. The curves were superimposed such that their peak positions coincided (a deviation in the shape of the curves indicates the presence of adsorption or dispersion).

and the algebraic equations determine the surface occupancies. The surface occupancies of the non-labeled species and the free surface are used in the solution of the transient response. The transient response for the labeled compound can be modeled by a system of partial differential equations (PDE). The PDE describes the concentration change of the labeled species in the gas phase and on the catalyst surface. The procedure followed to solve both the DAE and PDE has been described extensively in chapter 4.

The model as described by reaction equations 7.5 and 7.6 leads to the following equations for the steady-state:

**Steady-state equations (DAE)**

Gas phase equations:

\[
\frac{\partial X_{N_2O}}{\partial z} = -k_{decom}N_sX_{N_2O}\theta_\ast \left(\frac{1-\varepsilon}{\varepsilon}\right) \tag{7.7}
\]

\[
\frac{\partial X_{O_2}}{\partial z} = \frac{1}{2} k_{des}N_s\theta_O^2 \frac{RT}{P_t} \left(\frac{1-\varepsilon}{\varepsilon}\right) - k_{ads}N_sX_{O_2}\theta_\ast^2 \left(\frac{1-\varepsilon}{\varepsilon}\right) \tag{7.8}
\]

Surface equations:

\[
0 = 2k_{ads}X_{O_2}\theta_\ast^2 \frac{P_i}{RT} - k_{des}\theta_O^2 \tag{7.9}
\]

\[
0 = \theta_O + \theta_\ast - 1 \tag{7.10}
\]
Boundary conditions:

\[
X_{N,Y,O} = X_{N,Y,O,z=0} \quad \text{set by experimental conditions}
\]
\[
X_{O,Y} = 0
\]

Initial conditions:

\[
\theta_0 = 0 \quad \text{for } 0 < z < 1
\]
\[
\theta_* = 1 \quad \text{for } 0 < z < 1
\]

These steady-state equations have to be solved along the whole catalyst bed (for \( z = 0 \) to \( z = 1 \)). The equations describe the concentration of \( N_2O \) and \( O_2 \) in the gas phase, and the surface occupancies of the adsorbed oxygen atoms. In addition, the solution of this model defines the number of free sites still available for the labeled reactant \( (N_2^{15}O) \). It should be realized that this is a very important parameter since it has a major influence on the behavior of the labeled pulse. The molar fraction at the start of the catalyst bed is determined by the experimental conditions (2500 ppm \( N_2O \) in \( He \)). The concentration of \( O_2 \) at the inlet is zero since no oxygen was added to the reaction mixture. The surface occupancies at the beginning of the bed are of course not known. These occupancies are dependent on the reaction parameters, and therefore need to be determined by numerical solution of the equations at \( z = 0 \) (see chapter 4).

The next step in modeling the PEP profiles is setting up the equations describing the behavior of the labeled pulse as it passes through the catalyst bed. In principle, the same reaction model has been used as for the description of the steady-state. The only exception is that it is assumed that the adsorbed oxygen \( (^{15}O) \), formed after dissociation of \( N_2^{15}O \), does not desorb. Hence, readsoption of \( ^{15}OO \) also does not occur. This assumption is justified because it was shown in chapter 6 that the oxygen atoms present on the platinum surface of this catalyst are rapidly transferred to the support, where they spill-over. Once on the support the labeled \( ^{15}O \) atoms mix with the large pool of \( ^{16}O \) atoms present on and in the support, which leads to a permanent retention of the adsorbed \( ^{15}O \) atoms. This leads to the following equations describing the transient response:

\[\text{Non-steady-state equations for the labeled components (PDE)}\]

Gas phase equations:

\[
\frac{\partial X_{N,Y,O}^{15}}{\partial t} = -D \frac{\partial X_{N,Y,O}^{15}}{\partial z} - k_{\text{decomp}} N_{s} X_{N,Y,O}^{15} \theta_* \left( \frac{1 - \varepsilon}{\varepsilon} \right)
\]

Surface equations:

\[
\frac{\partial \theta_{s,Y,O}}{\partial t} = k_{\text{decomp}} X_{N,Y,O}^{15} \theta_* \frac{P_i}{RT}
\]
CHAPTER 7

Boundary conditions:

\[ X_{N_2O} = f(t) \quad \text{labeled N}_2^{15}\text{O pulse shape at z}=0 \]
\[ \theta_* = \theta_{*,ss}(z) \quad \text{for } 0 < z < 1 \text{ (steady-state amount)} \]

The equations have to be solved as a function of position and time. The numerical solution of such a PDE has been given in chapter 4. The amount of free sites (\(\theta_*\)) is determined by the steady-state (\(\theta_{*,ss}\)). This amount can actually be seen as a fixed parameter which is determined at each position in the reactor needed for the solution of the PDE. The shape of the labeled pulse was taken as a description for the change of the labeled N\(_2\)O concentration at the start of the catalyst bed. There is a problem with this approach since the pulse shape cannot be determined independently. The shape will always be influenced by the detection process, either by the PEP detector or by an external NaI detector. Therefore, it is impossible to determine the real shape of the pulse at the entrance of the catalyst bed. The pulse measured at the exit of the adsorber has been taken as an initial description of the pulse (see section 4 for a further treatment of this problem).

The combined DAE/PDE model has the following parameters which have to be determined:

- \(k_{\text{decom}}\) decomposition rate constant
- \(k_{\text{ads}}\) adsorption rate constant
- \(k_{\text{des}}\) desorption rate constant
- \(N_s\) total number of sites available for reaction

The rate constants for adsorption and desorption are only present in the steady-state description. However, they influence the transient response through determination of the amount of available free sites. The other variables present in the combined model are set by the experimental conditions. These parameters are the pressure (\(P_i = 101\) kPa), length of the catalyst bed (\(l = 0.041\) m), superficial velocity (\(v = 0.02\) m/s), and the bed porosity (\(\varepsilon = 0.41\)).

3.3 Modeling PEP profiles

The procedure used to simulate the PEP profiles consists of solving the mathematical equations describing the reaction sequence. Subsequently, the solution is convoluted with the detector sensitivity profiles. Although the method has been described in detail in chapters 4 and 5, a brief description will be given here for clarity. The procedure consists of the following steps:

1. Simulation of the detector sensitivity profiles. These profiles include the effects of positron range and photon scattering in the experimental setup. The sensitivity profiles that have been used here are given in figure 7.2.
2. Normalization of the PEP profile. The whole profile is normalized to the highest concentration measured. This value was determined after applying a moving
average of 21 points to the profile (non-averaged data were used in the remainder of the procedure).

3. Numerical solution of the equations describing the catalytic reaction sequence (equations 7.7 - 7.12). The input pulse is based on the shape of the injected $N_2^{15}O$ pulse. The pulse shape is measured directly behind the adsorber (accumulation of $N_2^{15}O$ during preparation, see experimental procedures), and does not include the effect of mixing (dispersion) in the tubing and in the first part of the reactor. To compensate for these effects it was assumed that a certain amount of dispersion occurred in the tubing and reactor. The resulting curve was calculated by numerical differentiation (see chapter 4). Using this procedure it was still difficult to correctly describe the pulse shape at the beginning of the catalyst bed.

4. Convolution of the numerical solution with the sensitivity profiles. The resulting simulated profile includes the non-idealities of the detection process.

5. Normalization of the simulated profile.

6. Comparison between the simulated and measured data (including the conversion level), and adjustment of the parameters accordingly (fitting).

A drawback of this procedure is that the measured and the simulated profiles have to be normalized before they can be compared. Normalization introduces an unwanted extra hidden fitting parameter, the normalization factor (maximum). This is not a problem for the mathematical solution since its maximum value is well defined. However, the measured data contain a large amount of noise which influences determination of the maximum value. To reduce the amount of noise the data were smoothed before determination of the maximum. In this case, this was an adequate procedure, since the adsorbed activity reached a constant level due to retention of $^{15}O$ on the catalyst (see
Figure 7.3. The N\textsubscript{2}O decomposition rate for the Pt/Al\textsubscript{2}O\textsubscript{3} catalyst compared with polycrystalline platinum. The decomposition rate of N\textsubscript{2}O was determined at different temperatures for the steady-state decomposition. The Pt/Al\textsubscript{2}O\textsubscript{3} rates were compared with results of Takoudis and Schmidt [8]. The rate was calculated from the rate equation given by the authors using the current N\textsubscript{2}O pressure. (O) Pt/Al\textsubscript{2}O\textsubscript{3}, (□) polycrystalline Pt.

If the response profile has a peaked shape the maximum may be ill-defined by this procedure, resulting in less accurate fits. Normalization is necessary because it is not possible to relate an absolute value for the concentration to the response of the detector. This is mainly due to the absence of a line source which fits in the oven to calibrate the system. In addition, the exact amount of tracer added to the reaction mixture can not be verified. These two points should be resolved if absolute quantities are required.

4 RESULTS AND DISCUSSION

4.1 Decomposition rate of N\textsubscript{2}O over Pt/Al\textsubscript{2}O\textsubscript{3}

The catalytic decomposition of N\textsubscript{2}\textsuperscript{15}O on platinum has to our knowledge only been studied for non-supported systems. Early studies with platinum metal indicated that decomposition only occurred at temperatures higher than 770 K [11]. A more recent study on polycrystalline platinum by Takoudis and Schmidt [8] showed that the steady-state decomposition occurred at temperatures around 675 K, as is also implied by the present results. The decomposition rate of N\textsubscript{2}O over Pt/Al\textsubscript{2}O\textsubscript{3} has been compared with the results obtained for polycrystalline platinum [8]. The reaction rate has been defined as the number of N\textsubscript{2}O molecules decomposed over the whole catalyst bed (average conversion). The rate is expressed as the number of converted N\textsubscript{2}O molecules versus the number of Pt surface atoms. The variation of the reaction rate with temperature is shown in figure 7.3. The rates have been calculated from the rate expression given by the authors (equation (7.13)), to accommodate the current experimental conditions. In the
study of Takoudis and Schmidt lower N$_2$O concentrations were used (10-100 times lower). The activity of the supported platinum catalyst is much lower than the activity of the platinum metal. However, the temperature dependency of the decomposition rate is identical. There is no direct explanation for the lower activity of the supported catalyst. A possible cause is an underestimate of the surface in the case of the metal catalyst. The exposed surface area of the platinum wire was merely based on geometrical observations. The surface area for the supported catalyst has been determined by CO adsorption which is likely to be more accurate. In addition, the lower N$_2$O concentration used might also prevent the inhibition by formed oxygen, which is likely to occur under the present conditions. The similar temperature dependency of the reaction rate implies that the value for the activation energy for the dissociation rate ($k_2$) should be identical. Takoudis and Schmidt found an activation energy of 146 kJ/mol for the dissociation of N$_2$O on platinum. The proposed rate expression was based on a Langmuir-Hinshelwood expression given by:

$$r_{N_2O} = \frac{k_2 K_{N_2O} P_{N_2O}}{1 + K_{N_2O} P_{N_2O}}$$

(7.13)

where,

- $r_{N_2O}$ reaction rate of the decomposition of N$_2$O
- $K_{N_2O}$ adsorption equilibrium constant (see equation 7.1)
- $P_{N_2O}$ N$_2$O pressure
- $k_2$ dissociation rate constant (see equation 7.2)

It was assumed that product inhibition did not occur and that an adsorption-desorption equilibrium existed for N$_2$O. They also concluded that the surface coverage of adsorbed N$_2$O is equal to unity at low temperatures (773 K). However, in a later study, Schmidt et al. [9] reported that N$_2$O does not chemisorb on platinum. Other studies also indicate that N$_2$O is only weakly adsorbed on metal surfaces [12,13].

The main objective of this study is therefore to model the decomposition reaction, without making any unrealistic assumptions about surface coverages.

### 4.2 Simulation of the transient response

The model equations formulated in paragraph 3.2 have been used to describe the transient response measured with the PEP detector. The symbols in figure 7.4 show the response at the beginning of the catalyst bed at 675 K and 825 K. The response at higher temperatures is characterized by a steep increase in the amount of $^{15}$O leading to a constant amount retained on the catalyst. At low temperatures the N$_2^{15}$O pulse is also visible. The observed plateau in the amount of $^{15}$O is caused by the efficient transfer of $^{15}$O atoms, formed by the decomposition, to the support. Once on the support the $^{15}$O atoms exchange with $^{16}$O preventing any desorption of $^{15}$O. The simulation of these profiles is shown by the solid lines in figure 7.4, which include the effect of the detector
Figure 7.4. Measured and simulated transient PEP response to a pulse of N$_2^{15}$O.
The Pt/Al$_2$O$_3$ catalyst was allowed to reach steady-state in a stream of He/N$_2$O at the indicated
temperatures. A pulse of N$_2^{15}$O was injected in the reaction mixture and the time dependent response of
the PEP detector was recorded. (—) Simulated profiles. The parameters were taken from the
simulations shown in figure 7.8.

sensitivity. The curves show that the current model does not correctly describe the
measurements. The passage of the N$_2^{15}$O pulse through the catalyst is still visible at both
the high and low temperature. The simulated profiles clearly overestimate the
contribution of gaseous N$_2^{15}$O to the response. This is especially apparent for the
simulated curve at 675 K. An explanation for this behavior is that the measured $^{15}$O
response also depends on the residence time of these $^{15}$O atoms in the detection volume.
The detection volume is defined by the section of the reactor which can be observed at a
certain detection position. The size of this volume is actually determined by the
sensitivity profile for this detection position. The effect of the residence time can be
envisioned as follows. The detector measures a fixed fraction of the number of
disintegrations in the detection volume for a given time interval. If the radioactive atoms
remain present (adsorbed) in this detection volume for the entire time interval the
maximum attainable response is obtained. However, moving atoms are only present for
a fraction of the time interval, therefore, a reduced amount of activity is measured.
The detector response to a moving source as compared to a non-moving static source
has been modeled to gain insight in the contribution of this effect. The modeling
procedure consisted of placing an $^{15}$O source at the center of the detector and
comparing its response with a moving $^{15}$O source. The response at the central detection
position (position 9) was deferred by incorporating the sensitivity profile for this position
in the calculations. The results of these calculations as a function of the flow rate (speed
of the moving source) are shown in figure 7.5. The response for the static source
(adsorbed phase) is maximal and is not influenced by the flow rate. The symbols in
figure 7.5 show the response for the moving source, which is much lower than that for
the static source. The initial low response at small flow rates is caused by the fact that the
source does not cross the detection section within the measurement interval. At high flow rates, the response is inversely proportional to the flow rate (solid line through the symbols in figure 7.5). This is expected since this relationship determines the residence time in the detection section. Examining the ratio between the adsorbed phase and the moving gas phase at the flow rate used here shows that the gas phase is detected 5 times less efficient than the adsorbed phase. Incorporation of this factor in the simulations should result in an improved description of the transient profiles. The results of these calculations are shown in figure 7.6. It can be seen that the results are adequately described in this case.

