Stellingen behorende bij het proefschrift

Towards a new propene epoxidation process
Transient adsorption and kinetics measurements applied in catalysis

door T.A. Nijhuis

1. Het gebruik van procestechnologische kennis binnen de katalyse, zoals het toepassen van een meertaps reaktorsysteem zoals bijvoorbeeld het riser-regenerator concept kan voor veel katalytische processen tot betere resultaten leiden (conversie en/of selectiviteit) dan met een conventionele reaktor behaald kan worden.

2. Wanneer bij de ontwikkeling van een nieuwe katalysator tegelijkertijd de procesvoering bekeken wordt, kan een op het eerste gezicht ‘slechte’ katalysator toch potentie hebben.
   (hoofdstuk 7 van dit proefschrift)

3. Bij het uitvoeren van experimenten in een TAP-systeem, is het zeer goed mogelijk dat in plaats van de gewenste reactiesnelheid als functie van de oppervlaktebezetting van de katalysator de reactiesnelheid gemeten wordt als functie van de axiale positie in de reactor.
   (hoofdstuk 3 van dit proefschrift)

4. Hoewel een TAP-systeem zeer geschikt is voor het bepalen van adsorptie- en diffusieparameters zal gezien de noodzakelijke korte tijdschaal van de experimenten deze geschiktheid beperkt blijven tot bepalingen met snel diffunderende gassen bij lage bezettingsgraden.
   (hoofdstuk 4 van dit proefschrift)

5. Een gesmolten-zout ‘katalysator’ voor de propeneepoxidatie is geen katalysator maar een radicalinitiator, aangezien het zout niet aan de daadwerkelijke reactie deelneemt en alleen helpt bij de start van een zichzelf instandhoudend autokatalytisch reactiemechanisme.
   (hoofdstuk 8 van dit proefschrift)
6. Hoewel een goede kennis van de literatuur essentieel is voor het doen van onderzoek, heeft dit echter als nadeel dat deze kennis van de literatuur zorgt voor een vernauwing van het blikveld, waardoor er minder snel tot nieuwe inzichten gekomen kan worden.

7. De verwachting van een promovendus omtrent de bouwtijd van nieuwe (complexe) apparatuur voor zijn/haar onderzoek moet meestal met een factor groter dan twee worden bijgesteld.

8. Hoewel dit tijdens een (promotie)onderzoek als verontrustend wordt ervaren, vergemakkelijkt het laat behalen van ‘goede’ resultaten het schrijven van een afsluitend verslag aanzienlijk.

9. Het inbouwen van nieuwe features in computerprogramma’s lijkt als eerste doel te hebben de verkoop van snellere computers. De beste functie van sommige nieuwe en ‘verbeterde’ computerprogramma’s is de mogelijkheid om de installatie ongedaan te maken.

10. De tijdsbesparing die betere computermogelijkheden bieden bij het schrijven van een proefschrift wordt meer dan ‘goedgemaakt’ door de hogere eisen die gesteld worden aan het uiterlijk van het geschrevene.

11. Een proefschrift is veel minder een uitprobeerseel dan het woord aangeeft.

12. De huidige Nederlandse fileproblematiek zou voor de overheid voldoende reden moeten zijn om de invoering van de vierdaagse werkweek te stimuleren.
Towards a new propene epoxidation process

Transient adsorption and kinetics measurements applied in catalysis

PROEFSCHRIFT

ter verkrijging van de graad van doctor
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Towards a new propene epoxidation process
Transient adsorption and kinetics measurements applied in catalysis

Proefschrift, Technische Universiteit Delft
- met samenvatting in het Nederlands

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Preface

Introduction

Propene oxide is one of the major bulk materials in use in the chemical industry. The production of propene oxide, however, by a direct oxidation reaction has not yet been accomplished. The only two production processes in use at the moment are the chlorohydrin process and the hydroperoxide process. The first of these processes has the disadvantage that it is environmental unfriendly, the latter has the disadvantage that a co-product is produced in a fixed stoichiometric amount. The original aim of this project, when it started four years ago, was the development of a direct epoxidation catalyst for propene. In the project the use of a new transient apparatus, referred to as Multitrack, for the fast testing of catalysts and the determination of reaction mechanisms on the catalyst was scheduled.

The building of a complex apparatus like Multitrack proved to be highly complex and took over almost three years to get the system operational. During this period the scope of the project shifted to the realization of the Multitrack system and the demonstration of such a powerful technique in the evaluation of processes occurring on or in a catalyst. The epoxidation of propene and ethene were investigated using the Multitrack system. Multitrack proved, however, to be less
suitable for this kind of reactions than was anticipated, since even very active catalysts did not meet the demand of a 1% conversion to a product, needed to accurately perform experiments. Subsequently both research subjects, Multitrack and the direct epoxidation of propene, were continued separately. In this thesis, therefore, two parts can be distinguished, chapter 1-4 for Multitrack and chapter 5-8 for the epoxidation of propene. The link between both subjects can be found in chapter 6, in which the transient epoxidation of ethene and propene will be discussed.

Outline

The first part of this thesis contains the development and application of the Multitrack system. Chapter 1 discusses the development of the Multitrack system, the type of experiments that can be performed, and the problems that arose during the startup. A crucial point in the successful application of Multitrack in catalysis is the method in which the measurements are evaluated. In order to get most out of the experiments, it is important to model the experiments. The modeling of Multitrack experiments is discussed in chapter 2. To demonstrate the potential of Multitrack, it was successfully applied to study two subjects: 1) the platinum catalyzed CO oxidation and 2) adsorption on and diffusion into microporous materials. The CO oxidation is discussed in chapter 3, in which it is shown that a new technique can provide new insights, even in such an in literature extensively discussed topic. The adsorption on and diffusion in zeolites is discussed in chapter 4. It is demonstrated that Multitrack is a powerful tool for the fast and accurate determination of the adsorption and diffusion parameters of gases on and into microporous materials.

The second part of this thesis deals with the epoxidation of propene. Chapter 5 discusses the current propene oxide production processes and their disadvantages. A discussion of silver catalysts, which are successfully applied in the direct epoxidation of ethene, is given, in which the problems are discussed related to the application of this catalyst in the epoxidation of propene. Possible alternative catalysts and processes are briefly discussed. A discussion on and experiments with an ethene-epoxidation-type silver catalyst is given in chapter 6. A recent development in catalysis is the use of highly dispersed gold catalysts. Supported on a titanium containing support material, these catalysts are able to epoxidize propene selectively at low temperature. The modes of operation of this type of catalyst, together with the design challenges for this type of catalyst are discussed in chapter 7. Finally, chapter 8 discusses the potential of a different type of 'catalysis' for the epoxidation of propene: direct oxidation in a molten salt mixture.

The most part of this thesis has been written with the intended publication of the chapters as separate articles in mind and can, therefore, be read separately. As a result some repetitions are present in this thesis.
Chapter 1

Multitrack

Summary

Inspired by the TAP (Temporal Analysis of Products) system developed by John Gleaves a new apparatus for studying catalysts on a very short time scale was developed at Delft University of Technology. This apparatus, Multitrack, is primarily designed to study catalytic gas-phase reactions in ultra-high vacuum with a very sensitive reaction product analysis, having a 1 µs time resolution. Experiments can be performed from ambient to 1273 K, using gas pulses ranging from $10^3$ to $10^9$ molecules, and with up to 3 ml of catalytic material. Gases can either be supplied using a continuous flow valve or using two high-speed gas-pulsing valves. Up to three compounds in the reactor effluent can be measured simultaneously. This chapter discusses the Multitrack set-up, the difficulties in the development of the system, and the possibilities of the system.
Introduction

The most conventional way of studying a catalytic reaction is by examining the steady-state performance of the catalyst. Although this kind of catalyst testing is the easiest type of experiments to perform, the major disadvantage is that only information is gathered on the general performance of the catalyst at the conditions of the experiment. To gain insight in the reaction kinetics or mechanism it is necessary to perform experiments using a number of different feed compositions and reaction conditions. These experiments refer to steady-state catalyst performances.

On the other hand, transient experiments give information on the catalyst under continuously changing conditions. Although the interpretation of a transient experiment is usually much more difficult than the interpretation of a steady-state experiment, the degree of information that can be gathered from one single transient experiment is also much greater. This additional information on a catalyst can be used to contribute to the better understanding of the reaction mechanism and kinetics and in such way help in the development of a more optimal catalyst (higher selectivity and/or activity). Moreover, dynamic conditions can be essential in the process, e.g. reactor startup and shutdown is in essence of a dynamic nature. Furthermore, some industrial processes are continuously run in the absence of a steady state to obtain the highest possible selectivities, e.g. FCC (Fluidized Catalytic Cracking) and the oxidation of butene to maleic anhydride.

The general definition of a transient catalytic reaction is a reaction in which the catalyst is subjected to changing process conditions, such as pressure, temperature, flow rate (WHHSV), and concentrations. Even though it is not usually identified as such, also batch experiments are transient experiments as in this case the concentrations surrounding the catalyst are changing, as a result of the activity of the catalyst. The other most commonly applied transient experiments are temperature programmed experiments, step-response, and pulse-response experiments.

In 1986 the TAP (Temporal Analysis of Products) system was introduced by Gleaves [1,2] as a way for the transient testing of catalysts. This apparatus consists of a small catalyst-containing reactor in an ultra-high vacuum system used for pulse-response experiments. The advantage of performing these pulse-response experiments in ultra-high vacuum is that this results in a very fast system with a high time resolution, provided the pulse-system and analysis system are also equipped for performing very fast experiments. This is the case for the TAP system. The excellent possibilities of this type of reactor system resulted in a large number of publications by different groups in which this technique was applied and provided new insights in the mechanistic aspects of various catalytic reactions. These publications cover a variety of different subjects, including: the epoxidation of ethene [3], the oxidation of methane to formaldehyde [4,5], the oxidative coupling of methane [6,7], the oxidation of propene to acrolein [8,9], the CO oxidation over
platinum [10,11], and the ammoxidation [12]. The application of the TAP system is of course not limited to these examples. In general it can be stated that the system is best equipped for the investigation of fast processes in catalysis, such as reaction kinetics, adsorption behavior, and diffusion.

Inspired by the successes of the TAP system, at the Delft University of Technology the plan emerged to build an advanced version of this system. This new system, called Multitrack (Multiple Time Resolved Analysis of Catalytic Kinetics), is described in this chapter, together with its possibilities and design challenges.

Description of the Multitrack system

The basic operation of the Multitrack system is similar to that of the TAP system and can be described as follows. From a gas supply section either a small gas pulse or a continuous flow is given to a reactor, which contains 0.05 to 2 ml of catalyst material. In the reactor the shape and composition of the gas pulse change due to processes such as diffusion, adsorption, and reaction. After the gas leaves the reactor, it reaches a large vacuum chamber. In this vacuum chamber, the bulk of the gas is removed immediately, a small portion travels as a molecular beam to the analysis section. This section consists of three mass spectrometers placed in line with this gas beam from the reactor. Each mass spectrometer analyzes one component in the gas beam with a time resolution of up to 1 μs. The main differences between Multitrack and the basic TAP system are the use of three mass spectrometers instead of one and an external instead of internal reactor design.

![Diagram of Multitrack system]

**Figure 1.**
*Schematical representation of the Multitrack set-up.*
The Multitrack system can be divided into four main parts: a high-speed gas-pulsing supply system, a catalytic reactor, a large vacuum chamber for the gas expansion, and an analysis section equipped with a very fast data acquisition system. In Figure 1 the basic layout of the Multitrack system is represented. A photograph of the Multitrack set-up is given in Figure 2.

Gas supply

The gas supply section consists of two high-speed pulse valves and one flow valve. The pulse valves are modified BV-100V valves from Newport Corporation. The valves were removed from their original housing and built into a small volume reactor assembly. The valves are thermostated at 333 ± 2 K to prevent differences in gas pulse size due to ambient temperature changes. It is possible to raise the temperature of the valves housing to 473 K, facilitating the pulsing of vapors of liquids with a boiling point up to this temperature. The valves have a pulse width (FWHH) of 100 μs and a maximum pulsing frequency of 50 Hz. The pressure inside the valves can be varied between 1 mbar to pressures as high as 10 bars. By varying the setting of the valve control units and adjusting the pressure inside the valve it is possible to change the gas pulse size from 10^5 to 10^8 molecules. The flow valve is a bellow sealed needle valve combined with a Bronkhorst Hi-Tec type F-201C (100 nml/min) mass flow controller in front to measure and regulate the gas flow. An important note should be made that when experiments are carried out using the
high-speed pulse valves, it is not necessary to use the flow system to provide a carrier-gas flow for the pulse. The gas pulse travels through the system by diffusion caused by a concentration gradient created by the pulse itself. The importance of the absence of a carrier gas is explained in more detail in chapter 2, where the modeling of experiments is discussed, and in chapter 4, where the Multitrack technique is applied for the determination of adsorption and diffusion parameters in zeolites.