The transient uptake of $^{15}$O and the pulse shape at the low temperature, as shown in figure 7.6, are dependent on the shape of the input pulse ($N_2^{15}$O). The exact shape of this pulse can not be determined with the PEP detector because of the non-idealities of the detection process. As mentioned, to overcome this problem the shape of the $N_2^{15}$O injection pulse has been used as the input function. This did not result in an adequate description of the profiles; the pulse seemed to be too narrow. Therefore, a certain amount of dispersion has been added to the initial pulse by numerical differentiation. Using this approach it was still not possible to unambiguously determine the input pulse. The dispersion factor had to be varied for each simulation. This introduces another unwanted fitting parameter. The amount of retained $^{15}$O (constant level in the figures) is independent of the pulse shape. If only this quantity is used during the fitting procedure, no extra parameter is introduced. The results presented in the next paragraph will
Figure 7.6. Measured and simulated transient PEP response to a pulse of N$_2^{15}$O after correction for the flow rate dependency of the gas phase activity. The Pt/Al$_2$O$_3$ catalyst was allowed to reach steady state in a stream of He/N$_2$O at the indicated temperatures. A pulse of N$_2^{15}$O was injected in the reaction mixture and the time dependent response of the PEP detector was recorded. (—) Corrected simulated profiles. The gas phase tracer was assumed to be detected less efficiently (5-fold) than the adsorbed tracer. The parameters used were taken from the simulations shown in figure 7.8.

Therefore only focus on modeling this quantity (the amount retained after 100 s) as a function of the position in the catalyst bed.

Another remaining uncertain factor is the exact location of the beginning of the catalyst bed. The accuracy of this position with respect to the detector varies between 1 and 2 mm. The position resolution of the current system is low because $^{15}$O is used as a tracer and because of the low density of the catalyst. The low resolution implies that a large section (7-10 mm) of the catalyst bed contributes to the signal of a single detection position. In addition, the highest amount of $^{15}$O is likely to be deposited at the beginning of the catalyst bed because there the N$_2^{15}$O concentration is the highest. This may result in large $^{15}$O concentration gradients at the beginning of the bed. These two factors will have a large influence on the shape of the resulting positions profiles ($^{15}$O concentration measured as a function of position at a specific time). It is therefore expected that the location of the catalyst bed front will also influence the profile shape. Simulations with assumed $^{15}$O concentration profiles have been carried out to evaluate the influence of this effect. The simulations consisted of setting up an $^{15}$O profile along the catalyst bed and analyzing the result after convolution with the sensitivity profiles for this system (figure 7.2). The $^{15}$O profile used for this analysis is shown in figure 7.7A. The concentration curve shows the amount of $^{15}$O retained on the catalyst after 100 s. This profile is based on the $^{15}$O concentration gradient which is expected at high N$_2^{15}$O conversion levels. Convolution of this profile with the sensitivity matrix is shown in figure 7.7B.
Figure 7.7. Influence of the position of the catalyst bed front on the simulated PEP profiles.
A. $^{15}$O concentration curve used to simulate the PEP response curves shown in B. The concentration indicates the amount of $^{15}$O adsorbed on the catalyst (Pt/Al₂O₃) as a function of position. B. Simulated effect of different starting positions of the catalyst bed. The activity distribution shown in figure A. was placed at several starting positions as shown by the vertical lines. This mimics the effect of not knowing the exact position of the catalyst with respect to the PEP detector. The distance between the starting positions is 1 mm. The effect on the simulated PEP response (convolution with the sensitivity matrix of figure 7.2) is shown.

Figure 7.7B shows the position profiles when the catalyst bed is placed at different positions (shifts of 1 mm) with respect to the detector. It can be seen that the position of the catalyst bed has a profound effect on the profiles. The shape of these curves is equal to the expected experimental curves. The difference is most profound at the beginning of the catalyst bed. This shows that the catalyst bed position has to be taken into account during the fitting procedure. The value for this parameter has been obtained as follows. First, the profile at high temperature was modeled since a large amount of $^{15}$O is retained, and therefore a substantial influence of the detector sensitivity is expected. The value
which gave the best fitting results was used as a starting point to model the profiles at lower temperatures. The value for the bed position was subsequently slightly varied such that optimal fits were obtained at each temperature. Consequently, a single value has been used for all the modeled profiles.

4.3 Modeling the decomposition of $N_2^{15}O$ over Pt/Al$_2$O$_3$

The equations used to model the amount of $^{15}O$ retained on the catalyst after 100 s during the decomposition of $N_2^{15}O$ have been given in paragraph 3.2. The equations (7.7-7.12) contain the following parameters which have to be estimated: $k_{\text{decom}}$, $k_{\text{ads}}$, $k_{\text{des}}$, $N_s$. Although the model only contains four parameters it is not possible to estimate their values unambiguously from the experimental profiles. Particularly, $k_{\text{ads}}$ (O$_2$ adsorption) and $N_s$ (number of sites) highly depended on their initial values, resulting in high error values for these parameters. The poor dependency of these estimates on the experimental data is likely caused by the normalization procedure and the small number of data points (17). It is therefore necessary to reduce the number of model parameters. The number of active sites ($N_e$) had no influence on the goodness of the fits. Therefore, the value for $N_s$ obtained at high temperature has been used to model the profiles at lower temperatures. This is an acceptable assumption because the number of sites should be independent of the temperature. The value for $N_s$ is given in Table 7.1. As mentioned, the value for $k_{\text{ads}}$ cannot be determined explicitly from the experimental data. A correct prediction of the profile at low temperature (675 K) can only be obtained with a high value for $k_{\text{ads}}$. At high temperature (800 K) good agreement with the experimental data can be obtained for every value for $k_{\text{ads}}$ by adjusting the other parameters. The value for $k_{\text{ads}}$ has been set to the value obtained at 675 K (see Table 7.1). It was assumed that this parameter is independent of temperature. This is justified since the adsorption of oxygen has been shown to be a non-activated process [14-17].

Using these values for $k_{\text{ads}}$ and $N_s$ the other two parameters have been estimated from the position profiles obtained at different temperatures. These results are shown in figure 7.8. The symbols represent the experimental data of the amount of $^{15}O$ retained on the catalyst as a function of the position in the catalyst bed. The main characteristic of the experimental profiles is the high amount of $^{15}O$ at the beginning of the bed. This indicates that formed oxygen (O$_2$) must have a strong inhibitory effect on the decomposition of $N_2^{15}O$. This explains the large value for the O$_2$ adsorption which was shown to be necessary to model the decomposition profiles. The solid curves in figure 7.8 give the results of the simulations. These simulations satisfactory predict the experimental data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{decom}}$</td>
<td>decomposition rate constant</td>
<td>From data fit</td>
</tr>
<tr>
<td>$k_{\text{des}}$</td>
<td>oxygen desorption rate constant</td>
<td>From data fit</td>
</tr>
<tr>
<td>$k_{\text{ads}}$</td>
<td>oxygen adsorption rate constant</td>
<td>4200</td>
</tr>
<tr>
<td>$N_s$</td>
<td>number of sites</td>
<td>500</td>
</tr>
</tbody>
</table>
Figure 7.8. Comparison between the simulated and measured PEP profiles for the decomposition of N$_2^{15}$O in the temperature range of 675 K to 825 K. The Pt/Al$_2$O$_3$ catalyst was allowed to reach steady-state in a stream of He/N$_2$O at the indicated temperatures. A pulse of N$_2^{15}$O was then added to the reaction mixture and the response of the PEP detector was recorded. The experimental profiles (O) show the $^{15}$O activity distribution after 75 s. The solid lines show the simulated response.

The values belonging to the estimated parameters are given in Table 7.2. The profiles measured by the PEP detector are obscured by the mediocre position resolution for the present system. Figure 7.9 shows the simulated $^{15}$O profiles not influenced by the detection process. It is apparent from these profiles that at low temperature only some N$_2^{15}$O decomposition takes place at the beginning of the catalyst bed and that the product O$_2$ must be inhibiting further decomposition downstream in the bed. Furthermore, the 'real' profiles are notably different from the measured profiles. Thus, without correction of the mathematical model by convolution with the sensitivity profiles of the detector it is not possible to obtain a satisfactory description of the measured data.
Figure 7.9. Simulated $^{15}$O activity profiles showing the actual distribution of the tracer along the catalyst bed.
The parameters obtained from the simulations shown in figure 7.8 have been used to generate the non-convoluted $^{15}$O concentration profiles. These profiles do not contain the non-idealities of the detection process.

The value for the $\text{N}_2\text{O}$ conversion at the reactor exit is also compared during the fitting procedure. Figure 7.10 shows the $\text{N}_2\text{O}$ conversion profiles as a function of position in the catalyst bed. At low temperature (675 K) the conversion is low and it increases with increasing temperature. The simulated conversion obtained at the reactor exit is given in Table 7.2. The simulation results can be compared with the measured conversion. As can be seen, these conversion levels are nearly identical.

The value for the oxygen desorption rate constant ($k_{des}$) is independent of the temperature as indicated in Table 7.2. This is not expected because desorption processes are usually activated which should lead to an increased desorption rate with increasing temperature. The apparent temperature independence of this value is probably a result of the small amount of oxygen that desorbs in this temperature range. It has been shown

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>$k_{decom}$ [m³/mol s]</th>
<th>Error</th>
<th>$k_{des}$ [1/s]</th>
<th>Error</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>0.035</td>
<td>0.02</td>
<td>1.1</td>
<td>0.6</td>
<td>3.5</td>
</tr>
<tr>
<td>725</td>
<td>0.7</td>
<td>0.1</td>
<td>0.4</td>
<td>0.06</td>
<td>11.4</td>
</tr>
<tr>
<td>750</td>
<td>2.1</td>
<td>0.2</td>
<td>0.8</td>
<td>0.00001</td>
<td>28.3</td>
</tr>
<tr>
<td>775</td>
<td>32.8</td>
<td>2.9</td>
<td>0.1</td>
<td>0.01</td>
<td>55.0</td>
</tr>
<tr>
<td>800</td>
<td>50.4</td>
<td>3.7</td>
<td>0.3</td>
<td>0.02</td>
<td>83.0</td>
</tr>
<tr>
<td>825</td>
<td>87.6</td>
<td>4.8</td>
<td>0.4</td>
<td>0.02</td>
<td>97.0</td>
</tr>
</tbody>
</table>
Figure 7.10. Simulated N₂O conversion along the catalyst bed.
The parameters obtained from the simulations shown in figure 7.8 have been used to generate the N₂O conversion profiles.

with temperature programmed desorption, that the maximum oxygen desorption rate from small platinum particles (2 nm) takes place at 950 K [18]. The platinum particles used here have the same size. In addition, the absolute value of \( k_{\text{des}} \) is much lower than that of \( k_{\text{adr}} \). As a result, the catalyst is likely to be completely covered with adsorbed oxygen under the decomposition conditions. The model shows that the oxygen coverage is close to unity.

Figure 7.11. Simulated and measured PEP profile of an \(^{15}\text{O}_2\) pulse injected on the catalyst operating under steady-state conditions at 725 K.
(○) The catalyst was allowed to reach steady-state in a stream of He/N₂O at 725 K. Instead of adding N₂\(^{15}\text{O}\), a pulse of \(^{16}\text{O}_2\) was injected in the reaction mixture and the response of the PEP detector after 75 s was recorded. (—) Simulated profile of an injected \(^{15}\text{O}_2\) pulse. The parameters used were taken from the simulations shown in figure 7.8.
The oxygen adsorption/desorption parameters have been verified by evaluating the response after injection of an $^{15}$O$_2$ pulse. The pulse has been added to the Pt/Al$_2$O$_3$ catalyst operating at steady-state conditions at 725 K. The measured PEP response is shown in figure 7.11. Under these conditions not all the oxygen is adsorbed on the catalyst and $^{15}$O$_2$ can be observed at the reactor exit. The profile has been simulated using the parameter values obtained at 725 K. As can be seen, the deviation between the experimental and simulated curves is small. It is therefore concluded that the adsorption/desorption of oxygen is correctly described by the model.

As mentioned, oxygen is strongly adsorbed inhibiting the adsorption and subsequent decomposition of N$_2$O. Various studies [19-23] on the decomposition of N$_2$O on Pt have shown that O$_2$ has a strong inhibitory effect on the decomposition. Alnot et al. [10] have shown that N$_2$O decomposes on a clean platinum surface at room temperature. However, the sticking coefficient for the dissociative adsorption of N$_2$O rapidly decreased with increasing oxygen coverage. Furthermore, the sticking coefficient for dissociative O$_2$ adsorption is higher than that for N$_2$O adsorption (factor 100 at 1100 K). Alnot et al. proposed that this difference between N$_2$O and O$_2$ was attributed to steric factors. In view of these results, Daniel et al. [24] showed strong steric effects in N$_2$O adsorption on rhodium. Dissociative N$_2$O adsorption terminated at an O-atom coverage of 0.25 monolayer, whereas dissociative O$_2$ adsorption continued up to 0.5 monolayer O-atom coverage. These results indicate that O$_2$ is more easily adsorbed dissociatively than N$_2$O, as is also apparent from the present results. Figure 7.11 shows that O$_2$ is adsorbed efficiently under steady-state N$_2$O decomposition conditions at 725 K. At this temperature the N$_2$O conversion is very low (10%) indicating that dissociative adsorption of N$_2$O is

![Figure 7.12. Comparison between the steady-state and pulse N$_2$$^{15}$O decomposition at 775 K.](image)

- The Pt/Al$_2$O$_3$ catalyst was allowed to reach steady-state in a stream of He/N$_2$O at 775 K. A pulse of N$_2$$^{15}$O was then added to the reaction mixture and the response of the PEP detector after 75 s was recorded. (©) The catalyst was pretreated in a stream of He where after a pulse of N$_2$$^{15}$O was injected in the He gas stream.
inefficient. To verify that N₂O decomposition is indeed higher on a clean surface, a pulse of N₂¹⁵O has been injected in a reaction mixture containing only helium. Under these conditions a larger amount of N₂¹⁵O is decomposed as shown in figure 7.12. However, even at non-steady-state conditions hindrance of the decomposition by formed O₂ still occurs, as indicated by the decrease in¹⁵O concentration. Thus, even small amounts of O₂ (< 18 nmol, amount of N₂O + N₂¹⁵O present in the pulse, versus 22 µmol Pt) still inhibit the reaction of N₂O with the platinum surface.

The values for the N₂O decomposition rate constant increase with increasing temperature. This indicates that this process is activated. Assuming an Arrhenius temperature dependence for k₅ (see figure 7.13) the activation energy is found to be 257 ± 23 kJ/mol. This activation energy is much higher than the value of 146 kJ/mol observed by Takoudis and Schmidt [8] for the dissociation of N₂O. Their value was based on a simple model assuming the absence of product inhibition. However, product inhibition does occur, even at low O₂ concentrations (figure 7.12). The high value for the activation energy probably indicates the large degree of hindrance experienced by N₂O molecules impinging on the oxygen covered platinum surface. The activation energy for k₅ is therefore higher than the value obtained for the dissociation energy of N₂O since k₅ is also dependent on the sticking probability of N₂O. The sticking probability of N₂O mainly depends on the amount of adsorbed oxygen on the platinum surface. Under the present conditions (high O_ads occupancy) it is likely that O₂ has to desorb before N₂O can adsorb dissociatively on the surface. This explains the high activation energy observed for this reaction step. Similarly, on rhodium it was observed that CO also strongly inhibits the dissociative adsorption of N₂O. In this case CO has to desorb before N₂O can react with the metal surface. In this study it was found that the apparent activation energy for N₂O decomposition on rhodium was as large as 209 kJ/mol, which is consistent with the value observed in this study.
5 CONCLUSION

The decomposition of N$_2^{15}$O over Pt/Al$_2$O$_3$ leads to the deposition of labeled oxygen on the catalyst surface. The resulting radioactivity profiles as measured with the PEP detector have been simulated with a mathematical model describing the reaction as a function of the position in the catalyst bed. Correct description of the experimental results could only be achieved when the detector sensitivity is taken into account. The combined approach allows determination of the kinetics under realistic conditions.

In the temperature range from 675 to 825 K the platinum is almost completely covered with oxygen. This inhibits the dissociative adsorption of N$_2$O at these temperatures. The apparent activation energy for the dissociative adsorption of N$_2$O (257 kJ/mol) is higher than the 146 kJ/mol reported earlier [8]. This difference can be ascribed to the inhibitory effect of adsorbed oxygen on the adsorption of N$_2$O, since this was not taken into account in the previous model [8]. Using only data obtained at the exit of the reactor, a lower value for the activation energy would also be obtained. Hence, the distribution of $^{15}$O over the catalyst bed as determined with the PEP technique gives better insight in the reaction kinetics.

6 SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAE</td>
<td>differential and algebraic equations</td>
<td></td>
</tr>
<tr>
<td>$f(t)$</td>
<td>labeled N$_2^{15}$O pulse shape at z=0</td>
<td></td>
</tr>
<tr>
<td>$K_{N_2O}$</td>
<td>adsorption equilibrium constant</td>
<td></td>
</tr>
<tr>
<td>$k_2$</td>
<td>dissociation rate constant</td>
<td>[molecules cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$k_{ads}$</td>
<td>adsorption rate constant</td>
<td>[m$^2$ mol$^{-1}$ s$^{-1}$]</td>
</tr>
<tr>
<td>$k_{decom}$</td>
<td>decomposition rate constant</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$k_{des}$</td>
<td>desorption rate constant</td>
<td></td>
</tr>
<tr>
<td>$k_i$</td>
<td>reaction rate constant of reaction step i</td>
<td>[mol m$^{-3}$]</td>
</tr>
<tr>
<td>$N_s$</td>
<td>total number of sites available for reaction</td>
<td></td>
</tr>
<tr>
<td>$O_{ads}$</td>
<td>amount of oxygen adsorbed on the platinum surface</td>
<td>[mol m$^{-3}$]</td>
</tr>
<tr>
<td>$P_{N_2O}$</td>
<td>N$_2$O pressure</td>
<td>[Torr]</td>
</tr>
<tr>
<td>PDE</td>
<td>partial differential equations</td>
<td></td>
</tr>
<tr>
<td>$P_t$</td>
<td>total pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>[J mol$^{-1}$ K$^{-1}$]</td>
</tr>
<tr>
<td>$r_{N_2O}$</td>
<td>reaction rate of the decomposition of N$_2$O</td>
<td>[molecules cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$T$</td>
<td>reaction temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$t$</td>
<td>variable in time</td>
<td>[s]</td>
</tr>
<tr>
<td>$u$</td>
<td>superficial velocity</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$X_j$</td>
<td>molar fraction of component j</td>
<td></td>
</tr>
<tr>
<td>$z$</td>
<td>variable in space</td>
<td>[m]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>void fraction of catalyst bed</td>
<td></td>
</tr>
<tr>
<td>$\theta_+$</td>
<td>fraction of free sites</td>
<td></td>
</tr>
<tr>
<td>$\theta_O$</td>
<td>fractional coverage of oxygen</td>
<td></td>
</tr>
</tbody>
</table>
\( \theta_{\text{ss}}(z) \) steady-state amount of free sites as function of position

* free site

7 REFERENCES


DECOMPOSITION OF $\text{N}_2^{15}\text{O}$ OVER ION-EXCHANGED ZSM-5 CATALYSTS

ABSTRACT

Positron emission profiling is an in-situ technique which can be used to determine the reaction pathway of reactants on the catalytic surface. The technique has been applied to the decomposition of $\text{N}_2\text{O}$ over metal ion-exchanged zeolites. Using the tracer $\text{N}_2^{15}\text{O}$ it was possible to determine the fate of the $^{15}\text{O}$ atoms formed by the decomposition. The $^{15}\text{O}$ atoms formed are efficiently exchanged with oxygen from the zeolite lattice. In Co- and Fe-ZSM-5 the exchanged $^{15}\text{O}$ is permanently retained on the catalyst. Cu-ZSM-5 is the only exception, $^{15}\text{O}$ also desorbs from the catalyst. The desorption of $^{15}\text{O}$O is clearly related to the nature of the active center and is not merely a property of ZSM-5.
1 INTRODUCTION

The control of nitrous oxide (N₂O) emission into the atmosphere is now considered to be of worldwide environmental concern. N₂O is responsible for ozone depletion and acts as a greenhouse gas. N₂O is nearly 270 times more potent in greenhouse warming than CO₂ [1,2], therefore, a decrease in its emission is very beneficial. The decomposition of nitrous oxide is considered to be one of the main catalytic approaches to its elimination from industrial effluents. Transition and precious metal cation-exchanged zeolites have been reported [3] as active catalysts [4-6] for the decomposition of nitrous oxide and the removal of NOₓ, even in the presence of water vapor. Among the transition metal-exchanged zeolites, Cu-ZSM-5 and Co-ZSM-5 are the most active.

The transient behavior of the decomposition of N₂O over metal-exchanged zeolites has been studied with radioisotopes like N₂¹⁸O and¹⁸O₂. The use of such isotopic step methods can reveal interesting information related to the N₂O decomposition reaction. Step switching experiments with N₂¹⁸O and N₂O have been performed to study the decomposition over Fe-mordenite [7]. The results demonstrated a high mobility of the oxygen formed by the decomposition. It appeared that lattice oxygen was involved in the decomposition mechanism and in the desorption of O₂. As decomposition occurs, the formed oxygen atoms may be introduced at one place in the zeolite lattice whereas O₂ may be formed and released from elsewhere (on the solid). Not all oxygen atoms in the zeolite lattice participate in the exchange only to a certain ratio of about 3-4 O/Fe site.

Positron emission profiling (PEP) is a recently developed detection system for positron emitters in a catalytic reactor. The technique is based on detection of gamma rays produced during the decay of a positron emitter. The decay produces two high energy photons which have enough energy to penetrate the reactor and the surrounding oven to reach the detector. The photons are detected coincidentally allowing the original position of the decaying atom to be deduced. As a result, the concentration (amount of radioactivity) can be determined as a function of time and position.

The PEP technique has been used here to follow the behavior of oxygen atoms produced by the decomposition of N₂O. As shown previously, the oxygen atoms are likely to have a strong interaction with the zeolite lattice which should be observable with the PEP technique. The tracer used should be the positron emitting counterpart of the reactant studied. Two possible positron emitters exist, namely¹⁸NNO and N₂¹⁵O. To study the behavior of oxygen only N₂¹⁵O is suitable. Using N₂¹⁵O it is possible to determine the reaction pathway of¹⁵O after its formation on ZSM-5 catalysts. It will be shown that the formed oxygen atoms are efficiently exchanged with the zeolite lattice of metal ion-exchanged ZSM-5 catalysts (Cu, Co, and Fe).

2 EXPERIMENTAL

2.1 Materials

The gases oxygen and helium were obtained from Hoekloos, and were used without further purification. The helium had a purity of 99.999%. The oxygen was supplied from a
cylinder containing a mixture of 2% O₂ in helium.
The ZSM-5 catalysts were prepared by coating glass beads with a small layer of ZSM-5 crystals. The exact preparation procedure of metal ion ZSM-5 catalysts has been described in chapter 2. Briefly, ZSM-5 coated beads were ion-exchanged with Cu, Co, and Fe containing solutions. The final catalysts were calcined in a mixture of 20% O₂ in nitrogen at 825 K for 24 hours. The exchange level for the various metal ions has not been determined because the ZSM-5 loading was very low. Since the glass beads also contain Si and small amounts of Al it is not possible to correctly determine the Si/metal ion ratio.

2.2 \( N_2^{15}O \) production
The production of \( N_2^{15}O \) has been described in chapter 3. Since the procedure was slightly modified, a brief description of the method will be given. Nitrogen gas was irradiated with 7 MeV deuterons in a cylindrical target to produce \( ^{15}O_2 \), \( N_2^{15}O \), and trace amounts of \( N_2O \). A beam current of 2 \( \mu\)A was used to produce the isotopes. The \( N_2^{15}O \) was selectively removed from the target effluent by adsorption on mordenite at 173 K. The adsorbed product (\( N_2^{15}O \) and \( N_2O \)) was removed by electrically heating the adsorbent in a stream of helium (40 ml/min). The resulting pulse was directly injected onto the catalyst. An adsorption time of 30 s was used to minimize the amount of non-labeled \( N_2O \) in the desorbed product. The higher beam current compensated the loss in radioactivity due to the shorter adsorption time. In this way, a sufficient amount of \( N_2^{15}O \) was adsorbed to perform PEP experiments. The amount of non-labeled \( N_2O \) present in the desorbed product is 18 nmol.

2.3 PEP experiments
A thorough description of the procedure to perform the PEP experiments is given in chapter 2, therefore, only a short description will be given here. The quartz reactor was loaded with 4 g of the ion-exchanged ZSM-5 catalyst, resulting in a bed length of 4 cm and was further filled up with glass beads of the same size (diameter 0.65 mm) on both sides of the catalyst bed. The catalyst was pretreated with a mixture of 2% O₂/He at 775 K for 1 hour. Subsequently, the feed was changed to helium only to remove residual O₂ from the reactor. The catalyst temperature was then allowed to reach the reaction temperature while in helium (40 ml/min).

PEP experiments were performed by direct injection of the adsorbed \( N_2^{15}O/N_2O \) onto the catalyst (pulse mode). Pulse experiments were performed because the loading of the coated zeolites was low, resulting in a low activity. Addition of a steady-state amount of \( N_2O \) has a detrimental effect on the \( N_2^{15}O/N_2O \) ratio, influencing the sensitivity of the PEP system. Because the amount of radioactivity in the injected pulse was not high the distance between the detection banks was adjusted to 160 mm (distance to the center of the reactor is 80 mm). A sampling time of 1 second was used for recording the PEP profiles. The PEP profile contains the \(^{15}O \) radioactivity measured at 17 equidistant positions in the reactor as a function of time. The profiles were corrected for the decay of
Figure 8.1. Time profiles for the decomposition of \( \text{N}_2^{15}\text{O} \) over Cu-ZSM-5, Co-ZSM-5, and Fe-ZSM-5 at 800 K.

The catalyst was pretreated in a stream of He at 800 K, after which a pulse of \( \text{N}_2^{15}\text{O} \) was injected in the He gas stream. The response of the PEP detector was recorded as a function of time. The response at the start of the catalyst bed is shown here.

\( ^{15}\text{O} \) during the analysis time. The results from the profile can be displayed as a function of time at a specific position in the reactor (time profile). The other possibility is that the results are displayed as a function of position along the catalyst bed at a specific time point (position profile).

3 RESULTS AND DISCUSSION

3.1 \( \text{N}_2^{15}\text{O} \) decomposition over Cu, Co, and Fe-ZSM-5

The decomposition of \( \text{N}_2\text{O} \) on ion-exchanged zeolites has been analyzed with \( \text{N}_2^{15}\text{O} \). The behavior of the labeled nitrous oxide can be followed with the PEP detector as it passes through the catalyst bed. Figure 8.1 shows the time profiles (response measured as a function of time at a specific position in the catalyst bed) for the three ZSM-5 catalysts measured at the beginning of the catalyst bed. The profiles have been recorded at a temperature of 800 K. This is the maximal permissible temperature; higher temperatures will result in melting of the glass beads. The main characteristic of the profiles is that radioactivity is retained on the catalyst. It is not possible to discriminate between \( \text{N}_2^{15}\text{O} \) and \( ^{15}\text{O} \) from these results only. At low temperatures (<600 K) no radioactivity is retained on the catalysts. For Cu-ZSM-5 activity starts to be retained at 650 K which is around the onset temperature for the decomposition reaction [2,4]. Thus, the retention of radioactivity on the catalyst is likely to be related to the decomposition of \( \text{N}_2^{15}\text{O} \). This suggests that \( ^{15}\text{O} \) is retained on the catalyst, and that the adsorption of \( \text{N}_2^{15}\text{O} \) is not responsible for the observed signal. The incorporation of oxygen atoms into the zeolite lattice has also been observed by Valyon et al. [7] during the decomposition of \( \text{N}_2^{18}\text{O} \) over Fe-mordenite. In chapter 6 it also has been shown that oxygen atoms formed after
decomposition of N$_2^{15}$O are very mobile. Hence, the formed $^{15}$O exchanges with $^{16}$O from the zeolite lattice resulting in retention of $^{15}$O atoms. The retention of $^{15}$O is not related to the method of N$_2^{15}$O addition to the catalyst which may result in non-steady-state behavior. With Cu-ZSM-5, the most active catalyst, the tracer has also been added to the catalyst operating under steady-state conditions. This as well resulted in retention of $^{15}$O on the catalyst (similar time profiles). The major difference between the profiles of the different ZSM-5 catalysts is that $^{15}$O is slowly removed from the Cu-ZSM-5 catalyst.

The time profiles show that Cu-ZSM-5 is the most active catalyst if the amount of retained $^{15}$O retained is related to the decomposition activity. The activity order Cu > Co > Fe corresponds to the order reported in literature [3,4]. The amount of radioactivity retained on the catalyst after 60 s at 800 K as a function of the position in the catalyst bed (position profiles) is shown in figure 8.2. This also shows that Cu-ZSM-5 is the most active catalyst. Fe-ZSM-5 hardly shows any decomposition activity at this temperature. The position profiles also show that N$_2^{15}$O is decomposed less efficiently at the end of the catalyst bed for Cu-ZSM-5. In contrast the activity of Co-ZSM-5 remains constant along the catalyst bed. The difference between Cu-ZSM-5 and Co-ZSM-5 may result from inhibition by oxygen or a limiting N$_2^{15}$O concentration. The latter is unlikely because the same curve shape has been observed at lower N$_2^{15}$O conversion, equal to the conversion level observed for Co-ZSM-5 at 800 K. In addition if the amount of N$_2^{15}$O is rate limiting the same curve shapes would be expected, since both catalysts show a first order dependency toward the partial pressure of N$_2$O [4]. This means that the decomposition of N$_2$O over Cu-ZSM-5 is inhibited by O$_2$. Oxygen inhibition for Cu-ZSM-5, and the absence of this inhibition for Co-ZSM-5 have also been observed by Kapteijn et al. [4]. Thus, the pulse experiments with N$_2^{15}$O correctly display the characteristics of the different metal ion ZSM-5 catalysts.
Figure 8.3. Time profiles for the decomposition of $\text{N}_2^{15}\text{O}$ over Cu-ZSM-5 at 800 K. The Cu-ZSM-5 catalyst was pretreated in a stream of He at 800 K, after which a pulse of $\text{N}_2^{15}\text{O}$ was injected in the He gas stream. The response of the PEP detector at the indicated positions was recorded as a function of time.

Towards the decomposition of $\text{N}_2\text{O}$.