Reactor

A schematic representation of a reactor in the reactor assembly is given in Figure 3. It is possible to use reactors of different sizes in the Multitrack system. The volume available for catalyst can be as large as 50 mm long and 14 mm in diameter. The temperature of the catalyst bed in the reactor can be measured by up to three thermocouples, depending on the reactor construction. The most commonly used reactor has an internal diameter of 7 mm and a bed height from 10 to 35 mm. The bed is held in the reactor by two stainless steel grids. The size of the grid mesh is selected to have the largest possible holes for the particles used, resulting in a minor influence on the gas pulse response in comparison to the influence on the pulse

![Diagram of Reactor Assembly]

**Figure 3.**
Schematical representation of the Multitrack reactor assembly.
response by the diffusional transport through the catalyst bed. The upper grid is lightly pressed on the catalyst bed by a thin tube, thus preventing movement of catalyst particles. The bottom of the reactor is pressed against the manifold of the gas supply section and is sealed by two Zalak O-rings.

The operating pressure of the reactor can vary from high vacuum (during normal operation) to up to 1 MPa. When the reactor is used at pressures higher than vacuum (>1 Pa), it is necessary to use a continuous gas flow in combination with either a small orifice or a special high pressure assembly at the reactor exit.

The temperature of the reactor can vary from room temperature up to 1300 K. The reactor is heated using a 1 meter long, 1 mm diameter Philips Thermocoax radiative heating element, supported by five rods placed around the reactor. Around the heating wire a hollow tube is placed in which continuously air is flowing to cool the outside of the reactor assembly. Between the heating element and the cooling tube a ceramic heat shield is located. The temperature profile within the reactor is uniform. The difference in temperature between the stainless steel reactor and the center of the catalyst bed is typically 2 K (reactor temperature of 873 K). At the maximum reactor temperature of 1273 K, this difference can be up to 5 K, at temperatures lower than 400 K, this temperature difference is usually less than 1 K. The axial temperature profile across the catalyst bed is similarly flat. A schematical drawing showing the locations of the thermocouples in the reactor is given in Figure 4. The thermocouple in the steel reactor wall is used for the temperature controller. The two other thermocouples are used to check whether the catalyst bed is uniformly heated after a change in temperature setpoint.

**Vacuum system**

The vacuum system can be divided into three parts: a main (reactor) chamber, an intermediate chamber (differential pumping stage), and an analysis section (see Figure 1). The reactor chamber has the shape of a horizontally placed hourglass. The 100 mm diameter tube in the middle is pumped by Balzers TPU 2200 turbomolecular pumps located on the two ends of the hourglass shape, each having a 2200 l/s pumping capacity, resulting in a pump down time constant in the order of 0.02 seconds. The reactor is located at the bottom of the middle tube in a special introduction system with a gate valve at the top. This gate valve allows for the
removal of the reactor and exchange of its contents without the need to vent the main vacuum chamber. The pressure is measured using a cold-cathode pressure gauge and is around $10^7$ mbar, when the reactor is in the main vacuum chamber. The reactor can be changed within 5 minutes using an automated procedure and an electronic elevator. The automated reactor change procedure uses an extra rotary vane vacuum pump to evacuate the reactor before it re-enters it into the main vacuum chamber. This entire procedure is handled using a personal computer. The main chamber is equipped with two extra flanges to allow future extensions to the Multittrack system. Such extensions can be in-situ analysis techniques like XPS, RAMAN, FTIR, etc.

The intermediate vacuum chamber is separated from the reactor chamber by a 2-mm orifice. This differential pumping stage is used to prevent interference in the detector chamber by pressure increases in the reactor chamber. The intermediate chamber is pumped by a Balzers TMH 65 turbomolecular pump with a pumping capacity of 65 l/s. The differential pumping chamber is built inside the reactor chamber to minimize the distance from the reactor exit to the analysis section.

The detector chamber, equipped with three mass spectrometers in line, is pumped by two Balzers turbomolecular pumps, one TPU 170 (170 l/s) and one TPU 240 (240 l/s). The detector chamber is separated from the intermediate chamber by a 4-mm orifice. The distance between the first of the mass spectrometers and the reactor exit is approximately 17 cm, the second and third mass spectrometer are located at 24 and 31 cm respectively. Minimization of the distance between reactor and mass spectrometers is important, as the signal measured is inversely proportional to the squared distance.

Analysis section

The analysis of the gases leaving the reactor is performed by three Balzers QMA 125 quadrupole mass spectrometers in line. The advantage of using three mass spectrometers is that it is possible to measure three components at the same time. When one mass spectrometer is used, it is impossible to measure more than one component because of the high sampling rate required, and the relatively slow switching between masses of a mass spectrometer. The ionization chambers of the mass spectrometers are placed exactly in line with the two orifices of the intermediate chamber and the reactor exit. Because each mass spectrometer ionizes only about 5% of the passing gas beam, this will hardly influence the signal measured. A greater influence on the ratio between the signals of each of the mass spectrometers is caused by the different distances to the reactor exit. The mass spectrometers make use of cross beam ion sources and an electron multiplier as detector. The mass spectrometers can be used from amu 1 to 200. By changing the size of the orifice between the reactor and the intermediate vacuum chamber, it is possible to alter the size of the gas beam from the reactor to the mass spectrometers. The adjustment in orifice size can be applied to drastically alter the sensitivity of the analysis system. The time needed for such an operation is approximately 15 minutes.
The signal from the electron multipliers is measured by custom-built electronics supplied by GH Design. These electronics are combined digital pulse counters and analog amplifiers. The analog amplifiers are only used in flow experiments with very large (>10 ml/min) gas flows into the vacuum system, when the signal from the mass spectrometers is too high for the pulse counters to process. It is possible to use the digital pulse counter signal as an internal calibration for the analog signal.

The electronics are able to measure at a maximum sampling rate of 1 MHz and can measure a maximum of 64000 points per mass spectrometer during a single run. The data acquisition system is also controlling the two pulse valves, and thus linking the timing of pulse valves to the data acquisition.

The main advantage of the digital electronics for the measurement of the pulses from the reactor is the very high signal to noise ratio. When measuring pulse responses it suffices to measure a single pulse without averaging or filtering. Another advantage of the digital data acquisition system is that fewer calibrations are needed to quantify the measurements. With standard analog data acquisition electronics, the main reason for calibrating mass-spectrometers is the varying amplification factor of the electron multipliers. However, as the digital electronics actually count the incoming molecules on these multipliers, the actual amplification factor is then irrelevant and, therefore, the varying amplification factor has no influence on the signal measured by the digital pulse-counters. An additional advantage of these electronics is that it is not necessary to switch between different measuring ranges of the mass spectrometers, as the pulse counter electronics cover the entire operating range.

The measurements are performed using a Pentium type personal computer, communicating with a special control unit. This allows for the setting of all relevant parameters (masses to be analyzed, valves timing, data acquisition rate, measuring time) on the personal computer. The measured data are transferred to the PC and can then be processed. The relevant temperatures and pressures of the experiments are automatically added to the data files created. The software being used is able to process standard TAP data files and can create TAP data files from Multitrack experiments. The advantage of this possibility is that it is easy to compare analogous measurements performed on a TAP and Multitrack.

Experimental description

The experiments that can be performed on the Multitrack system can be divided into four basic modes of operation: scan mode, single pulse mode, multiple pulse mode, and flow experiments.
Scan mode experiments

During experiments performed in the scanning mode, the mass spectrometers are not set to one mass (m/e), but they perform a sweep over a mass range. In this way the data collected consists of the fragmentation patterns of the gases leaving the reactor. Considering the fact that it takes about 0.5 seconds to perform a mass sweep from mass 1 to 200, it is necessary that the gas flow leaving the reactor does not change for this period of time. This can be done by using either the flow valve of the system instead of the pulse valves, or by pulsing very rapidly and thus creating a pseudo steady state.

Using the high sensitivity of a mass spectrometer, scan mode experiments can be performed to identify which products are formed by a catalyst. By measuring a scan of gases leaving the reactor, and then subtracting the fragmentation patterns of the feed gases, the fragmentation patterns of the products remain. By comparing these patterns to known fragmentation patterns of possible products, it is possible to determine (intermediate) products. An example of a scan mode experiment is represented in Figure 5. This figure demonstrates that the interpretation of a mass scan is not as straightforward as might have been expected. The scan in Figure 5 is the result of continuous pulsing of an oxygen/argon/carbon dioxide mixture in the absence of any reaction. It can be seen that not only the expected m/e ratios of 32, 40, and 44 are visible in the scan, but also significant signals at m/e ratios of 12, 16, 20, and 28 as secondary signals of the same gases, as a result of fragmentation and multiple ionization (m/e ratio 20 from Ar^{2+}). When more complex molecules are used in a reaction, the number of secondary signals as a result of fragmentation of

![Figure 5](image)

*Figure 5.* Example of a scan mode measurement. Measurement of an oxygen/argon/carbon dioxide mixture pulsed over inert material.
the molecules will increase, which can make the interpretation of the mass spectra difficult. Even more this will be the case as reactants and products are often similar, only differing one or two atoms in a molecule, therefore, having similar fragmentation patterns.

**Single pulse experiments**

Single pulse experiments are performed by pulsing a (mixture of) gas over a catalyst bed and measuring the response of this gas and/or possible products from a reaction. During this type of experiment each of the mass spectrometers is set to a different mass. The pulse response is then measured at a high sampling speed, usually in the order of 10 kHz. By modeling the measured pulse responses it is possible to evaluate aspects like diffusion, adsorption, desorption, and reaction on a catalyst. Since most of these phenomena take place at a very short time scale, it is necessary to have a high time resolution. An example of this type of experiment is given in Figure 6.

Single-pulse experiments are mostly used for the determination of the reaction kinetics or mechanism. The determination of a reaction mechanism using single pulse experiments is demonstrated in chapter 3 for the platinum-catalyzed CO oxidation. In chapter 4 the determination of the adsorption behavior on (in) zeolites is demonstrated. For the determination of reaction kinetics it is imperative that the pulse-responses can be modeled accurately. The modeling of single-pulse experiments is discussed in chapter 2.

**Figure 6.**

*Example of a single-pulse experiment. Steady-state results of CO oxidation with O₂ over Pt sponge at 573 K by pulsing 2.3*10⁹ molecules of O₂ at t=0 and 1.0*10⁷ molecules of CO at t=1 s over 291 mg of Pt sponge. At t=3.5 s the next O₂ pulse is given (from chapter 3 of this thesis).*
In the accurate measurement of a pulse-response in a single pulse experiment, the processing of the results can be very complicated, if the m/e ratio of the pulse response measured originates from more than one type of molecule leaving the reactor. In principle, it is possible to numerically separate a response of more than one type of molecule into the individual responses, provided additional information is available (unique pulse responses of some of the components in the combined response). The error in such numerically separated responses will, however, be larger than the error in a unique pulse response. Therefore, it is advisable to use scan mode experiments to determine unique m/e ratios for the reactant and product gases.

Multiple pulse experiments

Multiple pulse experiments are performed by repetitively pulsing one gas over a catalyst. This can be done with pulsing frequencies up to 50 Hz. During this continuous pulsing the mass spectrometers measure the pulses in one continuous run. In this case the actual shape of the measured pulses is less important than the change in the consecutive pulses and consequently lower sampling rates can be used (in the order of 1 kHz). By pulsing an adsorbing gas over a clean catalyst surface in a multiple pulse experiment, for example, the available surface area can be determined. The same can be done by having a gas react with another gas, which is preadsorbed on the surface. An example of a multiple pulse experiment is given in Figure 7. The application of multiple pulse experiments in the determination of the

![Figure 7](image_url)

*Figure 7.*

Example of a multiple-pulse experiment. Gas pulses of 1.0*10^16* molecules of CO are given over 291 mg of oxygen covered platinum surface at 333 K. Pulsing frequency: 1.33 Hz. Platinum surface area: 0.08 m²/g (from chapter 3 of this thesis).
number of active sites on a catalyst is demonstrated in chapter 3 for the platinum-catalyzed CO oxidation.