3.2 The behavior of $^{15}\text{O}$ in Cu-ZSM-5

In contrast to the other metal-exchanged zeolites, the retained $^{15}\text{O}$ is slowly removed in time from Cu-ZSM-5. Figure 8.3 shows the time profiles measured at several positions in the Cu-ZSM-5 catalyst bed. The profiles show that $^{15}\text{O}$ is removed at the beginning of the catalyst bed and is readsorbed again downstream. The $^{15}\text{O}$ has shown to be present as single oxygen atoms and not as adsorbed $\text{N}_2^{15}\text{O}$. Since only helium is present in the gas phase, removal of $^{15}\text{O}$ is most likely to occur via thermal desorption of $^{15}\text{OO}$ or exchange of $^{15}\text{O}$ with $\text{O}_2$. Exchange with $\text{O}_2$ can occur because the helium used contains small amounts of $\text{O}_2$ ($< 4$ ppm). The $\text{O}_2$ may also reoxidize the copper ions such that desorption as $^{15}\text{OO}$ can take place. In both cases, $^{15}\text{OO}$ is formed which must readsorb further downstream in the catalyst bed in order to explain the increased amount of $^{15}\text{O}$ at these positions, as shown in figure 8.3. The adsorption of $\text{O}_2$ on Cu-ZSM-5 has also been evaluated with $^{15}\text{OO}$. In this case, a pulse of $^{15}\text{OO}$ has been added to the helium stream instead of $\text{N}_2^{15}\text{O}$. In contrast to the pulse of $\text{N}_2^{15}\text{O}$ which also contains small amounts of non-labeled $\text{N}_2\text{O}$, the labeled oxygen pulse only contains $^{15}\text{OO}$ without any non-labeled oxygen. Addition of $^{15}\text{OO}$ to Cu-ZSM-5 showed that $^{15}\text{OO}$ readily adsorbs on this catalyst. Similar as in the $\text{N}_2^{15}\text{O}$ experiment, the adsorbed $^{15}\text{O}$ is retained on the catalyst and is removed slowly in time, as shown in figure 8.4. This is direct proof for the (re-)adsorption and desorption/exchange of $\text{O}_2$. In kinetic analyses [4,5] this was only assumed to describe the $\text{O}_2$ dependency. The adsorption/removal of $^{15}\text{O}$ on Cu-ZSM-5 after addition of $^{15}\text{OO}$ is similar to that after addition of $\text{N}_2^{15}\text{O}$. Hence, the $^{15}\text{O}$ deposited on Cu-ZSM-5 by $\text{N}_2^{15}\text{O}$ must be removed via a similar pathway, either by desorption of $^{15}\text{OO}$ or by exchange with $\text{O}_2$ producing $^{15}\text{OO}$. The formed $^{15}\text{OO}$ is capable of readsorbing further...
Figure 8.4. Time profiles for the desorption of $^{15}$O from Cu-ZSM-5 at 800 K.
The Cu-ZSM-5 catalyst was pretreated in a stream of He at 800 K. Subsequently, a pulse of $N_2^{15}$O was introduced. After all the $^{15}$O had decayed (10 min) the Cu-ZSM-5 catalyst was loaded with $^{15}$O by adding several pulses of $^{15}$OO to the He gas stream. After adsorption, the PEP response at the indicated positions was recorded as a function of time.

downstream in the catalyst bed.

The amount of $^{16}$O retained on Cu-ZSM-5 depends on two processes, namely the adsorption of new $^{15}$O (as $^{15}$OO) and the removal of already present $^{15}$O from the zeolite. The removal of $^{15}$O depends on the desorption or exchange rate, and on the exchange rate (mobility) of $^{15}$O within the zeolite lattice. This leads to the following equation:

$$\frac{dC_{ZSM}}{dt} = k_{ads}C_{gas} - k_{des}C_{ZSM}$$ (8.1)

where,

- $C_{ZSM}$ amount of $^{15}$O retained in the zeolite
- $C_{gas}$ amount of $^{15}$OO in the gas phase (supply of $^{15}$O)
- $k_{ads}$ $^{15}$OO adsorption rate constant
- $k_{des}$ $^{15}$OO removal rate constant

Solving this differential equation in time under assumption that the initial amount of $^{15}$O in the zeolite is equal to $C_0$ ($C^{-O} = C_0$) results in the following equation:

$$C_{ZSM} = \frac{k_{ads}}{k_{des}}C_{gas} - \frac{k_{ads}}{k_{des}}C_{gas}e^{-k_{des}t} + C_0e^{-k_{des}t}$$ (8.2)

Since both $k_{ads}$ and $C_{gas}$ are not known, this can be further simplified to:

$$C_{ZSM} = \frac{R+(C_0k_{des}-R)e^{-k_{des}t}}{k_{des}}$$ (8.3)

where, $R$ represents the factor $k_{ads}C_{gas}$. 

167
Figure 8.5. Influence of temperature on the removal rate of $^{15}$O.
(O) The catalyst was pretreated in a stream of $O_2$/He at 825 K, after which a pulse of $N_2^{15}$O was injected in the He gas stream at the indicated temperatures. The response of the PEP detector in time was modeled with equation (8.3). The rate of $^{15}$O removal at the different temperatures, obtained after fitting, are displayed.

The model has been applied to the time profiles of Cu-ZSM-5 measured at different temperatures. The influence of the temperature on removal of $^{15}$O is shown in figure 8.5. The removal of $^{15}$O decreases with increasing temperature. The removal is therefore not limited by the desorption of $^{15}$OO or by exchange with $O_2$, since both processes are expected to be more efficient at higher temperatures. It is more likely that the exchange of $^{15}$O within the zeolite is responsible for the observed temperature dependency. At higher temperatures the oxygen lattice atoms are more mobile and the $^{15}$O atoms which enter the lattice are therefore more easily “lost” within this lattice (a larger $^{16}$O pool is available for exchange). Thus, exchange of $^{15}$O within the lattice is the rate determining step in removal of $^{15}$O from Cu-ZSM-5. It is impossible to discriminate between the removal of $^{15}$O by exchange or by desorption as $^{15}$OO.

To further analyze the removal of $^{15}$O from Cu-ZSM-5 the effect of addition of CO to the reaction mixture was evaluated. The catalyst was pretreated with CO before addition of the $N_2^{15}$O pulse to the reaction mixture containing 0.1% CO in helium. Figure 8.6 shows the position profiles for the decomposition of $N_2^{15}$O over Cu-ZSM-5 in the presence and absence of CO. The amount of $^{15}$O retained on the catalyst is much higher when CO is present in the reaction mixture. Almost all $^{15}$O from the pulse is deposited on the catalyst. It was not possible to analyze the reactor effluent because the amount of $^{15}$O was too low. Hence, the radioactivity observed may be present as $^{15}$OO. The enhancement of the activity in the presence of CO has also been observed by Kapteijn et al. [4]. This enhancement by CO was attributed to the removal of oxygen from the active sites, since desorption of oxygen was shown to be a difficult step in the decomposition of $N_2$O. In this case, oxygen is removed through the formation of CO$_2$. It is therefore expected that the total amount of $^{15}$O on Cu-ZSM-5 will decrease in time, since it is removed as $^{15}$OO.
Figure 8.6. Position profiles for the decomposition of N₂¹⁵O over Cu-ZSM-5 pretreated with He or CO/He at 800 K.

(C) The response of the PEP detector after pretreatment in He (standard conditions). (C) The catalyst was pretreated in a stream of CO/He at 800 K, after which a pulse of N₂¹⁵O was injected in the CO/He gas stream. The response of the PEP detector after 75 s was recorded as a function of position. This response is the same as shown in figure 8.2.

However, the total amount of ¹⁵O on Cu-ZSM-5 remains constant as indicated in figure 8.7. The slight increase in radioactivity is due to slow movement of ¹⁵O towards the center of the detector. The sensitivity of the detector is higher at the center due to more reconstruction possibilities, resulting in a higher signal. Thus, it seems that ¹⁵O is not removed by CO as C¹⁵OO. It is not expected that the exchange of ¹⁵O from C¹⁵OO with oxygen from the zeolite lattice will be very efficient on Cu-ZSM-5. This exchange would be due to the formation and subsequent breakdown of labeled carbonates.

The rate of ¹⁵O removal has been modeled to ascertain that CO has no influence on the removal. The model has been applied to the time profiles obtained in the presence and absence of CO. The modeled profiles at two positions in the catalyst bed are shown in figure 8.8. From the estimated values in Table 8.1, it can be seen that the removal (kₐ₆ₗ) of ¹⁵O is not influenced by the presence of CO. A possible explanation for these results is that ¹⁵O is also removed by exchange with CO. It has been shown that CO forms stable

<table>
<thead>
<tr>
<th>Table 8.1. Estimated model parameters (equation 8.3) for the removal of ¹⁵O in the presence or absence of CO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>kₐ₆ₗ [10²/s]</td>
</tr>
<tr>
<td>C₀ [cps]</td>
</tr>
<tr>
<td>R [cps/s]</td>
</tr>
</tbody>
</table>
complexes with Cu$^+$ making exchange between $^{15}$O from the framework and $^{16}$O from CO possible. Hence, the $^{15}$O is transported along the catalyst bed as Cu$^{15}$O. The absence of any influence of CO on the removal of $^{15}$O is related to the efficient exchange rate of $^{15}$O within the zeolite framework which determines the rate of $^{15}$O removal.

There is no clear explanation for the unusual behavior of $^{15}$O atoms deposited on Cu-ZSM-5. The decomposition of N$_2^{15}$O is dependent on the metal ion used, indicating that the metal (ion) acts as an active site. The activity of the metals used is similar as observed in literature. Thus, N$_2^{15}$O adsorbs dissociatively on the active metal site leaving an $^{15}$O atom behind. The labeled oxygen rapidly exchanges with $^{16}$O from the zeolite lattice. This exchange is the cause of the retention of $^{15}$O in metal-exchanged zeolites.

This process has also been described by Valyon et al. [7] for the behavior of oxygen deposited by NO on Cu-ZSM-5. Oxygen atoms enter the zeolite at Cu$^+$, a site which acts as a porthole for oxygen entry. The oxygen is transported through the zeolite lattice to a Cu$^{2+}$ site where recombination and subsequent escape (as O$_2$) from the catalyst can occur. It is clear that the metal ion is involved in the escape of oxygen since removal is only observed for Cu-ZSM-5. The results also show that not all the lattice oxygen is involved in the transport process since this would result in a permanent retention of $^{15}$O atoms. Which indicates that oxygen is released in the vicinity or at the same site where it was initially deposited. Oxygen which is removed as $^{15}$O subsequently readsores at a reduced site where the exchange process reoccurs.

Evidently, this model explains the behavior of $^{15}$O in the absence of CO. However, in the presence of CO the amount of converted N$_2^{15}$O increases, due to an increased amount of reduced (Cu$^+$) sites [4]. This increase can be observed by the additional amount of $^{15}$O.
Figure 8.8. Comparison between the removal of $^{15}$O from Cu-ZSM-5 in a He and a He/CO atmosphere.

The Cu-ZSM-5 catalyst was pretreated in a stream of He (A) or He/CO (B) at 800 K, after which a pulse of N$_2^{15}$O was injected in the gas stream. The catalyst shown in B was continuously flushed with He/CO after addition of N$_2^{15}$O. The response of the PEP detector was recorded as a function of time. The measurement positions in the reactor are shown in the insert in figure B. The solid lines indicate the model fits (see equation 8.3).

deposited on the catalyst. However, addition of CO does not increase the removal of $^{15}$O neither does it remove $^{15}$O as C$^{15}$OO which would be expected. A conceivable rate limiting step in the removal of $^{15}$O from Cu-ZSM-5 is the transport of $^{15}$O in the zeolite lattice. The present results indeed indicate that this transport is the rate limiting step for the removal of $^{15}$O from Cu-ZSM-5. This explains the similar removal rate of $^{15}$O in the presence and absence of CO. However, this implies that $^{15}$O still can be removed as C$^{15}$OO. Even under steady-state conditions (equimolar amounts of CO and N$_2$O), only minor removal of radioactivity from the catalyst bed can be observed. It was technically not possible to analyze the reactor effluent to show the presence of C$^{15}$OO. A slow
Figure 8.9. Time profiles for the decomposition of N$_2^{15}$O over Cu-ZSM-5 at 800 K in the presence of CO.
The Cu-ZSM-5 catalyst was pretreated in a stream of CO/He at 800 K, after which a pulse of N$_2^{15}$O was injected in the CO/He gas stream. The response of the PEP detector at the indicated positions was recorded as a function of time.

Transport of $^{15}$O through the catalyst bed is still observed at steady-state conditions similar to the results shown in figure 8.9.
A possible explanation for the absence of C$^{15}$OO formation is the presence of two types of active sites in Cu-ZSM-5, namely, isolated Cu ions and clusters of Cu ions, and that the clusters are preferably reduced by CO. It is known that CO is only capable of reducing oxocations and oxide particles (Cu-clusters [8]). The presence of Cu-clusters is possible since overexchange has been shown to occur for Cu-ZSM-5 [4]. Overexchange for the catalyst studied here could not be determined due to the low ZSM-5 loading. The removal of $^{15}$O only occurs on isolated Cu-ions and takes place by either $^{15}$OO desorption or by exchange with O$_2$ or CO. This implies that not all $^{15}$O can be removed from the Cu-ZSM-5, which agrees well with the present results showing that removal of $^{15}$O levels off with increasing time. The $^{15}$O has previously been deposited by N$_2^{15}$O. The enhanced activity in the presence of CO can still be explained by an increase in the number of reduced sites. The observed readsorption of $^{15}$O on the catalyst may merely be due to the exchange of $^{15}$OO with the isolated Cu ions, which has been shown to be an efficient reaction for Cu-ZSM-5 [9]. This exchange may also be responsible for the readsorption of radioactivity observed when the N$_2^{15}$O pulse in injected in helium. Although the behavior of $^{15}$O in/on Cu-ZSM-5 remains unusual, the above mentioned sequence can explain the results found in this study.
4 CONCLUSION

The $\text{N}_2^{\text{15O}}$ decomposition reaction on various metal ion-exchanged zeolites displays a similar behavior, namely the incorporation of $^{15}\text{O}$ into the zeolite lattice. This results in an almost permanent retention of $^{15}\text{O}$ on the ZSM-5 catalysts. The retained amount is closely related to the activity of the catalyst. The following reactivity order for the metal ions has been found, Cu-ZSM-5 > Co-ZSM-5 > Fe-ZSM-5, which is similar to previous results. Cu-ZSM-5 is the only catalyst from which $^{15}\text{O}$ is slowly removed from the catalyst in time. This indicates that the desorption of $^{15}\text{O} \text{O}_2$ is related to the metal ion used, and is not just a property of the zeolite.

The unusual behavior of Cu-ZSM-5 in the presence of CO which promotes the activity but does not remove $^{15}\text{O}$ can be explained by a dual site model. The two types of sites that exist on Cu-ZSM-5 are isolated Cu ions and clusters of Cu ions. The isolated Cu-ZSM-5 ions are responsible for the removal of $^{15}\text{O}$ through exchange with O$_2$ or by desorption as $^{15}\text{O}_2$. The Cu clusters account for the enhanced activity and do not promote the removal of $^{15}\text{O}$ from the zeolite lattice by the formation of $^{15}\text{O} \text{O}_2$ or C$^{15}\text{O} \text{O}_2$. The isolated Cu ions are responsible for the removal of $^{15}\text{O}$ via $^{15}\text{O} \text{O}_2$ whereas the $^{15}\text{O}$ cannot directly be removed from these sites by CO.

5 REFERENCES


THE REDUCTION OF $^{13}$NO BY CO OVER Pt/Al$_2$O$_3$

**ABSTRACT**

The reduction of NO by CO over Pt/Al$_2$O$_3$ has been studied with positron emission profiling (PEP). With the use of positron emitters PEP allows the concentration of this isotope to be determined as a function of position and time through the catalyst bed. Using nitrogen labeled ($^{13}$NO) molecules it was shown that under reaction conditions two types of $^{13}$N containing species are present on the catalyst surface. The first species is $^{13}$NO which is efficiently adsorbed on platinum, even in the presence of CO. This $^{13}$NO is slowly converted to N$_2$ at low temperatures (425 K) which can be explained by slow dissociation of NO under these conditions. The other $^{13}$N containing species is situated on the support resulting in a long retention (>600 s). It is likely to be $^{13}$NCO which has been shown to be formed on the platinum surface followed by spill-over to the support where it is slowly removed by gas phase NO.
CHAPTER 9

1 INTRODUCTION

Removal of nitrogen oxides from combustion products belongs to the permanent challenges in the field of environmental catalysis. Reduction of NO\textsubscript{x} by various reductants, like hydrogen, ammonia, CO, and hydrocarbons has been frequently reported and is also employed in practice [1,2]. As CO and NO are simultaneously present in automobile emissions, their conversions over heterogeneous catalysts, predominantly supported noble metals, have been the subject of many studies [3]. Numerous studies have focused on the kinetics and mechanism of the NO - CO reaction and the adsorption and decomposition processes participating in N\textsubscript{2} formation. Application of various surface chemistry techniques to studies on polycrystalline and single-crystal surfaces [4] has provided understanding of the elementary surface processes on an atomic scale. These techniques mostly require ultra-high vacuum and are most suited for studying well characterized low surface area metals, whereas the active metal on practical catalysts is dispersed on high surface area oxide supports. For catalysts operating under realistic conditions it has been shown that isocynate species (NCO) are present on the support.

The reaction mechanism over platinum consists of the following steps if the formation of N\textsubscript{2}O is ignored. This seems to be allowable since no N\textsubscript{2}O was observed.

\[
\begin{align*}
\text{NO} + \ast & \xrightleftharpoons[k_1]{k_0} \text{NO}\ast \\
\text{NO}\ast + \ast & \xrightarrow{k_0} \text{N}\ast + \text{O}\ast \\
\text{CO}\ast + \text{O}\ast & \xrightarrow{k_3} \text{CO}_2 + 2\ast \\
\text{N}\ast + \text{N}\ast & \xrightarrow{k_4} \text{N}_2 + 2\ast
\end{align*}
\]  

The NO - CO reaction consists of the reversible adsorption of NO on the platinum surface. Adsorbed NO can dissociate forming adsorbed N and adsorbed O. This step is assumed to be rate limiting and can only occur in the presence of vacant sites. The production of CO\textsubscript{2} and N\textsubscript{2} occurs immediately after the dissociation of adsorbed NO. The desorption of N\textsubscript{2} formed via recombination of adsorbed N atoms is very efficient on platinum [5,6]. Positron emission profiling (PEP) is a recently developed detection system for positron emitters in a catalytic reactor under realistic conditions. The technique is based on detection of gamma rays produced during the decay of a positron emitter. The photons have enough energy to penetrate the reactor and the surrounding oven to reach the detector. This detection process allows determination of the concentration (amount of radioactivity) as a function of both time and position.

In this chapter the NO - CO reaction over Pt/Al\textsubscript{2}O\textsubscript{3} has been studied with PEP using $^{13}$NO as a tracer. Using this tracer it is only possible to follow the reaction pathway of $^{13}$N. It will be shown that NCO species are likely to be formed under the conditions used.
2 EXPERIMENTAL

2.1 Materials

CO and NO were obtained from Praxair, helium was obtained from Hoekloos. The gases were used without further purification. The helium had a purity of 99.999%. Both CO and NO were supplied from a cylinder containing a mixture of 5% CO in helium and 0.5% NO in helium respectively.

The 0.3 w% Pt/Al₂O₃ catalyst (density 0.45 kg/m³) was obtained from Johnson Mathey. The catalyst was characterized by CO adsorption. The platinum surface area determined by CO adsorption was 284 m²/g Pt. Assuming hemispherical platinum particles on the surface of Al₂O₃, the particle size was determined from the ratio between the platinum metal volume and surface area. This resulted in particles with an average diameter of 2 nm. The dispersion is defined as the number of adsorbed CO molecules divided by the total number of Pt atoms, resulting in a dispersion of 56%.

2.2 PEP experiments with ¹³NO

A thorough description of the procedure to perform PEP experiments is given in chapter 2, therefore, only a short description will be given here. The quartz reactor was loaded with 1.45 g of the 0.3% Pt/Al₂O₃ catalyst, resulting in a bed length of 4.1 cm, and was further filled up with glass beads (diameter 0.65 mm) on both sides of the catalyst bed. The catalyst was pretreated in He at 775 K for 1 hour. The catalyst temperature was then allowed to reach the reaction temperature while flowing with helium (40 ml/min). At the reaction temperature a mixture of 1.25% CO and 0.125% NO in helium was added to the catalyst. The catalyst was allowed to reach steady-state for at least 10 hours. Upon subsequent changes (rise) in temperature the catalyst reached steady-state in less than 60 minutes. The conversion of N₂¹⁵O over Pt/Al₂O₃ was investigated in a temperature range from 425 K to 525 K.

¹³NO was prepared as described in chapter 2. PEP experiments were performed by injecting ¹³NO in the reaction mixture to the catalyst. A sampling time of 0.5 s was used for recording the PEP profiles. The PEP profile comprises the amount of ¹³N measured at 17 equidistant positions along the axial axis of the reactor as a function of time. The profiles were corrected for the decay of ¹³N during the analysis time. The results from the measurements can be displayed as a function of time at a specific position in the reactor (time profile). The amount of radioactivity in the reactor effluent was measured with a separate, more sensitive, NaI detector. The composition of the reactor effluent was determined by GC analysis. This analysis detected both labeled and non-labeled components in the gas stream.

3 RESULTS

The reduction of NO by CO over Pt/Al₂O₃ has been analyzed in the temperature range from 425 K to 525 K. At these temperatures NO is totally converted to N₂ and CO₂. Figure
Figure 9.1. The amount of $^{13}\text{N}$ in the reactor effluent.

The Pt/Al$_2$O$_3$ catalyst was allowed to reach steady-state in a mixture of CO/NO in helium. Subsequently, $^{15}\text{NO}$ was injected in the reaction mixture. The curves display the course of the amount of $^{15}\text{N}$ in the reactor effluent as a function of time. This was recorded at different temperatures as indicated in the figure. GC analysis showed that all the activity was present as $^{15}\text{N}_2$.

9.1 shows the $^{13}\text{N}$ profiles measured at the reactor exit. These curves have been normalized for the initial amount of $^{15}\text{NO}$ added to the reaction mixture. An increase of the reaction temperature results in a narrower effluent curve shape. Analysis of the reactor effluent indicates that all radioactivity is present as $^{15}\text{N}_2$, no $^{15}\text{NO}$ nor $^{15}\text{N}_2\text{O}$ could be detected. This is consistent with the steady-state, which shows that all NO is converted to $\text{N}_2$ and CO$_2$.

The behavior of $^{15}\text{NO}$ in the catalyst bed has been recorded with the PEP detector. Figure 9.2 shows the resulting time profiles of $^{13}\text{NO}$. These profiles mainly show the amount of $^{15}\text{NO}$ adsorbed on the catalyst. The amount of $^{13}\text{NO}$ in the gas phase is also recorded but its contribution to the total signal is low. In the studied temperature range $^{13}\text{NO}$ is mainly adsorbed at the beginning of the catalyst bed. No radioactivity is observed further downstream. Almost all $^{13}\text{NO}$ is adsorbed in the first cm of the bed, and therefore only the response in this part of the catalyst is shown in figure 9.2. Only at high temperature (525 K) a pulse of a $^{13}\text{N}$ containing species passes through the whole catalyst bed. Since no adsorption of this species occurs, it is likely to be $^{15}\text{N}_2$. The profiles further show that a $^{13}\text{N}$ containing compound is retained on the catalyst. It is not possible to determine the nature of this component with the PEP detector. The amount of this species on the catalyst increases with decreasing temperature. The removal of this species shows the same temperature dependency.

The adsorbed $^{13}\text{N}$ containing compound is removed slowly from the catalyst. Closer examination of the initial curves at different temperatures shows that removal occurs at two different rates. This is evident from figure 9.3 in which the responses at the start of the catalyst are shown. The results show the presence of a temperature dependent (first part), and a nearly temperature independent (second part) removal.
Figure 9.2. Time profiles of the reduction of $^{13}$NO over Pt/Al$_2$O$_3$ at 425 K, 475 K and 525 K.

The catalyst was allowed to reach steady-state in a mixture of NO and CO in helium. A pulse of $^{13}$NO was added to the reaction mixture and the response of the PEP detector was recorded as a function of time. Since $^{13}$NO was only adsorbed at the beginning of the catalyst bed only these positions are displayed. The numbers correspond to the reconstruction position at which the signal was recorded. Position 3 is the first reconstruction position in the catalyst bed. The interval between two positions is 0.325 mm.
Figure 9.3. Comparison between the initial PEP curves at different temperatures. The catalyst was allowed to reach steady-state in a mixture of NO and CO in helium. A pulse of $^{15}$NO was added to the reaction mixture and the response of the PEP detector at the start of the catalyst bed was recorded as a function of time at 425 K, 475 K, and 525 K.

4 DISCUSSION

The mechanism of the reduction of NO by CO over platinum is given by equations (9.1-9.4), and starts with adsorption of NO on the metal surface. The adsorption of NO on Pt is hardly hindered by CO in the temperature range studied. $^{15}$NO which enters the catalyst is readily adsorbed in the first part of the catalyst bed (1 cm). This shows that the adsorption of NO is not rate limiting.

The PEP profiles indicate the presence of two distinct species on the catalyst which are removed at different rates. The first ($^{15}$N$_1$) which is removed within the first 300 s shows a temperature dependent removal. The rate increases with increasing temperature, and at high temperature $^{15}$N$_1$ is not present at all. The retention of the other $^{15}$N containing specie ($^{15}$N$_2$) does not show a temperature dependence and its removal rate is very low. The species $^{15}$N$_1$ which is retained at low temperature (<475 K) is likely to be $^{15}$NO since $^{15}$N will desorb after recombination with another adsorbed nitrogen (step 9.4). In addition, it has been shown that the dissociation of NO is the rate limiting step. The presence of $^{15}$N$_2$ in the target effluent is clearly related to the presence of $^{15}$N$_1$ on the catalyst. At low temperature the effluent profile shows a slow formation of N$_2$. At high temperature most of the $^{15}$NO is immediately converted to N$_2$ as is evident from the narrow N$_2$ formation pulse in the reactor effluent and the absence of $^{15}$N$_1$ (see figure 9.3).

Furthermore, at low temperature (425 K) a $^{15}$N containing molecule is desorbed and readsored further downstream in the catalyst bed (see figure 9.2). Again, the most likely candidate is $^{15}$NO (step 9.1) showing that this molecule must be present on the platinum surface at low temperature. $^{15}$NO could also be formed by recombination of adsorbed $^{15}$N and O, however, this is very unlikely because the removal of adsorbed O by CO is
very efficient at this temperature. It is not possible to completely rule out that $^{15}$N is the adsorbed species at low temperature. This can only be realized if N$^{15}$O is used as a tracer. If a complete description of the reaction pathway is to be deduced with PEP all the atoms in the reactant molecule have to be labeled successively.

The residence time of $^{13}$NO ($^{13}$N$_{ii}$) on the catalyst surface seems to be relatively long. The removal of $^{13}$NO shows an exponential decay in time; the residence time can be determined from this decay as is common in SSITKA (see chapter 1, [7-10]). The average residence time at 425 K is 60 s. Considering the supply of non-labeled NO in the reaction mixture, the platinum surface is completely covered with NO within 100 s. This indicates that the complete amount of injected $^{13}$NO is likely to be on the platinum surface. It can not be excluded that some of the adsorbed $^{13}$NO migrates to the support (spill-over).

With IR spectroscopy it has been shown that nitrogen containing species are present on the support during the NO - CO reaction [11,12]. The temperature dependent nature of $^{13}$N$_{ii}$ can be explained as follows. At low temperature the dissociation rate of NO is low and $^{13}$NO on the platinum surface is removed slowly. At high temperature the dissociation rate is fast such that removal of $^{13}$N through $^{13}$N$_{ii}$ formation is also efficient, resulting in a short residence time of $^{13}$NO on the surface.

The residence time of species $^{13}$N$_{ii}$ on the catalyst surface is much longer than that of $^{13}$N$_{i}$ (10NO). This indicates that this species must be present on the support. Several studies have reported the presence of a stable isocynate species (NCO) on the support. NCO is formed on the platinum surface after which spill-over to the support occurs. Once on the support a stable complex with Al$_2$O$_3$ is formed and NCO is removed slowly by NO from the gas phase as N$_2$ and CO$_2$ [11]. Therefore, $^{13}$N$_{ii}$ is likely to be $^{15}$NCO considering the
slow removal of this species. The temperature independency of the amount of formed NCO can be explained as each produced \(^{13}\)N has a certain chance to form NCO. Then the amount of NCO just depends on the amount of \(^{13}\)N formed which should be equal at each temperature since the NO conversion was 100%.

Based on the previous results the following mechanism is proposed for the reduction of \(^{13}\)NO by CO, as depicted in figure 9.4. The reaction starts with adsorption of CO and NO on platinum. The removal of \(^{13}\)NO through \(^{13}\)N\(_2\) formation depends on the dissociation rate of NO which increases with increasing temperature. The fate of the adsorbed N atoms is recombination with another N to give N\(_2\)(g), or reaction with CO to give isocynate (NCO). The NCO species can migrate to the support to form a stable support complex which slowly reacts with NO from the gas phase to give N\(_2\) and CO\(_2\). Adsorbed O atoms are removed by CO under formation of CO\(_2\).

5 CONCLUSION

The reaction of \(^{13}\)NO with CO produces two species which are retained on the catalyst. The first species is \(^{13}\)NO showing a temperature related retention on the surface. This can be explained by the temperature dependency of the NO dissociation rate; at low temperature this rate is low, and therefore the adsorbed \(^{13}\)NO is longer present on the surface. The residence time of the second species on the surface of the catalyst is too long for it to be solely present on the platinum surface. It is therefore proposed that this species migrates to the support. This slowly removed species is related to the formation of stable isocynate (NCO) on the support.