Flow experiments

Flow experiments are performed by continuously flowing a gas stream through the reactor. In this way the reaction is studied in steady state. When a reaction is studied in a steady-state situation, high sampling frequencies are not necessary. This situation allows for the possibility to have each of the mass spectrometers measure more than one component, by switching the setting of the mass spectrometers to each of the components to be measured alternately. This type of measurement gives the opportunity to check the performance of the same catalyst in the same reaction under both transient and steady-state conditions in a very short period of time. Another possibility is to perform step-response experiments by changing the composition and/or flow rate during the flow experiment.

If experiments are performed at pressures higher than ultra-high vacuum, it is necessary to use a continuous gas flow to maintain this higher pressure. The pressure is then set by the flow rate, when the leakage into the vacuum chamber is only dependent on the pressure in the reactor (in case of a fixed size orifice) or by a back-pressure regulator in case a high-pressure assembly is used. With the flow maintaining the higher pressure, it is possible to perform pulse-response experiments, by pulsing gas into the gas flow using the high-speed valves.

Design problems

The description of the Multitrack given in this chapter is of the system in its current configuration. However, to reach this configuration the design of the system had to be altered on a number of points to get a more optimal system. The next paragraphs will explain which problems occurred and how they were solved.

Vacuum system

Double pulse responses

The original vacuum system of the Multitrack system consisted of only two vacuum chambers with a single skimmer in between (the intermediate chamber was not present). When the first measurements were performed with this system, it turned out that all pulse responses consisted of two parts, a small very sharp and fast pulse followed by a very large and broad pulse. For a noble gas pulsed through a bed of silicon carbide this is shown in Figure 8.

The first idea for the cause of this phenomenon was that some by-passing of gas through the catalyst bed was occurring, causing the small first pulse. However, even pulse responses through an empty reactor showed this two-part pulse-response. A second possibility might have been that the pulse valves were working improperly. To study the cause of this occurrence it was, therefore, decided to
Figure 8.
Example of double pulse-responses as a result of a design flaw in the original vacuum system. Shown is the pulse response of neon through a 3 cm high bed of silicon carbide particles (400 μm) at 580 K.

examine the pulse response of an empty reactor in detail. This pulse-response is shown in Figure 9. As can be seen in this figure, also under these conditions a double pulse-response is obtained. The first response is clearly visible and there is a gap of a little over 1 ms between the first and the second response. Another indication is the width of the secondary pulse response. This width was almost identical when the pulse response of a reactor containing (400 μm) silicon carbide particles was compared with the response of an empty reactor. This indicates that the second pulse response is not characteristic for the reactor (content). It is clear that the molecules in the second pulse-response did not come straight out of the reactor and, therefore, there is no doubt that these molecules have collided at least once with one of the main vacuum chamber walls. This has to be the case since the free length of the molecules is in the order of a few meters. When the molecules have collided with one of the vacuum chamber walls, the distance traveled is significantly longer, which is consistent with the delay between the first and second pulse response. This view was confirmed by blocking the direct path from the reactor exit to the skimmer. This resulted in the disappearance of the first sharp pulse response in subsequent experiments.

The solution to the disturbance of the experiments by the indirect travelling gas was to introduce a third (pumped) intermediate vacuum chamber. The indirect travelling gas can be seen as gas flowing from the main vacuum chamber to the analysis chamber as a result of a pressure difference. The intermediate chamber will then 'catch' this gas, and the pressure increase in this chamber will be smaller than the pressure increase in the main vacuum chamber. Therefore, the amount of gas travelling indirectly from this intermediate chamber to the mass spectrometers will
Figure 9.
Pulse response in original vacuum system for argon through an empty reactor (323 K). A clear separation between the primary and secondary response is visible.

be negligible. After this modification was made to the Multitrack system, this very large second pulse response was no longer present.

Mass spectrometer signal
Another problem with the original vacuum system was that the signal measured by the mass spectrometers was insufficiently high to study products of reactions with a low conversion. For example, when the epoxidation of ethene was studied over a silver-catalyst yielding good results in a continuous flow reactor (15 % conversion, 60 % selectivity), no reaction products were visible in the preferred temperature range of 473 to 523 K. Only at temperatures above 600 K some CO₂ was visible. In literature Rigas et al. [3] reported on the same reaction studied in a conventional TAP system. Although in the TAP system the reaction also had very small conversions (maximum yield of most abundant product (CO₂) 1 %), all reaction products were clearly visibly in the desired temperature range.

Some fine-tuning of the mass spectrometers resulted in an increase in the mass spectrometer signal of up to 50 %. This was, however, by far insufficient. Increasing the voltage over the mass spectrometer electron multipliers is also useless because of the digital molecule counting principle of the electronics. The only possibilities to achieve a higher signal with the vacuum chambers with their original shape was to use either larger gas pulses or larger skimmers between the vacuum
chambers. The disadvantage to the first 'improvement' is that larger gas pulses would mean it would be impossible to perform experiments in the Knudsen diffusion regime, and as a result the modeling of the experiments would be complicated. The use of larger skimmers was not possible, as this would have caused significant peak tailing due to molecules reaching the mass spectrometers indirectly.

The solution to the problem was to bring the mass spectrometers closer to the reactor exit. This meant replacing the original main vacuum chamber, shaped like a 40 cm sphere with the two vacuum pumps on two opposing sides, the reactor at the bottom and the intermediate chamber connected to the top, as well as the 11 cm high T-shaped intermediate chamber. This replacement was necessary, as the signal at the mass spectrometers is inversely proportional to the squared distance from the mass spectrometers to the reactor exit. In the original design, the distance from the reactor exit to the nearest mass spectrometer was about 55 cm. The reconstructed main vacuum chamber is shaped like a horizontally placed hourglass with the intermediate vacuum chamber integrated into the main vacuum chamber. This new assembly resulted in a distance from the reactor exit to the first mass spectrometer of only 17 cm, which resulted in a mass spectrometer signal which was a factor of 10 higher than in the original design, making the set-up more suitable for studying low-yield reactions such as the ethene epoxidation.

Reactor assembly

Heating system

Part of the reactor assembly of the Multitrack system is located in ultra-high vacuum. This part consists of the reactor itself, the reactor heating system, and the external cooling tube. Due to the modular design of the reactor assembly and the vacuum, a difficulty to be expected is the proper transfer of heat between the heating tube and the reactor. The original heating tube consisted of a stainless steel pipe, heated on the outside by a 2-mm diameter, 1 meter long Thermocoax heating element. Adequate heat transfer from the heating tube to the reactor was provided by the use of a narrow fit between reactor and heating tube. A problem that arose soon, was to remove the reactor from the heating tube, especially after experiments had been performed at temperatures above 800 K. At these temperatures the reactor got stuck inside the heating tube as a result of the interaction between the two steel surfaces. A way to prevent this was to increase the distance between the reactor and the heating tube. However, because of the high vacuum now present between the reactor and the heating tube, it proved to be virtually impossible to accurately control the reactor temperature. The main cause was that the only way in which heat could be transferred from the heating tube to the reactor, was by radiative heat transfer. To have an adequate heat flow to the reactor, this meant that the heating tube should have a significantly higher temperature than the reactor. However, due to the high mass of the heating tube compared to the reactor, this resulted in an extremely sluggish temperature control. Attempts to solve this were made by filling
the space between reactor and heating tube using various conductive foils, but none of these seemed to be adequate.

An alternative solution was finally found by using a radiative heating element instead of a metal tube. The heating element that proved to work best, is a 1-mm diameter, 1 meter long Thermocoax heating element, which is wrapped around five steel rods placed on a circle around the reactor. This element is able to heat the reactor with a maximum rate of 30 K/min. Because of the small mass of this element, little temperature overshoot occurred. The maximum temperature this element can reach is about 1400 K, thus limiting the maximum reactor temperature to about 1300 K.

Reactor

The original reactor design of Multitrack did not include the use of support grids for the catalyst bed. From the start it was decided to use a safety grid on top of the reactor to prevent catalyst particles from being blown out of the reactor system. This is absolutely necessary as catalyst particles can destroy the two large turbomolecular pumps connected to the main vacuum chamber. The catalyst bed was held in place in the reactor by a layer of quartz wool at the top and bottom. However, after some of the experiments, the quartz wool at the bottom of the catalyst bed had migrated to the top. As a result, the catalyst bed shifted downwards, partly into the needle and pulse valves. This movement of the quartz wool was probably caused by small vibrations as a result of the pulsing of gases. Because particles can damage the pulse-valves, the use of a support grid below the catalyst bed was necessary, thus no longer making the use of quartz wool at the bottom of the bed obligatory. The use of quartz wool at the top of the catalyst bed had the disadvantage of allowing movement of catalyst particles induced by the pulsing of gases. As the reactor often consists of multiple zones of different particles, this can cause mixing of the separate zones, which is even more likely if the particle sizes and densities of the zones vary. This behavior was prevented by using a second grid immediately on top of the reactor bed, which is pressed onto the bed thus fixating the particles.

Conclusions

The most important possibilities of the Multitrack system are:
- identification of the rate determining step;
- determination of the number of active sites;
- determination of reaction kinetics and/or mechanism.

The major advantages of the Multitrack system over a conventional TAP system are:
- Few calibrations are needed for the mass spectrometers as separate ionized molecules are counted, instead of measuring an electrical current from the mass spectrometer electron multiplier;
• The noise in the measured signal is much lower, so the averaging of different experiments is no longer necessary;
• The sampling frequency can be up to 1 MHz (TAP: 100 kHz);
• Three masses can be followed simultaneously (TAP: one);
• The reactor can be changed using an automated procedure in a few minutes time, without venting the main vacuum chamber;
• In-situ analysis techniques can be added.

References

Chapter 2

Modeling Multitrack Experiments

Summary

Modeling the transient behavior of the Multitrack reactor system is necessary to obtain rate constants from experimental results. The models to be used for the behavior of gas pulses travelling through a reactor containing solid or porous particles are discussed, as well as an example of the modeling of a catalytic reaction. Using the platinum-catalyzed CO oxidation, it is shown that modeling can be used to reconstruct the behavior of the entire reactor from the integral behavior measured at the reactor exit. To facilitate the modeling process, it is recommended that experiments are performed in the Knudsen diffusion regime.
Modeling Multitrack Experiments

Introduction

Transient experiments such as performed using the Multitrack system can supply quantitative information on a catalyst, such as adsorption parameters, rate constants, and numbers of active sites. To extract these parameters from pulse responses measured, a model has to be used which incorporates all relevant processes occurring in the reactor. By fitting this model to measured pulse responses, the constants of the relevant processes can be determined.

Before any reaction or adsorption process can be modeled, first the basic characteristics of the reactor system should be known. The starting point for any modeling of reactor behavior is, therefore, the determination of the relevant transport processes throughout the reactor system. Once one is able to accurately describe how a non-adsorbing, non-reacting gas pulse travels through the Multitrack reactor system, this model can be extended to include other processes. This chapter will describe the modeling of pulse responses from a starting point of the simplest situation of an inert gas pulse travelling through a bed of non-porous particles, after which this model is gradually extended to include more difficult processes, such as reactions and diffusion into catalyst particles.

Modeling of diffusion only experiments with non-porous particles

Diffusion in catalyst bed

Experiments in a Multitrack or TAP system are preferably performed in the Knudsen diffusion regime to facilitate the modeling of a gas pulse through a catalyst bed. Performing experiments in this regime can be achieved by using very small gas pulses, such that the mean free path of the gas molecules is greater than the interparticle distance. The advantage of the Knudsen diffusion regime is that viscous flow and molecular diffusion can be neglected, and thereby simplifying the model significantly. The Knudsen diffusion regime implies that any influence of the reactor pressure on the diffusion coefficient is absent, as well as that diffusing molecules do not exert any mutual interaction. Furthermore, the Knudsen diffusion coefficient can easily be calculated and is concentration independent, thus facilitating the modeling. Another advantage is that no external mass transfer limitations around the catalyst particles can occur.