6 REFERENCES


EVALUATION OF
POSITRON EMISSION PROFILING

ABSTRACT

This chapter contains an evaluation of the application of positron emission profiling in heterogeneous catalysis. This in-situ technique is based on the detection of positron emitting molecules as they pass through the catalyst bed. This results in the determination of the concentration of the isotope as a function of position and time. Two types of information can be extracted from the data: qualitative and quantitative. Both aspects have been used in this thesis to deduce the mechanism and kinetics of catalytic reactions. The main focus is placed on the decomposition of N₂O, and the role of oxygen formed during this reaction. The data have successfully been modeled using a combination of a mathematical description of the reaction steps, and a model describing the detector sensitivity.
CHAPTER 10

1 INTRODUCTION

A major part of catalysis research is devoted to deduction of the mechanism and kinetics of the catalytic reaction taking place on the catalyst surface. Several techniques have been developed to achieve this goal. The most common methods are transient and isotopic techniques. In addition, several new methods are being developed enabling analysis of species on the catalyst under realistic conditions. Positron emission profiling (PEP) is a relatively new technique that combines the possibilities of the previously mentioned methods. The technique consists of addition of a pulse of radioisotopes (positron emitters) to the catalyst operating under steadystate conditions. The pulse only contains a minute amount of a positron emitting labeled reactant, and therefore, the pulse does not influence the steady-state reaction. The positron, which is the antiparticle of an electron, combines with an electron resulting in annihilation of both particles. The total energy of the particles is converted into two 511 keV photons emitted in opposite direction. The energy of the photons is high enough to penetrate the surrounding reactor and oven. The location of this annihilation event can then be determined via coincident detection of the emitted photons using two arrays (banks) of scintillation crystals. Each bank holds nine bismuth germanium oxide (BGO) crystals. The annihilation position is reconstructed from the intersection of the line which connects the two elements that detected a photon and the central axial axis of the reactor. In this way the activity (concentration) can be measured at 17 unique equidistant positions along the axial axis of the reactor. The distance between each measuring position is 3.25 mm. Hence, the course of the radio-isotopes through the catalyst bed can be followed with the PEP detector. This allows determination of the radioisotope concentration as a function of both position and time. As such, the PEP technique contains transient information (labeled pulse) about the catalytic reaction. The distribution of the isotope among the reaction products and the catalyst gives extra insight in the reaction mechanism (isotopic information). Furthermore information about the residence time of radioactive molecules and atoms on the catalyst surface can be extracted.

With the PEP technique the amount of the radioactive molecules in the catalytic reactor can be measured as a function of time and position resulting in a PEP profile of the catalytic reaction. The information contained in a PEP profile can be used to gain insight in the kinetics and mechanism of the catalytic reaction. Two types of information can be obtained from PEP profiles, qualitative and quantitative information. Each type will be discussed in more detail in the next paragraphs. At the end of this chapter some prospects for the PEP technique in relation to reaction kinetic research will be given.

2 QUALITATIVE INFORMATION

Qualitative information can be obtained from a PEP profile by direct interpretation of the radioactive atom distribution along the catalyst bed as a function of time and position. In this case the effects of positron range and photon scattering on the resulting profile can be discarded. The main consequence of positron range and photon scattering is that the
measured isotope concentration along the axial axis of the catalyst is smoothed. Thus, the absolute amount of the isotope at a specific position is not known, although trends in the distribution will be visible (e.g. high amount of radioactivity at the beginning of the catalyst bed versus a low amount at the end). Even though the exact position and amount of the radioisotope in the catalyst bed is not known much information can be obtained from the retention of the radioisotope on the catalyst. The retention of $^{15}$O emanating from $N_2^{15}$O has been used in this thesis to elucidate the role of oxygen during the decomposition of $N_2O$ over Pt/Al$_2$O$_3$ and ion-exchanged zeolites. It was shown that during decomposition the $^{15}$O atom was indefinitely retained on both catalysts. The retention of $^{15}$O was shown to be related to the transfer of $^{15}$O to the surface of the support or to the zeolite lattice. After this transfer the $^{15}$O atom exchanges with oxygen atoms from the support or lattice. Since the amount of oxygen atoms in these materials is very high, the $^{15}$O atom virtually gets lost in this large oxygen pool. This results in permanent retention of $^{15}$O on these catalysts. This conclusion could be drawn because the amount of retained $^{15}$O on the catalyst was related to the decomposition activity of the catalyst.

The qualitative interpretation of PEP data is usually not so straightforward as in the case of the $N_2O$ decomposition. In this reaction the number of reactants and products which contain the radioactive isotope is small (only $N_2^{15}$O and $^{15}$OO). When other catalytic reactions are considered the radioisotope is distributed among several components. This complicates the interpretation, because it is not possible to deduce the identity of the radioactive molecules with the PEP technique. This problem was also encountered during the interpretation of results concerning the reduction of NO by CO over Pt/Al$_2$O$_3$. The measured amount of radioactivity adsorbed on the catalyst could originate from $^{15}$N, $^{15}$NN, and $^{15}$NO. The products $^{15}$N or $^{15}$NN could be formed after dissociation of $^{15}$NO. Using results from other studies it was deduced that $^{15}$NO was the most likely source for the observed signal. A more conclusive evaluation could be obtained if also the N atom of NO is replaced by its positron emitting counterpart. In this case, the PEP profiles of $^{15}$NO and N$^{15}$O should be compared. If the retention of $^{15}$N is similar to that of $^{15}$O, then $^{15}$NO is the species present on the surface. A similar retention of $^{15}$N and $^{15}$O may seem unlikely because removal of these atoms does not solely depend on the dissociation of NO, but also on the removal rates of $^{15}$N and $^{15}$O from the catalyst. However if dissociation of NO is the rate limiting step, as proposed here, a similar retention should be observed. In conclusion, a full description of the reaction mechanism using only qualitative information from the PEP profiles, can only be obtained if all the atoms participating in the reaction are replaced by their positron emitting counterpart.

3 QUANTITATIVE INFORMATION

3.1 Introduction

The major aim of this thesis was the development of a method to model the transient data (profiles) obtained with the PEP technique in order to acquire reaction kinetic data.
CHAPTER 10

The solution of this problem consists of two modeling procedures:

1. Mathematical modeling.
   Solution of the mathematical model which describes the position and time dependency of the radioactive atom concentration in the catalytic reactor.

2. Monte Carlo modeling.
   Modeling of the detector sensitivity to a positron emitting source as a function of the position in the catalytic reactor.

The properties of the above mentioned modeling procedures will be discussed in more detail below.

3.2 Mathematical modeling

The mathematical model describes the steady-state catalyst occupancies of all species participating in the catalytic reaction, and the behavior of the radioactive molecules in the injected pulse. The steady-state is given by a system of ordinary differential equations and algebraic equations (DAE) which respectively describe the concentration of the reactants and products in the gas phase and on the catalyst surface. The course of the radioactive pulse in time and space is given by a system of partial differential equations (PDE). Both the DAE and PDE need to be solved simultaneously to give a correct modeling description of the PEP profiles. This combined system was solved numerically, using DASSL to solve the DAE, and the method of lines (LSODES and finite difference) for the solution of the PDE. The modeling results are thus dependent on the adequacy of the numerical methods, and the accuracy of the initial and boundary conditions. The accuracy of the latter conditions is determined by the experimental procedures and setup. For instance, the preparation method of the positron emitting tracer determines the shape of the input pulse which is used as a boundary condition in the PDE modeling. From a computational point of view the numerical solution of the PDE is the most demanding as compared to the DAE. The PDE system consists of numerous ODEs which have to be solved simultaneously. The number of ODEs depends on the number of radioactive reactants and products, and the number of grid points (see chapter 4). The accuracy of the method is enhanced by increasing the number of grid points, 160 grid points were used in the current model. In contrast, only several ODEs need to be solved for the DAE system. The number of ODEs only depends on the number of components in the system. Hence, most of the computation time is spent on the solution of the PDE. The dependency of the final solution (simulated PEP profile) on the results of the DAE and PDE is completely different. The simulated PEP profile highly depends on the results of the DAE since it serves as an initial condition for the PDE system. The results from the DAE calculation determine the surface occupancies of the non-labeled species on the catalyst, and the amount of available free sites. It is assumed that these occupancies do not change during addition of the labeled pulse, since this amount of labeled molecules is very small. The calculated occupancies as a function of the position in the catalyst bed are then used in the PDE calculation to determine the behavior of the labeled components. As a result, the relative (normalized) amounts of tracer on the catalyst and

188
in the gas phase are independent of the amount of tracer initially added. This in turn simplifies the fitting procedure because the exact amount of tracer added to the reactor does not need to be known (this amount was indeed not known in this study).

The accuracy of the numerical solution method is mainly determined by the accuracy with which the steady-state (DAE) can be determined. In addition, the accuracy of the method of lines (PDE solution) is mainly determined by the spatial approximation. In this case, finite difference formulas were used for the solution in the spatial direction. The precision of these formulas can easily be improved by using higher order formulas and more grid points. This does not pose a practical problem due to the rapid increase in processing power of personal computers. Hence, the error in the numerical solution of the PDE will be small and controllable (e.g. additional grid points). The accuracy of the DAE solution depends on the complexity of the modeled system and the initial conditions. The reaction systems used in this thesis are not complex, therefore, no problems were observed. The initial conditions of the DAE consist of determining the surface occupancies at the beginning of the catalyst bed using the known gas phase concentrations. In a study by Vonkeman et al. this was accomplished by treating it as a non-steady-state problem. The occupancies were obtained by allowing the system to reach a numerical steady-state. In this study, the occupancies were calculated by directly solving the DAE equations for the initial conditions (using the assumption that the concentration change at the start of the bed is zero). The results showed that the solution converged to consistent values for the occupancies. Thus, the DAE system can be numerically solved in an efficient and accurate manner. However, because the mathematical solution mainly depends on the solution of the DAE, a better description of the reaction system might be appropriate. For example, the effects of dispersion may be added to the DAE equations.

3.3 Monte Carlo modeling

The main purpose of the Monte Carlo calculations is to add the effects of the detector sensitivity to the mathematical solution. The Monte Carlo model determines the effects of photon scattering and positron range on the position resolution of the PEP detector. The main contributions influencing the position resolution are photon scattering in the detection crystals and the range of the emitted positrons in the catalyst bed. The influence of the detection crystals is closely related to their physical properties like composition and geometry. These properties are fixed to the setup of the PEP detector. The only factor which can easily be influenced is the range of the positrons in the catalyst. This range should be as small as possible such that the annihilation position is close to the position of the positron emitting molecule. The factor with the largest influence on the positron range is the density of the catalyst. The density of frequently used catalysts is low, because the carrier material used to prepare the catalyst (e.g. Al₂O₃, SiO₂) has a low density. A solution to this problem is to coat the catalyst on more dense material. This approach was used in this thesis to study the catalytic properties of ion-exchanged ZSM-5 catalysts. The zeolitic catalyst was coated on glass beads during the
synthesis of ZSM-5. The resulting catalyst has a much 10-fold higher density than the original catalyst. In addition, the pressure drop over the catalyst bed is low compared to a bed packed with small ZSM-5 crystals.

The Monte Carlo simulations were used to construct sensitivity profiles. These profiles describe the sensitivity of the detector to a positron emitting source as a function of its axial position between the two detection banks. Convolution of these profiles with the mathematical solution results in a profile which can be compared with the experimental PEP profile. This approach was used to model the reaction kinetics of the decomposition of \( \text{N}_2^{15}\text{O} \) over Pt/Al\(_2\)O\(_3\). The modeling results showed a strong adsorption of \( \text{O}_2 \) on the platinum surface. This was also evident from the qualitative results, since a strong adsorption of \( ^{15}\text{O} \) was observed at the beginning of the catalyst bed.

### 3.4 Improvements

Several improvements of the experimental setup can be made to aid the quantitative modeling of the PEP results. The following points will be discussed here: position resolution, position of the catalyst bed, pulse width of the injected tracer, and influence of the carrier gas velocity.

**Position resolution:** Increasing the position resolution will limit the smoothing effect of the detection process on the actual distribution of the tracer along the catalyst bed. The position resolution of the system may be improved by using a catalyst with a high density, or a reactor tube with a small internal diameter. Both aspects will reduce the range of the positrons in the catalytic reactor. In addition, better alignment of the crystals will also increase the position resolution.

**Catalyst bed position:** The position of the catalyst bed has a significant influence on the measured profile (chapter 7). In addition, the position of the catalyst bed needs to be known to simulate the sensitivity profiles. The exact position of the catalyst bed with respect to the detector is difficult to determine in the current setup. The first limiting factor is that the boundary between the catalyst and the inert material, used to fill the reactor, is not sharp enough. This could be solved by placing a frit between the catalyst and the inert. A second limitation is that the exact position of the start of the catalyst bed is not known. The position of the catalyst could be determined by relating the position of a point source in the oven to the position of the catalyst/inert interface. This requires a point source that can be fitted in the oven of which its position is exactly known.

**Pulse width:** To ease the mathematical modeling a narrow tracer pulse is preferred. In addition, the actual shape of the tracer pulse just before it enters the catalyst bed should be known. With the current setup it is difficult to determine the pulse shape, since the response to the fast moving pulse is low. This could be improved by limiting the effects of dispersion in the reactor before the tracer enters the catalyst by adjustment of the linear flow rate, or by a different reactor design. In this case, the pulse can be measured just before it enters the reactor with a sensitive detector.

**Carrier gas velocity:** As shown in chapter 7 and 9 the response to the moving tracer in the gas phase is much lower compared to the same amount of tracer adsorbed on the
catalyst. The response is also a function of the gas velocity. Increasing the gas velocity decreases the response to the tracer. Mathematical modeling may be simplified by increasing the carrier gas velocity such that the response of the gas phase is negligible. In this case, the response does not need to be included in the modeling procedure.

3.5 Limitations

A method has been developed to simulate the PEP profiles with a mathematical model describing the catalytic reaction convoluted with the detector sensitivity profiles. The method has proven to be successful in predicting the results of the decomposition of N$_2$O over Pt/Al$_2$O$_3$. The results showed that it was necessary to perform a convolution of the mathematical model with the detector sensitivity profiles. However, prediction of time dependent results remained difficult. These simulation results mainly depended on the shape of the initial pulse. Attempts were made to model the results of the $^{13}$CO oxidation over Pt/Al$_2$O$_3$, and the adsorption/desorption of N$_2^{15}$O on ZSM-5. These results also showed that these simulations depended on the tracer pulse shape. The width of the time profile measured with the PEP detector at the beginning of the catalyst bed was similar to that of the injected pulse for these experiments. As mentioned, the shape of the tracer just before it enters the catalyst bed can not be measured accurately with the PEP detector. Therefore, the pulse shape was estimated from the pulse measured directly after the synthesis equipment with the addition of a certain amount of dispersion. Consequently, the fitting results were also dependent on the dispersion value, since this was an unknown parameter. These results imply that the pulse shape will always play an important role in the simulation results when the retention of the tracer is of the same magnitude as the pulse width. Hence, the PEP system is not suited to evaluate systems with high surface reaction rates (efficient removal of the labeled atom).

Considering the above mentioned limitation of PEP, the reduction of $^{15}$NO by CO over Pt/Al$_2$O$_3$ appears to be a suitable reaction to be studied with the PEP technique. The retention of $^{15}$N on the platinum surface is long enough that resemblance with the injected pulse is negligible (this is especially true for the low temperature results). Since chapter 9 was a preliminary study on this system, modeling would require additional reaction profiles at different temperatures.

3.6 Possibilities for PEP in catalysis

Reviewing the results described in this thesis and the limitations of the PEP system, it is possible to specify some areas in catalysis research which may benefit from the PEP technique. The main strength of PEP lies in its ability to measure the concentration of a tracer under realistic conditions, and its use of isotopes to follow the reaction sequence. In principle there are no limitations to the conditions under which the catalyst is operated. It is possible to examine catalytic reactions under high pressure and at high temperature under steady-state conditions. These conditions are difficult to realize when using surface science techniques to elucidate the reaction mechanism of a catalytic reaction.
Isotopes have long been used to verify reaction mechanisms, therefore, the PEP technique has competition from techniques applying this analysis route. For example, it is possible to develop a transient method based on detection of isotopes via mass spectroscopy. A PEP comparable system can be obtained by measuring the isotope distribution in the effluent with a mass-spectrometer for different catalyst quantities (varying the bed length). Such a system would be more sensitive, and the amount of isotope retained on the catalyst can be obtained from the mass balance. Thus, for catalytic systems with high surface reaction rates such an analysis system would be the choice. A distinct advantage of PEP is that the retained amount can be monitored directly. The slow removal of the isotope from the catalyst surface will result in a very low concentration at the reactor exit. Therefore, it is difficult to determine this concentration accurately. Hence, in this case PEP is the technique of choice.

The above mentioned advantage of PEP can be used to analyze reaction systems where exchange with the catalyst plays an important role. For example, oxidation reactions over metal oxides can involve transport of adsorbed oxygen into the lattice, and removal of lattice and surface oxygen by the reactants (Mars and Van Krevelen reaction mechanism). Thus, radioactive oxygen admitted to this system will be slowly removed from the catalyst. PEP can be used to measure the overall oxygen removal rate and to determine the amount of lattice oxygen involved in the oxidation reaction. Another field for PEP research is studying of catalysts operated under extreme conditions. Such a system is Fischer-Tropsch catalysis which is operated at high pressure to obtain hydrocarbons from CO and hydrogen. In this reaction CO is adsorbed on the catalyst surface from which carbon is formed by disproportionation. The adsorbed carbon reacts with hydrogen, and the hydrogenated carbon further reacts to produce lengthy hydrocarbons. Using $^{11}$CO this reaction can be followed with PEP. Removal of $^{11}$C from the catalyst surface is not expected to be rapid, furthermore, readsoption of the reaction products, will result in a long retention of $^{11}$C. This makes the reaction ideal for PEP. Although it is only possible to analyze the overall retention of $^{11}$C, a model can be used to verify the reaction mechanism.
APPENDIX: SENSITIVITY MATRICES

A.1 Introduction

Modeling PEP experiments involves solving a combined PDE/DAE model. This mathematical model describes the steady-state reactions (DAE) and the transient (PDE). The transient equations describe the evolution of the labeled pulse through the reactor. The surface coverage of the non-labeled species and the number of free sites is taken from the steady-state. The procedure to solve this system numerically is given in chapter 4. The numerical solution describes the concentration of the labeled species at a specific position in the reactor. The PEP detector does not measure the concentration with an infinite accuracy. The detection process determines the average activity of a range of positions. The contribution of the activity at a specific position to the response measured at a certain reconstruction position is given by the sensitivity profile. Each reconstruction position has its own sensitivity profile. Since there are 17 reconstruction positions, the response of the whole detector is given by a matrix containing all the sensitivity profiles. Each column of this matrix describes the position sensitivity of a reconstruction position. The sensitivity depends on several factors like the reconstruction position, the positron emitter used, the density of the catalyst/inert, and the composition and shape of the oven. The sensitivity profiles were simulated with EGS4, since it is not possible to obtain these profiles experimentally. Including these sensitivity profiles (matrix) in the mathematical solution will give a more detailed description of the experimental data. The effect of the detector response was added to the mathematical solution by convolution with the sensitivity matrix.

The sensitivity matrices have been calculated with EGS4. The calculated sensitivity matrices used in this thesis are given in this appendix. A short description of what was taken into account in the EGS4 simulations will be described in the next section. The numerical values of the matrices will not be shown, since it is more illustrative to show a graphic representation of the profiles. The graphs show the position dependency of every reconstruction position.

A.2 Modeling

The sensitivity profiles for each reconstruction position were calculated with EGS4. The calculations contain the influence of the positron range and photon scattering. A simplified description of the simulation system is shown in figure A.1. A more detailed figure is shown in chapter 5. Figure A.1 shows the position of the catalyst bed with respect to the detection elements of the PEP detector. The positrons are emitted from a cylindrical slab with an energy related to the isotope used. The positrons are transported through the catalyst/inert, and the surrounding reactor/oven if their energy is still high enough, until annihilation occurs. Annihilation produces two high energy photons which
Figure A.1. Schematic of the simulated geometry of the reactor/catalyst system. The figure shows the position of the catalyst bed with respect to the PEP detector. The width of the catalyst bed is 41 mm. The bed is enclosed by inert material on both sides. The density of both the catalyst and inert can be chosen during the simulation. The source has a cylindrical shape with an infinitely small length (slab). The properties of the positron emitter can also be varied. The oven is not shown in this setup but is included in the simulation. A full description of the simulated setup is given in chapter 5.

are then transported. Since the energy of the photons is high the chance that they will interact with the reactor/oven is small. Therefore, most of the interactions will occur in the detection elements (BGO crystals). In contrast, transport of positrons involves a large amount of interactions. This means that a large amount of the simulation time is spent on determining the positron range. To obtain statistically meaningful results a large amount of positrons needs to be simulated at every source position. With the current computational power it takes a month to calculate the sensitivity profiles for the whole detector. To decrease the computation time by 50% a symmetrical setup was assumed, in this case only half of the detector response needs to be simulated. This assumption is true for the PEP detector, however, the catalyst bed was not always situated in the center of the detector. This discrepancy was overcome by inserting some additional profiles at the center of the catalyst bed. The inserted profiles are identical to the sensitivity profile measured at position 9 (center). The effect of this procedure is shown in figure A.3.

A.3 Sensitivity matrices

All the matrices used in this thesis are shown in the figures of this Appendix. Each matrix is accompanied by a short explanation. Figure A.2 shows the calculated sensitivity profiles for an $^{15}$O containing positron emitter (tracer) present in the Pt/Al$_2$O$_3$ catalyst. This tracer clearly demonstrates the effect of the positron range on the sensitivity profiles. As can be seen, the position resolution for $^{15}$O molecules in the catalyst bed is very poor. At the interface an increased amount of the positrons is stopped on the side of the beads. The higher density of the beads stops the positrons escaping from the lower density region (catalyst). The enhanced stopping in the glass beads medium causes the increase in the position resolution and peak height towards the sides of the detector. The sudden jump in the peak height of the profile in the glass beads medium can thus be explained.
by the increased stopping power of the glass beads.
The catalyst bed is not always situated in the center of the detector. This is also true for
the Pt/Al₂O₃ bed used during the decomposition of N₂¹⁵O. The simulations have been
performed in such a way that at least one side of the catalyst is described accurately by
the setup. The interface at the start of the bed (left side) should be described accurately
because significant changes in tracer concentration occur here. Because the tracer is
one of the reactants the largest amount of adsorption/reaction will take place at the
beginning of the catalyst, since the concentration is highest here. To compensate for the
effect that the catalyst bed end is not positioned symmetrically with respect to the
beginning of the catalyst, additional profiles are inserted at the center of the matrix. The
procedure is as follows. The profile simulated for position 9 (center of the detector) is
inserted at position 10. The other profiles, including the profile at position 10, are all to
the right. This insertion is repeated until the simulated bed end coincides with the
experimental bed end. In this case two profiles were inserted, as shown in figure A.3. In
addition, all the profiles were smoothed by fitting the profiles with a smoothing spline.
The sensitivity profiles for reconstruction positions 10 and 11 are not correct, however, it
is expected that the error will be small.
Figure A.4 shows the sensitivity profiles for ¹¹C containing positron emitters which are
present in the catalyst. The profiles display the same features as shown in figure A.2,
however, they are less pronounced. This is caused by the lower energy of the positrons
emitted by ¹¹C. The range of the positrons in the catalyst and the glass beads does not
differ as much as for ¹⁵O. Thus the stopping power of both materials is almost identical,
Figure A.3. Modified sensitivity profiles for each reconstruction position for $^{15}$O containing tracer molecules.
Sensitivity profile curves are for a quartz reactor containing Pt/Al$_2$O$_3$ (bed length 41 mm) surrounded by glass beads on both sides inside the aluminum oven. The modified sensitivity profiles are based on the profiles shown in figure A.2. Additional profiles were inserted at the center to compensate for the asymmetry of the catalyst bed with respect to the detector.

resulting in a small increase in the position resolution and peak height when going from the catalyst to the glass beads.

Figure A.4. Simulated sensitivity profiles for each reconstruction position for $^{11}$C containing tracer molecules.
Sensitivity profiles are for a quartz reactor containing Pt/Al$_2$O$_3$ (bed length 35 mm) surrounded by glass beads on both sides inside the aluminum oven. The distance between the center of the reactor and the detection arrays was 170 mm. The response of the whole detector (17 reconstruction positions) is recorded for a $^{11}$C cylindrical source with a radius of 5 mm and zero width placed in this system at intervals of 0.25 mm.
Figure A.5. Simulated sensitivity profiles for each reconstruction position for \(^{15}\text{O}\) containing tracer molecules.

Sensitivity profiles for a reactor filled with glass beads only. The distance between the center of the reactor and the detection arrays is 80 mm. The response of the whole detector (17 reconstruction positions) is recorded for an \(^{15}\text{O}\) cylindrical source with a radius of 5 mm and zero width placed in this system at intervals of 0.25 mm.

The results shown above indicate that a difference in the density of the catalyst and the inert should be avoided, since it causes a change in the position resolution and complicates the calculation of the sensitivity matrices. To eliminate this effect the catalyst (ZSM-5) was coated on the glass beads (inert). This catalyst was used to investigate the diffusion/adsorption/decomposition of \(\text{N}_2^{15}\text{O}\) in/on ZSM-5. Figure A.5 shows the sensitivity matrix for this catalytic system. As can be seen, the peak height still increases going from the center to the sides of the detector. This shows that the positron range is not solely responsible for this effect since it does not change using catalyst coated glass beads. Another explanation is that the small distance between the source and the detection arrays causes this effect.

It has been shown in chapter 5 that the position resolution depends on the distance between the source and the detection arrays. The main reason for this effect is an increased amount of mis-reconstructions between opposite across lying detection crystals separated by several detection elements. This can easily be demonstrated by showing the sensitivity profiles only including reconstructions between opposite and opposite-adjacent detection elements. Figure A.6 shows the resulting profiles in which no variation in the peak height occurs. The profiles for the different reconstruction positions are nearly identical now and the position resolution is also better (narrower profiles). This might lead to the conclusion that it is more straightforward not including every possible reconstruction (detection possibility) when this setup is used. However, this is not true because the signal to noise ratio of a measured PEP profile is dependent on the activity of the tracer and the number of possible reconstructions. The amount of radioactivity which can be used during experiments is restricted due to the limited linear
Figure A.6. Simulated sensitivity profiles for each reconstruction position for $^{15}$O containing tracer molecules (onl reconstructions between opposite an opposite-adjacent detection crystals are considered).

Sensitivity profiles for a reactor filled with glass beads. Only reconstructions between opposite and opposite-adjacent detection crystals are shown. The distance between the center of the reactor and the detection arrays is 80 mm. The response is recorded for an $^{15}$O cylindrical source with a radius of 5 mm and zero width placed in this system at intervals of 0.25 mm.

detection range of the PEP detector. Therefore, the tracer activity cannot be increased to compensate the reduction in the signal to noise ratio when a large number of possible reconstructions are discarded. Because the simulated profiles always need to be corrected with the detector sensitivity profiles for the detector it is better to include all possible reconstructions. This in turn will increase the reliability of the experimental profiles. This procedure has been used in all the results presented in this thesis.
SAMENVATTING

TOEPASSING VAN POSITRON EMISSION PROFILING IN DE KATALYSE
DE ONTLEDING VAN N₂O

Inleiding

Katalysatoren worden veelvuldig gebruikt om chemische reacties sneller en bij lagere temperatuur te laten verlopen. Het meest bekend is de toepassing van een katalysator in de auto om schadelijke stoffen, zoals koolmonoxide en stikstofoxide, om te zetten in niet schadelijke stoffen. Het basisprincipe van de meeste katalysatoren berust op adsorptie van de reactanten op het katalysatoroppervlak, waarna deze reageren tot de gewenste eindprodukten. Het verbeteren van de werking van bestaande katalysatoren is alleen mogelijk als het reactiemechanisme op het katalysatoroppervlak bekend is. In de katalyse wordt onderzoek gedaan naar de kinetiek en het mechanisme van katalytische reacties. Dit gebeurt meestal door de samenstelling van de reactanten te veranderen en vervolgens de invloed op de produkt samenstelling te bekijken. De katalysator wordt dan dus als een zwarte doos beschouwd. Eigenlijk is er behoefte aan een techniek die onder reële omstandigheden de concentraties van reactanten en van tussen- en eindprodukten in het katalysatorbed kan bepalen. Omdat de katalysator zich in een reactor bevindt met daaromheen een oven, is het lastig om ter plekke concentraties te meten. In de medische wereld is men al eerder tegen dit probleem aangelopen. Dit heeft geresulteerd in de ontwikkeling van een techniek waarmee structuren in het menselijk lichaam zichtbaar gemaakt kunnen worden. Deze techniek (positron emission tomography, PET) is gebaseerd op het meten van toegediende radioactieve moleculen in het lichaam met een speciale detector. Deze detector meet de positie van de radioactieve moleculen in drie dimensies, zodat de verdeling van het isotoop in een levend orgaan bepaald kan worden. Een soortgelijke techniek zou licht kunnen werpen op het gedrag van reactanten op de katalysator tijdens een chemische reactie. Hiertoe is een één dimensionale variant op de PET techniek ontworpen, namelijk positron emission profiling (PEP). Voor katalytische reacties is het namelijk niet nodig om in drie dimensies het concentratieverloop te bepalen, omdat de grootste concentratieveranderingen in de axiale (lengte) richting plaatsvinden.

De PEP techniek is gebaseerd op het toevoegen van een zeer kleine hoeveelheid radioactief (10⁻¹³ mol) reactant aan het reactiemengsel naar de katalysator. De katalysator bevindt zich gedurende dit proces in evenwicht, zodat de radioactieve reactant meedoet met de reactie die plaatsvindt op de katalysator. De gebruikte radioactieve moleculen vervallen snel en zenden tijdens dit proces een positron uit. Een positron is het antideeltje van een elektron en contact tussen deze twee deeltjes kan leiden tot annihilatie. Door dit annihilatieproces worden twee fotonen (lichtkwanten) geproduceerd met een energie van 511 keV die in tegenovergestelde richting uit elkaar
bewegen. De fotonen hebben voldoende energie om de reactor en de oven te penetreren, en worden vervolgens opgevangen door de PEP detector. Deze detector bestaat uit twee detectiebanken, waarin zich negen scintillatiekristallen bevinden die de fotonen absorberen. Wanneer in de bovenste en in de onderste detectiebank tegelijkertijd een foton wordt gedetecteerd, wordt de annihilationpositie bepaald door de verbindingslijn van de twee kristallen die een foton gedetecteerd hebben en het midden van de reactor. Het afzonderlijk meten van meerdere annihilationgebeurtenissen leidt tot een concentratieprofiel van het radioactieve atoom als functie van tijd en positie in de reactor. De positron straler wordt ingebouwd in de reactant, zodat het gemeten concentratieprofiel informatie geeft over de verdeling van de reactant in het katalysatorbed. Uit deze concentratieprofielen kan na mathematische bewerkingen informatie over het reactiemechanisme verkregen worden. Dit proces wordt beschreven in het eerste deel van dit proefschrift (hoofdstuk 4 en 5). In het tweede deel wordt de procedure gëëvalueerd aan de hand van experimentele resultaten verkregen met ontleding van lachgas (N₂O) over een platina katalysator (hoofdstuk 6 en 7).