The effective Knudsen diffusion coefficient for diffusion through a porous medium can be calculated from the following equation [1]:

\[ D_{kn} = \frac{\varepsilon_b \cdot 2{\overline{r}}}{\tau_b} \frac{8RT}{3} \left( \frac{\pi M}{\varepsilon_b} \right)^{\frac{1}{2}} \]  

(1)
with $D_{Kn}$ Knudsen diffusion coefficient, $\varepsilon_b$ bed porosity, $\bar{r}$ average interparticle distance, $\tau_b$ bed tortuosity, $R$ gas constant, $T$ temperature, and $M$ molecular mass of the molecule considered. The average interparticle distance can be estimated from the average particle radius $r_p$ using:

$$\bar{r} = \frac{2\varepsilon_b}{3(1-\varepsilon_b)} r_p$$

(2)

In calculating the Knudsen diffusion coefficient, the bed tortuosity can be seen as a fitting parameter, as shown by Huinink [2] in modeling TAP experiments, since it is very difficult to determine it experimentally. Alternatively, the often used approximation of $\tau_b = 1/\varepsilon_b$ can be taken. This latter possibility was preferred, as this will always result in realistic values of 2 to 3 for the tortuosity, whereas using the tortuosity as a fitting parameter can result in physically unrealistic values to compensate for errors in the model used.

**Basic TAP-reactor model**

The gas transport through a bed of particles is modeled by diffusion of a gas pulse through a packed bed. Figure 1 demonstrates this model schematically, with the gas pulse given directly to the bottom of the bed. This model is commonly used to describe TAP-reactor experiments [2,3]. The differential equation for the model in Figure 1 reads:

$$\varepsilon_b \frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial z^2}$$

(3)

with $C_z$ being the concentration at axial position $z$, $D$ diffusion coefficient, $z$ axial position, and $t$ time.

In this equation the left-hand side stands for the concentration build-up at axial position $z$ and the right-hand side stands for the diffusion into and out of this position. Because no other driving forces are present except for the concentration gradient, no other terms, such as a velocity term, are present in the equation. Although it might be argued that the gas travels through the bed by a pressure gradient, which is clearly present, the separate introduction of a pressure-induced flux-term is not necessary, as in the Knudsen diffusion regime a pressure gradient is identical to a concentration gradient. Therefore, the gas fluxes of the pressure and
concentration gradients are the same. The boundary conditions for differential equation 3 are:

\[
t = 0: \quad C_z = 0 \quad (4)
\]
\[
z = 0: \quad -D \cdot \frac{\partial C_z}{\partial z} = \delta(t) \quad (5)
\]
\[
z = L: \quad C_z = 0 \quad (6)
\]

where \( L \) is the total bed height.

In boundary condition 5 the gas pulse given to the reactor is assumed to be a Dirac pulse \( \delta(t) \). This assumption of an ideal pulse is realistic because the width of the input pulse is three orders of magnitude shorter than the measured response. As long as the time steps used for the modeling are larger than 100 \( \mu s \), the width of the original pulse peak at half height, the ideal pulse assumption is allowed. Should experiments be performed with extremely thin catalyst beds (smaller than approximately 5 mm bed height) or an otherwise special reactor content, causing the pulse responses to be narrower than 100 ms, it will be necessary to use the actual input pulse shape instead of the ideal pulse. The assumption in equation 6 to set the concentration at the reactor exit to zero can be justified because the concentration at the reactor exit (the main vacuum chamber) is kept very low by the vacuum pumps. Furthermore, even if the reactor chamber were not continuously evacuated, the concentration at the reactor exit would not reach a significant value after a gas pulse is given. This is easily seen since the volume of the main vacuum chamber is four orders of magnitude larger than volume of the reactor. The error made in the numerical approximation of equation 6 to set the concentration at the reactor exit to zero can, therefore, be neglected. The only problem this boundary condition causes is that it is not possible to determine the concentration at the reactor exit from the model. This is solved by using the flux at the reactor exit for the modeled pulse response instead of the concentration. This flux is directly related to the measured concentration by the mass spectrometers as these measure the concentration in the passing molecular beam over a user specified time interval (= 1/sampling frequency). In this way boundary condition 6 can be used without any (numerical) problems.

The model was numerically solved in Fortran using the DSS/2 and LSODES libraries [4] in Fortran. The proper numerical solution was validated by comparing the outcome to the analytical solution published by Zou et al. [5]. The diffusion coefficient of the model was fitted to the measurement using the Levenberg-Marquard parameter estimation method, in which the sum of squared residuals between model and measurement was minimized. A detailed description of this fitting procedure is given by van de Linde et al. [6]. The results of both measurement and modeling using this first simple model are shown in Figure 2, for an argon pulse given to a reactor containing a 30 mm bed height of 230 \( \mu m \) silicon carbide particles at 314 K. As can be seen in Figure 2, the model is inadequate.
Improvement reactor-model

Zou [5] has presented a number of alternatives for the basic TAP reactor model. One of these models, which resembles the actual Multitrack reactor geometry more closely is schematically drawn in Figure 3. This model consists of a small mixed volume in front of the packed bed in the reactor. The gas pulse is given to this volume and passes from there to the packed bed. In this case the bed is more or less acting as a flow restrictor to the empty space and the gas is passed to the catalyst bed over a much larger period of time. This reason makes this model closer to the actual situation since the reactor does contain a small empty volume between the pulse valves and the catalyst bed. It is possible to depict the empty volume as ideally mixed, because the Knudsen diffusing coefficient in this volume is an order of magnitude larger than the diffusion coefficient in the packed bed. Therefore, the mixing in the empty volume is fast compared to the diffusion through the packed bed.
Modeling Multitrack Experiments

bed. For this model the differential equation describing the concentrations through the bed is still equation 3, as the situation throughout the packed bed has not changed. The boundary conditions for this new model are different:

\[ z=0: \quad h_{eq} \frac{\partial C_m}{\partial t} = D \frac{\partial C_z}{\partial z} \quad (7) \]

\[ C_z = C_m \quad (8) \]

\[ z=L: \quad C_z = 0 \quad (9) \]

\[ t=0: \quad C_z = 0 \]

\[ C_m = 0 \quad (10) \]

\[ \text{pulse: } C_m := C_m + \delta(t) \quad (12) \]

with \( C_m \) the concentration in the empty volume between the pulse valves and the reactor. \( h_{eq} \) is defined to be the effective equivalent height of the empty volume (the volume of the empty space divided by the cross sectional area of the packed bed).

Boundary condition 7 expresses the change in concentration in a stirred tank (left hand side) being controlled by the flux into the packed bed (right hand side). Boundary condition 8 at \( z=0 \) expresses equal concentrations for empty volume and beginning of the packed bed, since it is impossible to have two different concentrations for the same component at the same location. The pulse given by the valves directly enters the empty volume and can be seen as a simple increase in concentration in this volume (equation 12). The empty volume between the pulse valves exit and the packed bed beginning can easily be calculated from the reactor design.

The advantage of this model is that it takes into account the disturbance by the empty volume before the catalyst bed of the Dirac pulse given to the reactor. The differential equations of this model were solved similar to the first model. In Figure 4 it can be seen the results of best fit for the diffusion coefficient in this model are in good agreement with the measurement. In Table 1 the calculated diffusion

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**Table 1.**
Calculated diffusion coefficient in Multitrack reactor bed, together with the tortuosities for the models calculated from the diffusion coefficients using equations 1 and 2, assuming Knudsen diffusion. (Reactor filled with 230 μm SiC particles, 314 K, Argon)

<table>
<thead>
<tr>
<th></th>
<th>Diffusion coefficient (m²/s)</th>
<th>tortuosity (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic model</td>
<td>9.5*10⁴</td>
<td>7.4</td>
</tr>
<tr>
<td>Improved model</td>
<td>30.5*10⁴</td>
<td>2.3</td>
</tr>
<tr>
<td>Knudsen (τ=1/εₜ)</td>
<td>30.4*10⁴</td>
<td>2.3</td>
</tr>
</tbody>
</table>

---

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coefficients from the best fits of both models are given, together with the Knudsen coefficient calculated from equations 1 and 2. Table 1 shows the excellent agreement between the Knudsen diffusion coefficient and the fitted diffusion coefficient of the advanced model, whereas the simple model yields a much lower diffusion coefficient. This lower diffusion coefficient of the simple model is a result of the model adapting to the significant tailing of the measured pulse response. The fact that the simple model calculates the peak maximum at a later time is a result of this too low a diffusion coefficient. The simple model could describe the peak maximum better if a lower ‘weight factor’ were to be given to the points in the tail of the response. This would, however, only improve the description of the peak maximum and not the overall fit. The tortuosity obtained using the improved model is realistic, whereas the tortuosity from the basic model fit is usually not likely.

Three conclusions can be drawn from the modeled responses in Figures 2 and 4 and the diffusion coefficients in Table 1:

- It is necessary to use the improved model to describe Multitrack experiments and to calculate parameters from the experiments;
- The experiments are performed in the Knudsen diffusion regime. This facilitates the modeling significantly, as viscous flow and viscous diffusion do not have to be taken into account;
- The gas pulse given does not arrive at the reactor bed as sharp as it is delivered by the pulse valves. This can be seen even clearer from Figure 5, where it is demonstrated that the major part of the pulse response measured is directly determined by the emptying of the volume in front of the bed.
When studying real short time phenomena it is necessary to use a reactor with a smaller empty volume before the catalyst bed, for example by filling this space with glass beads. Another possibility is to use a larger diameter bed, as this reduces the relative height of the empty space in front of the reactor bed ($h_{eq}$) in equation 7. The advantage of obtaining a smaller $h_{eq}$ is an increasing time resolution of the system. The broad entrance peak of systems with a large $h_{eq}$ makes short time-scale phenomena disappear in the broadening effect of the empty volume in front of the reactor.

Although the fact that the model used is able to predict a pulse response measured, the presence of the Knudsen diffusion regime during the experiments was double-checked by pulsing a number of different gases over a bed of silicon carbide particles and then determining the diffusion coefficient for each of the experiments using a fitting procedure. This check was made as all modeling in this thesis is based on the assumption of Knudsen diffusion, and the absence of this diffusion regime would make the results obtained of any modeling work doubtful. Figure 6 demonstrates these diffusion coefficients in a plot of the diffusion coefficient as a function of the inverse squared root of the mass of the gases used. As can be seen from equation 1 this type of plot should result in a straight line with a slope equal to $c_0/\tau_0 \cdot \frac{2}{3} \cdot \sqrt{\frac{8RT}{\pi}}$. The linear correlation in Figure 6 ensures the presence of the Knudsen diffusion regime. Using experiments with different pulse sizes, it was determined that this linear correlation was obtained with gas-pulse sizes of up to $2 \times 10^9$ molecules, making this the upper limit for performing experiments in the Knudsen diffusion regime.

![Figure 5.](image_url)

*Comparison between concentration in pre-bed volume and flux leaving reactor. Calculated using the improved model for the measurement shown in Figure 4.*
Figure 6.
Knudsen diffusion coefficients obtained from the model best-fits for pulses of different gases over bed of SiC particles as a function of the inverted square root of the molar masses.

Modeling of experiments with porous particles

In the preparation of a catalyst, one usually uses a porous support material to create a catalyst with a large active surface area per volume. Modeling an experiment performed with such a catalyst is more complicated as the concentration gradient into the particle has to be taken into account. When modeling experiments with porous particles, it is allowed to neglect the axial transport through the particles. This simplification is valid when the diffusion coefficient in the particles is much smaller than the diffusion coefficient between the particles in the bed. This is the case when the pore diameter of the particles is smaller than about one tenth of the particle diameter. The previously described model for non-porous particles has to be expanded with an extra dimension to represent the concentration profiles into the particles, which results in the following equations (on the assumption of spherical particles):

\[
\varepsilon_b \frac{\partial C_{z}}{\partial t} = D \cdot \frac{\partial^2 C_{z}}{\partial z^2} - (1 - \varepsilon_b) \cdot D_p \cdot A_{sp} \cdot \frac{\partial C_{r,z}}{\partial r}
\]

(13)

\[
\varepsilon_p \frac{\partial C_{r,z}}{\partial t} = D_p \cdot \frac{\partial^2 C_{r,z}}{\partial r^2} + \frac{2}{r} \cdot D_p \cdot \frac{\partial C_{r,z}}{\partial r}
\]

(14)
with $D_p$ diffusion coefficient in particle, $A_{sp}$ specific surface area of particle, $r$ radial position in particle, $C_{rz}$ concentration in particle at axial position $z$ and radial position $r$, and $\varepsilon_p$ particle porosity. It should be noted that equations 13 and 14 only express the diffusion of non-adsorbing gases into a porous particle. The more complex situation of the diffusion of adsorbing compounds into a porous material is discussed in chapter 4.

Equation 13 is similar to equation 3 with an extra term added on the right-hand side for the diffusion of the bulk gas phase into the particles. Equation 14 has on the left-hand side the concentration build-up at position $r$ in the particle and on the right side the diffusion to and from that position. The boundary conditions for equations 13 and 14 for $C_z$ remain unchanged compared to the non-porous model (equations 7-11). The boundary conditions for $C_{r,z}$ are:

$$\begin{align*}
  r=0: & \quad \frac{\partial C_{r,z}}{\partial r} = 0 \\
  r=R: & \quad C_{r,z} = C_z \\
  t=0: & \quad C_{r,z} = 0
\end{align*} \tag{15, 16, 17}$$

with $R$ the particle radius of the catalyst particles.

By solving these differential equations, it is possible to calculate as a function of time both the concentration profiles in the axial direction through the reactor and the concentration profiles in the particles.

![Figure 7](image.png)

*Figure 7.* Comparison between pulse response through a bed of porous and non-porous particles (argon pulse through 11.5 mm of 250 μm particles, 298 K, porous: γ-alumina and zeolite 13X, non-porous: silicon carbide) (measurements for γ-alumina and zeolite 13X overlap).
In Figure 7 the experimental results of an argon pulse over a packed bed of porous (silicon carbide) and non-porous (gamma alumina and zeolite 13X) particles are compared. The particle size is equal for each of the three materials. As can be seen, the influence of the porosity of the particles is relatively small. This gives the opportunity, when using a porous catalyst, to start the modelling first with the assumption of a non-porous catalyst. This is preferred, as the computation time necessary to calculate diffusion into particles is much longer than in the case of non-porous particles. The reason for this is that when calculating a concentration profile with porous particles, the number of differential equations is multiplied by the number of gridpoints in the particle. For example, in the case of diffusion through a bed of non-porous particles, the number of differential equations to solve is typically 101 (100 axial gridpoints plus the stirred tank) for each time step. In the case of porous particles, the typical number of differential equations to solve is 2201 (20 radial gridpoints into particle x 100 axial gridpoints + 100 axial gridpoints for the bulk gas phase + the stirred tank equation).

The effect of the porosity of particles on the measured pulse response is determined by the time constant of the diffusion into the particles compared to the time constant of the diffusion through the bed. This time constant ($t_c$) can be calculated from equation 18:

$$ t_c = \frac{L_c^2}{D} $$

(18)

The characteristic length $L_c$ is in the case of diffusion into the particles equal to the particle diameter, for the diffusion through the packed bed the characteristic length is equal to the bed height. As the diffusion coefficient $D$ is partly determined by the pore radius and the particle radius, the time constant is effectively set by the ratio between pore radius and particle diameter for the diffusion into the particles, and by the ratio between particle diameter and bed height for the diffusion through the packed bed.

In case of diffusion through a bed of alumina particles, shown in Figure 7, the time constant for diffusion into the particles is small compared to the time constant for diffusion through the packed bed. This means that diffusion into the particles is fast compared to the transport through the bed, and therefore Figure 7 shows more or less the worst case for peak broadening due to porous particles. Effectively no concentration gradient in the macropores exists, and the porosity of the particles is only raising the overall reactor porosity, however, without changing the cross-sectional area of the reactor available for axial diffusional transport. As a result the pulse response is only slightly broadened.

In case the time constant for diffusion into the particles is very large (very small pores) compared to that for diffusion through the catalyst bed, the gases have little chance to diffuse into the particles. This can be seen by the experiment performed using zeolite 13X in Figure 7. The pulse response measured is almost
Modeling Multitrack Experiments

identical to that of the experiment using alumina. In this case only the macroporosity of the binder material has an influence, explaining the similarity in the pulse responses over zeolite 13X and γ-alumina. The small zeolite pores result in a negligible influence on the pulse broadening. If one, therefore, uses a porous catalyst with the active material in micropores pores to study a reaction, this also means that the catalyst will be very inefficient. Therefore, it is advisable to only use a non-porous or macroporous catalyst for performing transient measurements on either a TAP or Multitrack system. One very clear exception to this statement has to be made: when adsorption, which often is an essential part in catalysis, occurs followed by the diffusion process, diffusion into micropores has to be taken into account. In this case the diffusion in the micropores occurs by the adsorbed phase. This diffusional process is able to occur because of the longer ‘contact time’ between molecules and pores due to the adsorption process. This type of ‘activated’ diffusion into the particles is shown in Figure 8. In this figure the pulse responses of propane and argon over uncalcined (as synthesized) (effectively non-porous) and calcined (porous) silicalite-1 are shown. The pulse response of Argon (non-adsorbing) does not change when the zeolite is calcined, effectively demonstrating a gas does not measurably diffuse into small micropores. Propane, on the other hand, does diffuse into the pores of the calcined silicalite-1, as a result of the possibility of propane to diffuse into the particles as an adsorbed species instead of in the gas phase. An extensive discussion on this subject will be given in chapter 4.

For intermediate pore-size catalysts it is necessary to incorporate diffusion into the particles, even when no adsorption is occurring. Simplification of the model by assuming the pore content to be ideally mixed with the surrounding gas phase (as

![Figure 8](image)

**Figure 8.**

*Pulse responses of argon and propane over a bed of silicalite-1, before and after in-situ calcination of the silicalite. (pulse response at 423 K)*

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can be done with macroporous materials) or neglecting diffusion into the particles (as can be done with microporous materials in the absence of adsorption), will result in a unsatisfactory model description of the experiment. Which catalysts are defined as intermediate pore size (mesoporous) for the modeling of Multitrack experiments is set by the value of the time constant from equation 18. If this time constant is within one order of the width of the pulse response, the pore size of the catalyst should be called intermediate and modeling of the concentration profiles within the particles is necessary.

**Modeling of reactions: CO oxidation**

The CO oxidation over macroporous platinum sponge was used as a model reaction to describe the performance of Multitrack in case of a reaction taking place. The reaction steps determined to be of significance are the reversible adsorption of CO, the dissociative adsorption of oxygen, a reversible reaction on the catalyst surface via the Langmuir-Hinshelwood mechanism, and the desorption of the CO₂ produced. The determination of these reaction steps is described in detail in chapter 3 of this thesis. The steps can be represented by the following reaction equations.

\[
\begin{align*}
\text{CO} & \xrightleftharpoons[k_2]{k_1} \text{CO}_{\text{ad}} \\
\text{O}_2 & \xrightarrow[k_3]{k_3} 2 \text{O}_{\text{ad}} \\
\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} & \xrightarrow[k_4]{k_5} \text{CO}_2 \text{ad} \\
\text{CO}_2 \text{ad} & \xrightarrow[k_6]{k_6} \text{CO}_2
\end{align*}
\] (a) (b) (c) (d)

The differential equations describing this reaction are (non-porous particles):

\[
\begin{align*}
\varepsilon_b \frac{\partial C_{\text{CO}_2}}{\partial t} &= D_{\text{CO}_2} \cdot \frac{\partial^2 C_{\text{CO}_2}}{\partial z^2} - k_1 \cdot (1 - \varepsilon_b) \cdot N_s \cdot C_{\text{CO}_2} \cdot \theta_{\text{CO}_2} + k_2 \cdot (1 - \varepsilon_b) \cdot N_s \cdot \theta_{\text{CO}_2} \\
\varepsilon_b \frac{\partial C_{\text{O}_2} \cdot \text{ad}}{\partial t} &= D_{\text{O}_2} \cdot \frac{\partial^2 C_{\text{O}_2} \cdot \text{ad}}{\partial z^2} - k_4 \cdot (1 - \varepsilon_b) \cdot N_s \cdot C_{\text{O}_2} \cdot \theta_{\text{O}_2} \\
\varepsilon_b \frac{\partial C_{\text{CO}_2} \cdot \text{ad}}{\partial t} &= D_{\text{CO}_2} \cdot \frac{\partial^2 C_{\text{CO}_2} \cdot \text{ad}}{\partial z^2} + k_6 \cdot (1 - \varepsilon_b) \cdot N_s \cdot \theta_{\text{CO}_2} \\
\frac{\partial \theta_{\text{CO}_2}}{\partial t} &= k_1 \cdot (1 - \varepsilon_b) \cdot C_{\text{CO}} \cdot \theta_{\text{CO}_2} - k_2 \cdot (1 - \varepsilon_b) \cdot \theta_{\text{CO}_2} - k_4 \cdot \theta_{\text{CO}_2} \cdot \theta_{\text{O}_2} + k_6 \cdot \theta_{\text{CO}_2} \\
\frac{\partial \theta_{\text{O}_2} \cdot \text{ad}}{\partial t} &= 2 \cdot k_3 \cdot (1 - \varepsilon) \cdot C_{\text{O}_2} \cdot \theta_{\text{CO}_2} - k_4 \cdot \theta_{\text{CO}_2} \cdot \theta_{\text{O}_2} + k_5 \cdot \theta_{\text{O}_2}
\end{align*}
\] (19) (20) (21) (22) (23)

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\[ \frac{\partial \theta_{\text{CO}_{2}z}}{\partial t} = -k_s \cdot (1 - \varepsilon_b) \cdot \theta_{\text{CO}_{2}z} + k_4 \cdot \theta_{\text{CO}z} \cdot \theta_{\text{O}_{2}z} - k_5 \cdot \theta_{\text{O}_{2}z} \]  

(24)

With \( \theta \) the surface coverage on the catalyst for each of the components ([ ] for vacant sites), \( N_s \) conversion factor from gas-phase concentration to surface sites on catalyst, \( k_i \) for the reaction and adsorption/desorption rate constants. The boundary conditions for the three reactants in the gas phase are for each component identical to equation 7-12. The boundary condition for the surface coverages of the components consist only of an initial value at \( t=0 \). The value depends on the experiment that is performed.

Reaction experiments with porous catalysts can also be modeled. The number of differential equations will, however, become increasingly large. In case of the transition from one component diffusing through a bed of non-porous particles to a bed of porous particles, differential equation 3 is converted into differential equations 13 and 14. In the case of the CO oxidation (equation 19 to 24), equation 19 to 21, representing the gas phase transport of each of the component have to be expanded in a similar manner as equation 3 was to obtain equations 13 and 14. If the transport across the catalyst surface (surface diffusion) is neglected, equations 22 to 24 are then indexed for both radial position \( r \) and axial position \( z \), to obtain the complete set of differential equations for the CO oxidation on a porous catalyst.

In the Multitrack system the CO oxidation over platinum sponge was studied. Platinum sponge has the advantage of having a relatively high surface area with a macroporous structure. As described earlier a macroporous structure has the advantage of the entire surface area of the catalyst being available for the reaction. The modeling of this reaction was done using equation 19 to 24. Although the platinum sponge has a porous structure, it was not necessary to take this pore structure into account in the modeling, since the sponge only has macropores. Although in principle it is possible to determine all rate constants in equations 19 to 24 by fitting these differential equations to Multitrack experiment, this has not been done. The main reason for this decision is that a large amount of experiments and modeling is necessary to determine these constants, as it is impossible to fit all parameters on a single experiment. Instead it was decided to focus on the determination of the mechanistics of the reaction, as can be found in chapter 3 of this thesis. The determination of rate constants by fitting a model to experiments was applied to a less complicated situation, the adsorption and desorption of gases on a sorbent material, which can be found in chapter 4. As in this study the initial conditions were exactly known and the possible processes are limited to adsorption, desorption, and diffusion, the modeling was less complicated.

Modeling of the platinum-catalyzed CO oxidation was applied to one important aspect of the CO oxidation study, the double CO\(_2\) pulse-responses during experiments occurred after a switch was made from pulsing oxygen-only to pulsing oxygen and carbon monoxide alternately. As mechanistic or kinetic models proved to be inadequate to describe this type of behavior, the reactor behavior had to be
investigated. By solving equations 19 to 24 subsequently for each of the oxygen and carbon monoxide pulses given, this reactor behavior was modeled. The rate constants to be used in the equations were not known. It was, therefore, decided to use estimates for these rate constants from the work of Dekker [7] on the CO oxidation. Although these rate constants were obtained using a different catalyst under different conditions, the use of these estimates would insure that the values used are likely to be realistic. Figure 9 demonstrates the result of these subsequently modeled pulses.