**Synthese positron stralers**

Om het reactie-evenwicht niet te verstoren dient bij de synthese van radioactieve reactanten zo weinig mogelijk niet radioactief reactant gevormd te worden. Voor ³⁵NO en N₂¹⁵O (de radioactieve isotopen van NO en N₂O) zijn nieuwe syntheseroutes ontwikkeld, zodat ze in de PEP techniek gebruikt konden worden. De in de literatuur beschreven synthese van radioactief lachgas (N₂¹⁵O) voldeed niet aan de eisen die door de PEP techniek gesteld worden. Het grootste nadeel was de aanwezigheid van aanzienlijke hoeveelheden niet radioactief lachgas. Er is voor gekozen radioactief lachgas te produceren door stikstof te bestralen met deuteronen in de aanwezigheid van een kleine hoeveelheid zuurstof. Het resulterende N₂¹⁵O werd selectief afgevangen met een zeoliet, was zeer zuiver en bevatte slechts een kleine hoeveelheid niet radioactief N₂O. Tijdens deze synthese is informatie verkregen over de vorming van N₂O in een mengsel van stikstof met een kleine hoeveelheid zuurstof. Het blijkt dat N₂O direct wordt gevormd door de reactie van ozon met stikstof. Dit heeft belangrijke implicaties voor radicaalreacties die zich in de atmosferaar aanspelen als gevolg van bestraling door de zon. Het is bekend dat ook in dit geval ozon geproduceerd wordt, dat met de aanwezige stikstof tot N₂O kan reageren. De in de atmosferaar aanwezige N₂O zorgt voor een versterkt broeikaseffect.

**Mathematische bewerking van PEP resultaten**

De mathematische bewerking van PEP profielen bestaat uit twee stappen. Ten eerste dienen de reacties die plaatsvinden op de katalysator met een wiskundig model beschreven te worden. Zo'n wiskundig model bestaat uit een aantal differentiaal vergelijkingen (ODE), die de concentraties van reactant en produkt op het katalysatoroppervlak beschrijft voordat de radioactieve reactant wordt toegevoegd. Een tweede set differentiaal vergelijkingen beschrijft het verloop van de radioactieve puls door het
Samenvatting

Katalysatorbed (PDE). Deze differentiaal vergelijkingen worden simultaan numeriek opgelost. Dit proces is beschreven in hoofdstuk 4. Ten tweede dient de positie resolutie van de PEP detector bepaald te worden, zodat deze aan het wiskundig model toegevoegd kan worden. Het wiskundig model bepaalt de concentratie van het radioactieve molecule met een oneindige positiewaarschijnlijkheid. De PEP detector meet echter niet zo nauwkeurig, hetgeen resulteert in beeldvervanging. Dit proces kan men vergelijken met de situatie waarin een verziend persoon zijn bril is vergeten en vervolgens moet lezen. Om hiervoor te corrigeren zijn de positie-gevoeligheidsprofielen van de detector met Monte Carlo simulaties bepaald (hoofdstuk 5), en vervolgens door convolutie aan het wiskundig model toegevoegd. In analogie met het voorbeeld komt dit overeen met het opzetten van een bril. De op deze manier verkregen concentratieprofielen worden vergeleken met de experimentele resultaten. Het wiskundig model bevat verschillende reactieconstanten, die bijgesteld kunnen worden aan de hand van deze vergelijking. De grootte van de reactieconstanten geeft aan met welke snelheid de verschillende reactiestappen verlopen, zodat inzichtelijk wordt welke stap voor de katalytische reactie belangrijk is.

Ontleding van lachgas

Lachgas is een zeer actief broeikasgas, 300 maal krachtiger dan CO₂. Daarom dient emissie van dit gas voorkomen te worden. Een methode hiervoor is de katalytische ontleding over een platina katalysator (Pt/Al₂O₃). Het platina metaal in deze katalysator is in kleine deeltjes over het oppervlak van het dragermateriaal (Al₂O₃) verdeeld. In hoofdstuk 6 wordt deze reactie op een kwalitatieve manier behandeld. Dit betekent dat alleen het gedrag van de positron straler op de katalysator onderzocht is. Voor deze PEP experimenten werd zuurstof gelabeld N₂O gebruikt, zodat het gedrag van zuurstof bestudeerd kon worden. Als N₂₁⁵O op de katalysator wordt ontled, ontslaat er een geadsorbeerde zuurstof atoom op het platina en wordt de stikstof (N₂) afgesplitst. De stikstof wordt direct met de gasstroom door de reactor afgevoerd. Het geadsorbeerde zuurstof atoom kan samengaan met een ander geadsorbeerde zuurstof atoom, en dit produkt desorbeert van het oppervlak zodat zuurstof gas gevormd wordt. Uit de resultaten van de PEP experimenten bleek dat het gevormde zuurstof atoom niet van de katalysator verwijderd werd. De enige verklaring voor dit gedrag bleek de sterke mobilitéit van zuurstof atomen te zijn. Deze mobilitéit zorgt ervoor dat het gevormde zuurstof atoom zich over het platina oppervlak naar het dragermateriaal beweegt. Omdat het dragermateriaal veel zuurstof atomen bevat en de temperatuur hoog is (500 °C), vindt er uitwisseling plaats tussen de gevormde radioactieve en de niet radioactieve zuurstof van het dragermateriaal. Door deze uitwisseling blijft de zuurstof achter op de drager en desorptie van ¹⁵O van de drager vindt niet plaats. Deze resultaten toonden eenduidig aan dat zuurstof van het platina naar de drager migreert (spill-over). De hoge mobilitéit van zuurstof is ook waargenomen tijdens de ontleding van radioactief lachgas over zeoliet katalysatoren (hoofdstuk 8). De atomaire zuurstof werd in dit geval uitgewisseld met zuurstof uit het zeoliet rooster. Het optreden van uitwisseling is
bewezen doordat de gelabelde zuurstof niet met koolmonoxide verwijderd kon worden. De reactietemperatuur was hoog genoeg voor de oxydatie van CO met de gelabelde zuurstof.

Hoofdstuk 7 beschrijft de kwantitatieve behandeling van de ontleiding van radioactief lachgas. De mathematische procedure voor de bewerking van PEP resultaten is hier met succes gebruikt voor het verkrijgen van kwantitatieve gegevens (reactieconstanten). De tijdens de ontleiding gevormde zuurstof adsorbeerde zeer sterk op het platina en verhinderde de adsorptie van nieuw N₂O. Dit werd bevestigd door de hoge waarde voor de N₂O adsorptiewarmte. De adsorptie van N₂O is uiteindelijk bepalend voor de snelheid van de ontleidingsreactie.

De reductie van NO door CO

Met behulp van de positron straler ¹³NO is de reductie van NO door CO met de PEP techniek onderzocht. De ontleiding van NO in geadsorbeerde stikstof en zuurstof op platina bleek de limiterende stap voor deze reactie te zijn. De desorptie van stikstof gas door het samengaan van twee geadsorbeerde stikstof atomen is op platina een snelle stap. De geadsorbeerde stikstof was eveneens zeer mobiel en migreerde naar de drager. Op de drager werd een stabiel ¹⁵N bevattend complex gevormd (waarschijnlijk ¹³NCO). Dit verdween langzaam door reactie met NO uit de gasfase, waarbij N₂ en CO₂ gevormd werden.

Evaluatie

Een evaluatie van de PEP techniek is te vinden in hoofdstuk 10. Tevens worden daarin de mogelijkheden van de PEP techniek aangegeven. De slechte positieresolutie van het detectiesysteem bemoeilijkt de kwantitatieve interpretatie van de resultaten. De gevolgde mathematische procedure geeft een goede beschrijving van de resultaten, maar is nog afhankelijk van de experimentele condities. De kwalitatieve interpretatie is lastig, omdat alleen het radioactieve atoom met de PEP detector gevolgd kan worden. Daarom is het aan te bevelen met verschillende radioactieve moleculen te werken waarin steeds een ander atoom is vervangen door een positron straler.

Het belangrijkste voordeel van de PEP techniek is dat de concentratie van reactanten en produkten op de katalysator direct gemeten kan worden onder reële condities. Het gebruik van isotopen geeft additionele informatie over het gevolgde reactiepad van de reactanten op de katalysator. De migratie van atomair zuurstof van het platina oppervlak waar het door ontleiding van N₂O gevormd wordt naar de drager, kon voor het eerst eenduidig met de PEP techniek aangetoond worden.

Simon van der Linde
DANKWOORD

Je promotieonderzoek op twee universiteiten uitvoeren heeft voor- en nadelen. Het grootste nadeel is dat je altijd moet reizen en vaak moet slepen met spullen die voor een katalyse lab zo gewoon zijn, maar op een natuurkundig lab domweg ontbreken. Een voordeel is dat wanneer je problemen hebt, je daarmee op twee plaatsen terecht kunt. Bovendien, als je het goed uitkijkt, heb je twee keer zoveel kans op het eten van taart. Voor de hulp die ik van beide kanten ontvangen heb wil ik een aantal mensen bedanken.

Ik wil beginnen in Delft met mijn ineens twee promotoren, Jacob Moulijn en Freek Kapteijn. Jacob, jouw vertrouwen dat het proefschrift er wel zou komen heb ik altijd gewaardeerd. Freek, dank je wel voor de vrijheid die je me gaf om gewoon mijn eigen gang te gaan. Met jouw kritische kijk op de katalyse resultaten is het proefschrift van een “nu bijna fysicus” sterk verbeterd.

Voor de totstandkoming van dit proefschrift was de goede samenwerking met de vakgroep Deeltjesfysica van de Technische Universiteit Eindhoven onmisbaar. Martin de Voigt, de interesse in mijn werk als ik weer een dag in de “PEP control room” zat heb ik bijzonder op prijs gesteld. Leo IJzendoorn, jouw deur stond altijd open als ik wetenschappelijke en praktische problemen had met de PEP detector. Onze discussies en je ideeën waren zeer waardevol voor mij. Bedankt ook voor je neus voor goede studenten.

De interpretatie van PEP experimenten bleek een lastige klus. Albert Mangrus, onze discussies hieromtrent waren voor mij belangrijk, en jouw gedetailleerde kennis van je eigen detector en EGS4 heeft mij veel werk bespaard. Bruce Anderson, het delen van bundeltijd heeft mij goed geholpen, en de bewegende bakjes van de hexaan-synthese opstelling gaven mooie tracer pulsen naar de PEP detector.

Behalve een goed werkende PEP detector is ook de beschikbaarheid van positron emitters onontbeerlijk voor het doen van een goed experiment. Jeroen de Goeij bedank ik voor zijn altijd parate kennis van radiochemie, en voor de plezierige samenwerking bij het N2O (helaas geen 15O) artikel. Wim Jansen, mijn enige eigen student, zonder jouw hulp en inzet bij de produktie van het gelabelde lachgas (deed zijn naam niet altijd eer aan) was mijn proefschrift een stuk dunner geweest. Ik wil Peter van der Ven bedanken voor zijn hulp bij de bereiding van 15NO, en voor het vele heen en weer lopen van de bunker naar het B-lab.
DANKWOORD

Veel steun bij de produktie van de gelabelde tracers kreeg ik van de Bedrijfsgroep van het cyclotron. In het bijzonder wil ik Frits, Jan, Erik, en natuurlijk Rinus noemen. Rinus, jij stond 's morgens vroeg al klaar om "Delft" te helpen met het versnellen van die lastige deuteronen. Ik heb het samen draaien aan de vele potmeters van het cyclotron altijd erg gezellig gevonden. Alle medewerkers van Cygne wil ik bedanken voor de vele extra vijf minuten die ik steeds weer nodig had voor het laatste experiment.

Waar is hij, in Eindhoven of in Delft? Na de lange, drukte dagen in Eindhoven was het vaak gezellig "thuis komen" in Delft. De prettige werksfeer en samenwerking, maar ook de borrels, fietsweekenden, het zeilen en skiën, waren voor mij van grote betekenis in het hele promotiegebeuren. Hiervoor bedank ik al mijn collega's van Industriële Katalyse. In het bijzonder wil ik Jolinde, Xander, Marion, Bastiaan en mijn kamergenoten bedanken voor de gezellige babbels, jullie interesse en hulp.

Promoveren, maar vooral het schrijven van het proefschrift is niet altijd even gemakkelijk. De laatste loodjes waren in dit geval ook de zwaarste. Onmisbaar is dan iemand die je hierin helemaal steunt. Lieve Liek, hiervoor ben ik je erg dankbaar.

Simon
LIST OF PUBLICATIONS

PUBLICATIONS

The behaviour of titania supported iron oxide catalysts in butene dehydrogenation.

The behaviour of titania supported iron oxide catalysts in butene dehydrogenation.

Mathematical treatment of transient kinetic data: Combination of parameter estimation with solving the related partial differential equations.

Production of \([^{15}\text{O}]-\text{N}_2\text{O}\) by deuteron irradiation of nitrogen.

PRESENTATIONS


PEP in heterogeneous catalysis: Decomposition of \(\text{N}_2\text{O}\) over Pt/Al\(_2\)O\(_3\), KNCV katalyse (1998).


PUBLICATIONS IN PREPARATION

Synthesis of \(^{15}\text{NO}\) by reduction of \(^{15}\text{NO}_3\) produced by proton irradiation of water.

Decomposition of \(\text{N}_2^{15}\text{O}\) over Pt/Al\(_2\)O\(_3\). Spill-over of \(^{15}\text{O}\) formed during the decomposition.
Decomposition of $\text{N}_2^{15}\text{O}$ over $\text{Pt/Al}_2\text{O}_3$. Modeling.

Properties of the PEP detector. Prediction of the detector response by Monte Carlo simulations to aid the data interpretation.

Decomposition of $\text{N}_2^{15}\text{O}$ over metal ion-exchanged ZSM-5.

The reduction of $^{13}\text{NO}$ by CO over $\text{Pt/Al}_2\text{O}_3$.
CURRICULUM VITAE

Simon van der Linde, geboren 29 juli 1967 te Kaldenkirchen.

1990-1991  Stage bij de vakgroep Moleculaire Celbiologie (Prof. dr. H.O. Voorma), Universiteit Utrecht: Translation initiation mechanism of Semliki Forest Virus leaders.

aug. 1992  Doctoraal examen, met genoegen.
1993-1994  Militaire dienstplicht, gedeeltelijk vervuld in het Centraal Militair Hospitaal: An evaluation of specific blood markers that are indicative of muscular damage during exercise and training.
1994-1999  Promotieonderzoek bij de vakgroep Chemische Procestechnologie, Industriële Katalyse, Technische Universiteit Delft (Prof. dr. J.A. Moulijn), onder begeleiding van Prof. dr. F. Kapteijn.

vanaf 1999  Wetenschappelijk medewerker bij de afdeling Ademprotectie en Luchtmisvertering, TNO, Rijswijk.
THE DECOMPOSITION OF N₂O