In Figure 9 it can be seen that the model is able to describe the occurrence of double pulse responses measured. That these double pulse responses are indeed the
cause of a reactor-technical aspect, and not of a kinetic origin, can be better understood when one not only examines the pulse responses calculated by the model, but also the calculated catalyst surface compositions in between the pulses. The experiment yielding the double pulse response in this model had, prior to the CO pulse producing the double CO₂ pulse response, three distinct zones. First (nearest to the pulse valves) an oxygen covered zone, second a clean catalyst (no significant surface coverages of either CO or oxygen), and third another oxygen covered zone. As CO travels slower through the catalyst bed than CO₂, due to continuous adsorption-desorption of CO, the CO₂ produced in the first zone leaves the reactor slightly before the CO₂ produced in the third zone. This reactor behavior was confirmed using isotopic experiments with ¹⁸O₂. The detailed discussion on this behavior in the transient CO-oxidation over platinum can be found in chapter 3 of this thesis.

Conclusions

- Using the model described by Zou, Multitrack pulse responses can be described accurately.
- Experiments with porous particles can be modeled as non-porous in a first approximation to facilitate the modeling process.
- Diffusion into macropores in Multitrack experiments occurs instantaneously. As a result, macroporosity contributes only to the total porosity of the bed.
- Diffusion into micropores can be neglected unless adsorption is occurring.
- Intermediate pore size catalysts should be modeled with the concentration profiles in the particles included into the model, as is the case for micropores if adsorption occurs.
- By minimizing the value of $h_{eq}$ (pre-catalyst bed empty volume / reactor cross sectional area) the time resolution of the reactor system can be improved.
- Accurate modeling of reaction and transport in the Multitrack reactor system allows for the possibility to reconstruct the situation at every axial reactor position from the measured integral reactor behavior.

Symbols

- $A_{sp}$: specific surface area of particles \( m^2_{\text{surface}} / m^3_{\text{volume}} \)
- $C$: concentration diffusing gas \( \text{mol/m}^3 \)
- $D$: diffusion coefficient \( \text{m}^2/\text{s} \)
- $D_{kn}$: Knudsen diffusion coefficient \( \text{m}^2/\text{s} \)
- $D_p$: diffusion coefficient in particle \( \text{m}^3/\text{s} \)

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\( h_{eq} \)  volume of empty volume before packed bed / cross sectional area of packed bed
\( k \)  rate constant
\( L \)  bed length
\( L_c \)  characteristic length
\( M \)  molecular weight of species
\( N_s \)  number of sites
\( r \)  radius
\( \bar{r} \)  average interparticle radius
\( R \)  gas constant, 8.314
\( t \)  time
\( t_c \)  time constant (for diffusion)
\( T \)  temperature
\( z \)  vertical coordinate
\( \delta(t) \)  ideal pulse
\( \varepsilon \)  porosity
\( \tau \)  tortuosity
\( \theta \)  surface coverage

subscripts
\( a \)  adsorption
\( b \)  packed bed
\( d \)  desorption
\( lh \)  reaction via Langmuir-Hinshelwood mechanism
\( p \)  particle
\( r \)  position indicator in porous particle
\( m \)  indicates pre-bed mixed volume
\( z \)  axial position indicator
\( CO \)  regarding CO
\( CO_2 \)  regarding CO\(_2\)
\( O_2 \)  regarding O\(_2\)

References

Chapter 3

The Platinum-Catalyzed CO Oxidation

Summary

The platinum catalyzed oxidation of carbon monoxide was studied using a new fast transient technique, referred to as Multitrack, to evaluate the possibilities of this technique and to investigate the reaction mechanism. The experiments indicate that the reaction takes place according to the Langmuir-Hinshelwood model. From experiments performed using oxygen-18 isotope, it was shown that the desorption of carbon dioxide produced at the platinum surface is a kinetically relevant step influencing the reaction rate. Although the Multitrack technique, and other TAP-like techniques, are generally used to evaluate fast reactions, it was shown that in transient experiments with fast reactions the catalyst surface composition can vary through the position in the bed, as sequential gas pulses show a moving reaction front like behavior. This behavior can cause pulse responses having more than one maximum in a pulse experiment, which is often erroneously attributed to multiple surface reactions.
The Platinum-Catalyzed CO Oxidation

Introduction

The oxidation of carbon monoxide over platinum sponge was chosen as a model reaction to evaluate the Multitrack system. Multitrack is an advanced version of a TAP (Temporal Analysis of Products) apparatus, and has been designed in our laboratory to study reactions at a very short (millisecond) time scale. The oxidation of carbon monoxide over platinum has already been studied extensively on several TAP systems [1,2]. The advantages of this reaction are that the reaction is fast, making optimal use of the Multitrack systems capabilities, and the only by-product reported is carbon. A review on this reaction is given by Engel and Ertl [3]. In their review the following individual reaction steps involved with this reaction are listed:

\[
\begin{align*}
\text{CO} & \xrightleftharpoons[k_2]{k_1} \text{CO}_{\text{ad}} \\
\text{O}_2 & \xrightarrow{k_3} 2 \text{O}_{\text{ad}} \\
\text{O}_{\text{ad}} + \text{CO}_{\text{ad}} & \xrightarrow{k_4} \text{CO}_2 \\
\text{O}_{\text{ad}} + \text{CO} & \xrightarrow{k_5} \text{CO}_2 \\
\text{O}_2 + 2 \text{CO}_{\text{ad}} & \xrightarrow{k_6} 2 \text{CO}_2
\end{align*}
\]

(a) (b) (c) (d) (e)

The reaction steps are formulated on the assumption that all oxygen molecules adsorb irreversibly dissociatively on the platinum surface. In the temperature range of this study (300-650 K) this assumption is valid, since dissociative adsorption of oxygen occurs on all platinum group metals at temperatures above 100 K [4]. Recombination and desorption of adsorbed oxygen atoms take place only at temperatures above 700 K [3], so this reversible step can be neglected in the temperature range of this study. The carbon dioxide produced is weakly bonded to the platinum surface and assumed to desorb immediately after formation at temperatures above 300 K [5].

Reaction c is of the Langmuir-Hinshelwood reaction model, whereas reactions d and e are of the Eley-Rideal type. In the review of Engel and Ertl [3] it is assumed that the only relevant kinetic model for the CO oxidation over platinum in steady state is the Langmuir-Hinshelwood model. This means that only reactions a, b, and c are relevant. Not all studies support their view, as shown by Bonzel and Ku [6] at higher temperatures (T > 473 K), where the CO₂ production rate is not inhibited by a high CO surface coverage, possibly indicating an Eley-Rideal model. Therefore, in this study both reaction models will be taken into account.

Experimental

The CO-oxidation experiments were performed in the Multitrack system. This system consists of a small reactor (7 mm inner diameter, 10 mm bed height), located
in an ultra high vacuum chamber \(10^{-6}\) Pa, to which gas pulses in the order of \(10^6\) to \(10^7\) molecules can be given with a pulse width of about 100 \(\mu\)s using high speed gas pulsing valves. The gas leaving the reactor can be analyzed for three components simultaneously with a sampling frequency of up to 1 MHz using three mass spectrometers in line. The size of the gas pulses is determined by giving a large number of gas pulses and determining the pressure drop from the gas supply volume of the pulse valves using a high accuracy pressure transducer. The gas supply volume of the pulse valves is accurately known. The gases used have a purity of at least 99.995%. The sensitivity of the mass spectrometers for each component is determined by pulsing the relevant gas and measuring the total integrated pulse response at the mass spectrometer. It should be noted that the mass spectrometer is measuring m/e ratios, which can be the result of fragmentation of more than one component. A detailed description of Multitrac and the various possible experiment types and operating procedures is given elsewhere [7].

The platinum selected for the reaction was platinum sponge, 99.9 % purity, supplied by Johnson Matthey. It consisted of 2 \(\mu\)m spheres sintered together to form 40-100 \(\mu\)m particles (Figure 1). The use of platinum sponge as a catalyst has the advantage of a macroporous structure, making the occurrence of pore diffusion limitation unlikely, and a relatively high platinum surface area without using a support that might influence the reaction studied. The surface area calculated from SEM micrographs is about 0.070 m\(^2\)/g. No difference was visible in the micrographs between fresh and used catalyst. The surface area of the fresh platinum was 0.081 m\(^2\)/g, as determined using krypton adsorption measurements and the BET-
theory. The number of surface Pt atoms in the (100) crystal plane is $1.29 \times 10^{19} / m^2$, assuming a fcc structure with a 0.393 nm lattice constant. The amount of platinum used in the reactor was 0.291 g, giving a total number of available surface sites of $2.7 \times 10^{17}$ for the area calculated from the SEM micrographs and $3.1 \times 10^{17}$ for the area from the krypton BET measurement. The platinum was diluted using 0.628 g of 230 μm SiC (carborundum) particles. Blank experiments were performed with a reactor containing only SiC to confirm that neither reactor nor silicon carbide had any catalytic activity in the CO oxidation. Prior to use, the platinum was in-situ oxidized at 773 K and reduced at 673 K to remove possible contaminants. The in-situ treatment was carried out by pulsing each gas for two hours, with a pulse-size of $10^{17}$ molecules at a rate of 2 Hz. The platinum-sponge (fresh) was analyzed using XPS (X-ray Photoelectron Spectroscopy). Only minor amounts of carbon, oxygen, sodium, and indium were detectable on the catalyst surface. An influence of these contaminants can be expected to be negligible. Nitrogen, which might take part in the catalytic process, if it were present in the form of nitrates, was not detectable.

The experiments performed using this catalyst are of both the single and multiple-pulse type. The multiple-pulse experiments were done by precocovering the catalyst using either CO or O₂ and thereafter immediately pulsing O₂ and CO, respectively. The multiple-pulse experiments were performed in the temperature range of 328 to 423 K. The size of the gas pulses given is $1.0 \times 10^{17}$ molecules for the CO pulses, O₂ was pulsed as a mixture of 20 vol% in argon, resulting in O₂ pulses of $2.3 \times 10^{16}$ molecules.

Single-pulse experiments were performed in order to accurately monitor the pulse shapes of the gases leaving the reactor. The gas pulses used for the single-pulse experiments were identical to those used in the multiple-pulse experiments. Additional single-pulse experiments were also done with 100 % O₂ and with $^{18}$O₂ (99.5 % isotopically pure, $3 \times 10^{16}$ molecules per pulse). Since the experiments were done in the Knudsen diffusion regime, there is no difference in experimental results between measurements performed with either pure O₂ or diluted O₂ in argon.

Results

Multiple-pulse experiments

In Figure 2 mass spectrometer signals are shown of a multiple-pulse measurement in which CO is pulsed over oxygen covered platinum. It is possible to calculate the amount of CO₂ produced and CO reacted from this figure by integrating the area under the individually measured pulse-response curves. From the integration of individual pulses a graph as shown in Figure 3 (pulsing oxygen over CO-precovered platinum) can be created. By adding these values for the entire multiple-pulse experiment, the total amount of adsorbed CO or O₂ on the platinum before and after each multiple-pulse series is calculated. In the case of pulsing O₂ over platinum precovered with CO, the amount of adsorbed CO is determined by
the CO₂ produced. The amount of O₂ reacted plus adsorbed on the platinum is obtained by calculating the difference between the amount of O₂ pulsed and the amount measured by the mass spectrometer. The calculated amounts of gas (CO and O₂) consumed and amounts of carbon dioxide produced are given in Table 1.

![Graph showing CO and CO₂ over time](image)

**Figure 2.**
*Example of a multiple-pulse experiment. Gas pulses of 1.0*10⁷ molecules of CO are given over 291 mg of oxygen covered platinum surface at 333 K. Pulsing frequency: 1.33 Hz. Platinum surface area: 0.08 m²/g.*

<table>
<thead>
<tr>
<th>T (K)</th>
<th>CO multiple-pulse (oxygen covered Pt)</th>
<th>O₂ multiple-pulse (carbon monoxide covered Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO used (10⁷ molecules)</td>
<td>CO₂ produced¹ (10⁷ molecules)</td>
</tr>
<tr>
<td>328</td>
<td>6.1</td>
<td>3.1</td>
</tr>
<tr>
<td>333</td>
<td>6.1</td>
<td>3.2</td>
</tr>
<tr>
<td>338</td>
<td>5.8</td>
<td>2.9</td>
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<tr>
<td>343</td>
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<td>3.2</td>
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<td>5.9</td>
<td>2.9</td>
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<tr>
<td>393</td>
<td>5.7</td>
<td>3.0</td>
</tr>
<tr>
<td>423</td>
<td>5.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

¹: equals oxygen adsorbed on platinum when CO pulsing starts
²: equals adsorbed carbon monoxide at the start of O₂ pulsing

Table 1.
Results of series of multiple-pulse experiments over 291 mg Pt sponge. The values given are the total amounts of reacted or produced gas during the entire multiple-pulse experiment. (accuracy +/- 10%)
Figure 3.
Consecutive pulsing of O$_2$ over a CO precovered platinum surface (291 mg of Pt sponge). The Figure represents the amount of product and reactant gases measured at the reactor exit after a single gas pulse (the integrated area of a single pulse) versus the number of the gas pulse given. Pulse size: 2.3*10$^{16}$ molecules. (338 K).

Single-pulse experiments
The basic type of single-pulse experiments was executed by covering the catalyst with oxygen and then pulsing CO or covering the catalyst with carbon monoxide and then pulsing O$_2$. A less standard type of single-pulse experiment is performed by covering the platinum catalyst with either oxygen or carbon monoxide and thereafter pulsing O$_2$ and CO alternately. Figure 4 demonstrates the steady state that is achieved after pulsing both gases repeatedly for a long time. This steady state is the same, independent of the initial platinum coverage. In this Figure it should be noted that the small peak in the CO signal, which coincides with the maximum of the CO$_2$ signal, is not actually due to CO, but a fragment of the CO$_2$ created by the mass spectrometer. Similar effects are also visible in the other figures, when both CO and CO$_2$ are present. Figure 4 shows that the CO$_2$ produced is measured slightly earlier than the CO pulse. As most experiments were performed with an excess amount of CO, the steady-state surface coverage of the platinum will predominately exist of carbon monoxide. When pulsing CO and O$_2$ over initially CO covered platinum, one immediately reaches steady state. In case of the alternate O$_2$/CO pulsing experiments over an initial oxygen covered surface, the excess CO is able to slowly change the surface from oxygen covered to carbon monoxide covered. Initially one, therefore, observes a 100 % CO conversion and a matching amount of
Figure 4.
Steady-state results of CO oxidation with O\textsubscript{2} over Pt sponge at 573 K by pulsing 2.3*10\textsuperscript{6} molecules of O\textsubscript{2} at t=0 and 1.0*10\textsuperscript{7} molecules of CO at t=1 s over 291 mg of Pt sponge. At t=3.5 s the next O\textsubscript{2} pulse is given.

CO\textsubscript{2} produced. At about the third or fourth cycle (depending on the temperature), the shape of the pulse response of the CO\textsubscript{2} produced after a CO pulse starts to be divided into two distinct parts, seemingly indicating two different reactions taking place, as shown in Figure 5. Depending on the conditions, the split pulse-response is observed in two or three consecutive CO pulse-response measurements.

Experiments using \textsuperscript{18}O\textsubscript{2}

Before the experiments yielding the double CO\textsubscript{2} response were repeated with labeled oxygen, the steady-state situation was measured first. Figure 6 shows the measured mass signals in the 'steady-state' situation after alternately pulsing \textsuperscript{18}O\textsubscript{2} and C\textsuperscript{18}O. It can be seen that not only the expected C\textsuperscript{18}O\textsuperscript{18}O is produced, but also the isotopes C\textsuperscript{16}O\textsubscript{2} and C\textsuperscript{18}O\textsubscript{2} are present. The experiment resulting in two maximums in the CO\textsubscript{2} response, repeated with \textsuperscript{18}O\textsubscript{2} pulsed over initial \textsuperscript{18}O covered platinum, is shown in Figure 7D. In the Figures 7A to 7D the gradual formation of the double pulse-response is visible, after the consecutive C\textsuperscript{18}O pulses. The fifth C\textsuperscript{18}O pulse (7E) is the steady-state situation, when all precoversd \textsuperscript{16}O has been used. The pulse responses of the intermediate \textsuperscript{18}O\textsubscript{2} gas pulses are not shown. It should be noted that the small amount of C\textsuperscript{18}O visible in pulse responses 7A to 7C, are CO fragments of CO\textsubscript{2} created by the mass spectrometers.
The Platinum-Catalyzed CO Oxidation

Figure 5.
Results of CO oxidation with O₂ over 291 mg of Pt sponge (0.08 m³/g) at 573 K by pulsing 2.3×10¹⁶ molecules of O₂ at t=0 and 1.0×10¹⁷ molecules of CO at t=1 s over 291 mg of Pt sponge. At t=3.5 s the next O₂ pulse is given. Figure represents the fifth combination of an O₂ pulse followed by a CO pulse after saturation of the platinum surface with oxygen.

Discussion

Reaction model

As can be seen in Table 1, pulsing of O₂ over platinum covered with carbon monoxide at a temperature of 328 K does not produce any carbon dioxide. This shows the very strong adsorption of CO on the platinum maintaining all sites occupied and thus inhibiting the adsorption of oxygen. This indicates that at 328 K the mechanism for the reaction of O₂ with pre-adsorbed CO is according to the Langmuir-Hinshelwood model, as the Eley-Rideal model does not need free sites for oxygen adsorption. This is supported by the experiments done at higher temperatures. As can be seen in Figure 3 a fully CO-covered surface is hardly reactive towards O₂. When carbon monoxide is desorbing, free sites become available, and the oxidation reaction starts. The Langmuir-Hinshelwood model with respect to O₂ is likely as oxygen needs to be dissociated on the platinum metal sites. At low temperatures the limiting factor in this reaction is the absence of sites for oxygen adsorption caused by the slow desorption of carbon monoxide.
Figure 6.
Steady-state results of CO oxidation with $^{18}$O$_2$ over 291 mg of Pt sponge (0.08 ml/g) at 573 K by pulsing $2.3 \times 10^6$ molecules of $^{18}$O$_2$ at $t=0$ and $1.0 \times 10^7$ molecules of CO at $t=1$ s over 291 mg of Pt sponge. At $t=3.5$ s the next $^{18}$O$_2$ pulse is given (results compiled from 3 identical measurements).
Figure 7.
Results of C\textsuperscript{16}O oxidation with \textsuperscript{18}O, over initial \textsuperscript{16}O covered Pt sponge (573 K done by pulsing alternately 3*10\textsuperscript{16} molecules of \textsuperscript{18}O\textsubscript{2} and 1.0*10\textsuperscript{17} molecules of C\textsuperscript{16}O over 291 mg of Pt sponge. Shown are the pulse responses of the first five CO pulses given.
The Platinum-Catalyzed CO Oxidation

An oxygen-covered platinum surface behaves quite differently. When pulsing CO over an oxygen covered platinum surface carbon dioxide is immediately produced. The absence of an initial inhibition of the reaction by a fully oxygen covered surface indicates that the reaction of CO with adsorbed oxygen atoms takes either place according to the Eley-Rideal model or oxygen is not able to fully cover the platinum surface. As CO only needs a single site to adsorb on platinum, while oxygen needs at least two adjacent vacant sites to adsorb on platinum, it is well possible that under all conditions sufficient vacant sites will be available for the CO adsorption on the platinum surface allowing Langmuir-Hinshelwood kinetics.

In Figure 3 one can see that the production of CO$_2$ on the platinum surface shows three maximums. Similar results were obtained from other experiments in the temperature range from 333 to 393 K. This is a puzzling observation, which has also been made by Huinink [2] in his TAP experiments. A possible explanation, which was suggested by Huinink, is based on different platinum clusters (different crystal planes?) having a slightly different reactivity. A second explanation for this reaction behavior might be the oscillatory reaction effect, as described by Ertl [8] to occur on single-crystal platinum surfaces. The multiple-maximums phenomenon is not observed at higher temperatures, because the reaction rates then become too fast and this very small difference in reactivity is no longer of any significance.

Number of active sites

If both the amounts of CO$_2$ produced in Table 1 are added and then compared to the amounts of oxygen and carbon monoxide used, it can be seen, that the amount of oxygen and CO used, correspond nicely to the amount needed for the CO$_2$ produced within the accuracy (10-20 % error) of the experiments. The number of CO$_2$ molecules produced during one multiple pulse experiments should be equal to the number of active sites available on the catalyst. When the amounts of produced carbon dioxide are compared to the calculated number of platinum surface atoms from the SEM micrographs (2.7*10$^{17}$) or B.E.T. measurement (3.1*10$^{17}$), it can be seen that these are in good agreement with the adsorbed amounts calculated from the multiple-pulse experiments.

Isotopic mixing at the catalyst surface

Figure 6 shows, that in the steady-state situation when pulsing C$^{16}$O and C$^{18}$O$_2$ sequentially, three types of CO$_2$ are produced on the catalytic surface: C$^{18}$O$\cdot$, C$^{16}$O$^{18}$O, and C$^{16}$O$_2$, whereas only one type C$^{16}$O$^{16}$O might have been expected. The production of C$^{18}$O$_2$ (and C$^{16}$O$_2$) indicates that splitting of a C-O bond takes place. This can occur in two ways:

1. CO decomposes on the surface and produces C$_{ads}$ and O$_{ads}$;
2. CO$_2$$_{ads}$ produced decomposes to CO$_{ads}$ and O$_{ads}$, (i.e. the reverse of the CO$_2$ producing reaction).

The possibility of decomposition of CO or CO$_2$ in the gas phase is very unlikely at the low reaction temperatures of the experiments and is, therefore, not taken into
account. The possibility of the isotopic mixing occurring over small amounts of contaminants on the catalyst is unlikely, since the isotopic mixing occurs at a similar (or higher) rate as the \( \text{CO}_2 \) production. Possibility 1 is not likely to be the main cause because of the following reasons:
- no \( \text{CO}_2 \) production is seen, when only CO is pulsed over the platinum sponge.
- during the \( ^{18}\text{O}_2 \) gas pulse a significant amount of \( ^{18}\text{O}_2 \) is produced, and it is not likely that the decomposition of CO is induced by the presence of oxygen. This amount of \( ^{18}\text{O}_2 \) is far greater than is possible from the small amount of \( ^{16}\text{O} \) present as impurity in the \( ^{18}\text{O}_2 \) used.

\[ \text{Figure 8.} \]
\[ \text{Schematic representation of the mechanism for the CO oxidation. The shaded area's represent a platinum surface. The oxygen atoms marked with a * denote oxygen-18.} \]
The second possible explanation for the occurrence of the three CO\textsubscript{2} isotopes is based on the following mechanism, which is schematically shown in Figure 8. Adsorbed CO reacts with adsorbed oxygen to form adsorbed CO\textsubscript{2}. This is a very fast and reversible reaction. The adsorbed CO\textsubscript{2} can then dissociate to give adsorbed CO and O. In the decomposition of CO\textsubscript{2}, both oxygen atoms are identical and have an equal chance to be split off. The O\textsubscript{ads} at the surface can then be either from the CO or the original adsorbed O atom. By this pathway it is possible to form C\textsuperscript{18}O\textsubscript{2}, that can then produce C\textsuperscript{18}O\textsubscript{2} without dissociation of CO. Since this mechanism is able to produce adsorbed \textsuperscript{16}O from adsorbed C\textsuperscript{16}O during the reaction between C\textsuperscript{16}O and \textsuperscript{18}O\textsubscript{ads}, it should also be possible to produce C\textsuperscript{16}O\textsubscript{2}. The C\textsuperscript{16}O\textsubscript{2} is produced simultaneously with both other types of CO\textsubscript{2}. As C\textsuperscript{18}O\textsubscript{2} can only be produced by a Langmuir-Hinshelwood model (i.e. reaction only at the surface), it is concluded that all CO\textsubscript{2} produced from the reaction between CO and adsorbed O atoms is produced in this way. The Eley-Rideal model does not need adsorption of CO, so it can be expected that this reaction is faster. This would imply that the isotopes C\textsuperscript{16}O\textsubscript{2} and C\textsuperscript{18}O\textsubscript{16}O that can be produced using this same mechanism should be measured in front of the isotope C\textsuperscript{16}O\textsubscript{2}. As all types of CO\textsubscript{2} isotopes are produced simultaneously the main mechanism is most likely the Langmuir-Hinshelwood type.

The proposed mechanism involves the production of carbon dioxide on the platinum surface, on which the carbon dioxide remains adsorbed for some time and has the possibility to decompose. In literature the carbon dioxide desorption is thought to be instantaneous, which would contradict this mechanism. However, recently CO\textsubscript{2} surface species on platinum have also been observed by Somorjai and Rupprechter [9] in the CO oxidation at low pressures using a new SFG (Sum Frequency Generation) method, an interface specific vibrational spectroscopy.

To verify the assumption in the proposed mechanism, that isotopic mixing of the carbon dioxide is caused only by the carbon dioxide produced on the surface and not by carbon dioxide re-adsorbing on the catalyst and subsequently reacting with oxygen, an experiment was performed in which C\textsuperscript{18}O\textsubscript{2} and \textsuperscript{16}O\textsubscript{18}O were pulsed simultaneously over the catalyst at 523 K. This experiment showed that only very small amounts of C\textsuperscript{16}O\textsubscript{16}O were produced (less than 0.1 \%) and that no detectable amounts of C\textsuperscript{16}O\textsubscript{2} were visible, indicating that the CO\textsubscript{2} adsorption on the catalyst is slow. This again confirms that the isotopic mixing does not occur over contaminants on the catalyst, since in that case the isotopic mixing would have been caused by CO\textsubscript{2} re-adsorbing on a (contaminant) mixing site after it had been produced. Therefore, in that case this experiment should also have shown significant isotopic mixing rates.

The ratio between the amounts of C\textsuperscript{16}O\textsubscript{2}, C\textsuperscript{16}O\textsubscript{16}O, and C\textsuperscript{18}O\textsubscript{2} produced ranges from approximately 2:4:1 (573K) to 2:6:1 (373 K). According to the proposed mechanism the amount of C\textsuperscript{16}O\textsubscript{2} and C\textsuperscript{18}O\textsubscript{2} should be equal. That this is not the case can be explained, apart from the very small amount of \textsuperscript{16}O present in the \textsuperscript{18}O\textsubscript{2}, by the fact that a vacuum system will never be 100 \% leaktight. As even very low partial pressures of oxygen present in the vacuum can and will adsorb on the platinum, all
air leaking into the system will cause an extra amount of C\textsuperscript{18}O\textsubscript{2} produced. Alternatively the amount of excess \textsuperscript{18}O can have originated from oxygen bonded (either as O\textsuperscript{2} or as CO\textsubscript{2}) to the small amount of sodium contaminant present. The isotopic ratios observed give direct information on the scrambling rate in respect to the rate of desorption. If the isotopic scrambling (i.e. both formation and decomposition) of the CO\textsubscript{2} is very fast compared to the desorption of CO\textsubscript{2}, the ratio C\textsuperscript{16}O\textsubscript{2} : C\textsuperscript{18}O\textsubscript{16}O : C\textsuperscript{18}O\textsubscript{2} should be 1 : 2 : 1 on statistical considerations. If the desorption and isotopic mixing of CO\textsubscript{2} occur at the same rate, it is easily calculated that the ratio C\textsuperscript{16}O\textsubscript{2} : C\textsuperscript{18}O\textsubscript{16}O : C\textsuperscript{18}O\textsubscript{2} should be 1 : 6 : 1. From the observed ratios (2 : 4 : 1 (573 K), 2 : 6 : 1 (373 K)) we conclude that the rates are of the same order of magnitude. This isotopic mixing of the CO\textsubscript{2} produced was also found by Huinink [2], who performed comparable experiments on a conventional TAP system with CO and \textsuperscript{18}O\textsubscript{2} using a platinum sponge catalyst.

Multiple maximums in pulse-response artifact

In Figure 5 a double pulse response for carbon dioxide is seen, which might be interpreted as the result of two reactions taking place. These two reactions seem to have different activation energies, as the time between the first and second maximum in the CO\textsubscript{2} signal increases with an increasing temperature. An explanation for the two different reactions cannot be given on the basis of these experiments only. It was, therefore, decided to examine this phenomenon in more detail using isotopically labeled O\textsubscript{2}. At first sight, this multiplicity in pulse response (Figure 5) might seem similar to those shown in Figure 3, however, these results cannot be compared directly. In the case of Figure 5 the reaction rates were measured at high temperatures, where the multiple-pulse experiments do not show more than one maximum. Furthermore Figure 3 shows an experiment, where O\textsubscript{2} is pulsed over a CO covered surface, and Figure 6 shows a CO pulse over an oxygen covered surface.

In Figures 7A-7E the first five pulse responses of the C\textsuperscript{18}O pulses of an experiment in which alternately \textsuperscript{18}O\textsubscript{2} and C\textsuperscript{18}O are pulsed over platinum precovered with \textsuperscript{18}O\textsubscript{2} are shown. In the Figures A to D the gradual formation of a double pulse-response is visible. The measurement shown in Figure 7D shows a well-resolved double pulse response for the C\textsuperscript{18}O\textsubscript{2} signal, similar to the result in Figure 5. However, in Figure 7D the C\textsuperscript{18}O\textsubscript{16}O signals do not show a double pulse responses. Only one peak is found, at the same location of the first peak in the C\textsuperscript{18}O\textsubscript{2} signal. This indicates that the first peak in the CO\textsubscript{2} is a product of freshly added \textsuperscript{18}O, whereas the second peak is a result of the reaction of C\textsuperscript{18}O with \textsuperscript{18}O with a longer residence time on the surface. If this statement is correct, the fact that there is C\textsuperscript{18}O\textsubscript{2} present in the first maximum of the CO\textsubscript{2} production, can be explained by the isotopic mixing that is occurring as described earlier. The difference in reactivity between ‘fresh’ and ‘old’ oxygen, is not due to two different reaction mechanisms, such as an Eley-Rideal and a Langmuir-Hinshelwood mechanism, occurring simultaneously, since it is not likely that these mechanisms can make a distinction in which oxygen atom to react

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with, based on the residence time on the surface of the oxygen atom. Furthermore, such a dual mechanism occurrence, would always result in double pulse responses, which is not the case as is shown in Figure 7.

There are a few other possible explanations for a different reactivity between the ‘fresh’ and the ‘old’ oxygen on the surface. These explanations might be the following:

- Platinum has two different kinds of reactive zones for the CO oxidation, possibly different crystal planes. It is, however, unlikely that these zones will cause such a sharp distinction between freshly added oxygen and oxygen with a longer residence time on the surface.

- Besides surface, subsurface oxygen is taking part in the reaction. Subsurface oxygen could cause an additional amount of oxygen to be available at a slightly later time and thus be responsible for the second maximum in the CO\textsubscript{2} pulse response. However, the amount of sites (adsorbed oxygen) calculated to take part in the reaction from the multiple-pulse experiments are in good agreement with the number of surface sites calculated from SEM or BET. If subsurface oxygen takes part in the reaction, the amount of CO\textsubscript{2} produced when pulsing CO over oxygen-covered platinum should be much higher.

- The reaction is taking place according to a ‘moving reaction front’ model, i.e. the reaction rate is so fast, that the adsorption (and reaction) immediately takes place, when the pulsed gas arrives at the catalyst bed. This last mechanism is discussed in the next section.

Explanation of the moving reaction front model

In experiments where the adsorption and/or reaction of a component on a surface is taking place at a much higher rate than the transport in the axial direction, under certain conditions one can have a reaction zone moving as a front through the catalyst bed. This can be compared to processes taking place in adsorption columns.

Figure 9A illustrates what is occurring with the oxygen on the surface when CO is pulsed repeatedly over an oxygen covered platinum surface, if the reaction is taking place according to the moving reaction front model. If, however, CO and O\textsubscript{2} are pulsed alternately over an initially oxygen covered platinum surface, a different situation is occurring (Figure 9B). The catalyst bed has three zones, after the first combination of a CO pulse followed by a smaller O\textsubscript{2} pulse in respect to the CO pulse has been given (cycle number 1b):

I. an oxygen covered zone, with oxygen from the last added oxygen pulse;
II. a partial CO covered zone, from the CO pulses;
III. an oxygen covered zone, with oxygen residing on the surface for a longer time, from the initially fully covered surface.

When a new CO pulse is given, zone I will immediately produce CO\textsubscript{2}, and become partially CO covered, zone II will increase in CO coverage, and zone III will produce CO\textsubscript{2}, when the CO arrives at that zone. The CO pulse is able to reach zone III, because the amount of oxygen available in zone I is insufficient to consume all CO,
Figure 9.
Schematic representation of the moving reaction front model. A) Pulsing CO over an initial oxygen covered catalyst bed; B) pulsing CO (excess) and O₂ alternately over an initial oxygen covered catalyst bed, left: after CO pulse, right, after O₂ pulse. The gray area represents oxygen covered platinum. The white area is either a clean platinum surface or platinum covered by CO. The numbers denote the cycle number. Initial condition is fully oxygen covered.

due to the larger size of the CO gas pulses. Since there is an adsorption/desorption process taking place for the CO traveling through the bed, the CO₂ produced in zone III will be produced later than the CO₂ produced in zone I, which can explain the double pulse response in Figure 5.

When the experiment as described above is performed with platinum precovered with¹⁸O₂ and the oxygen pulsing is then performed with¹⁸O₂, zone I will then consist of ¹⁸O covered platinum and zone III will consist of ¹⁸O covered platinum. This is consistent with the experiment shown in Figure 7, where first the isotopically mixed CO₂ is produced (zone I) and thereafter unlabeled C¹⁶O₂ only (zone III).

The same model can explain why CO₂ is formed during both the O₂ and CO pulses in the steady-state situation of pulsing O₂ and excess CO over platinum (Figure 4). In this case the platinum will be mainly CO covered, since this is available in excess. During an O₂ pulse this will logically produce CO₂ after this pulse the first section of the catalyst bed will remain oxygen covered and, therefore, produce CO₂ during the next CO pulse. This also explains why the CO exits the reactor before the CO does, as the first CO molecules entering the reactor will be converted to CO₂. The slower 'travelling' of the CO molecules cannot be explained by the adsorption/desorption process of the CO on the platinum alone, as this process would cause the pulse-response curve to mainly flatten out, and not cause the first molecules to exit the reactor at a later time.

To confirm the moving reaction front model, simulations were carried out. Due to the complexity of this modeling, the details are discussed elsewhere [10]. The
model used a very high CO adsorption rate compared to the diffusional transport of CO through the catalyst bed. As an example, one of the results of the numeric modeling is demonstrated in Figure 10. In this figure the result is shown for a CO pulse over a platinum surface with the surface coverage as shown in cycle 3b of Figure 9b. It should be noted that this analysis is rather qualitative than quantitative and that a large amount of different constants in the model will have to be determined independently before a ‘fit’ of the simulation to the experiments will be possible. It is, however, clear from this figure that qualitatively the moving reaction front model is quite able to describe double CO$_2$ pulse responses obtained during some measurements.

The CO-oxidation reaction at higher temperatures in the Multitrack system takes place most likely according to a moving reaction front type reaction model. This has some consequences for fast reactions investigated in this or a similar set-up, like a TAP apparatus. For example, when one gives a number of CO pulses over an oxygen covered catalyst, one then does not measure the reaction as a function of the surface coverage, what is the general assumption, but as a function of the location in the reactor.
Conclusions

- The CO oxidation takes place via the Langmuir-Hinshelwood model, with the following set of equations:

\[
\begin{align*}
\text{CO} & \xrightleftharpoons[k_2]{k_1} \text{CO}_{\text{ad}} \\
\text{O}_2 & \xrightarrow[k_2]{k_3} 2 \text{O}_{\text{ad}} \\
\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} & \xrightleftharpoons[k_4]{k_3} \text{CO}_{2\text{ad}} \\
\text{CO}_{2\text{ad}} & \xrightarrow[k_5]{k_6} \text{CO}_2
\end{align*}
\]

- The CO\textsubscript{2} is produced from adsorbed carbon monoxide and oxygen on the catalyst by an equilibrium reaction of which the forward and reverse occurring reactions are faster than the CO\textsubscript{2} desorption. This implies that the rate of desorption of CO\textsubscript{2} from the platinum surface should be taken into account as a separate step in the reaction mechanism.

- The local surface coverage of components on the catalyst can vary strongly, even in a small reactor. This type of behavior can be simulated according to a moving reaction front model.

- The moving reaction front model is able to describe the occurrence of double pulse responses observed experimentally.

References

7. Chapter 1 of this thesis.
10. Chapter 2 of this thesis.
Chapter 4

Transient Adsorption Measurements

Summary

Using pulse-response experiments the adsorption and desorption of a number of gases on silicalite-1 and ZSM-5 was measured in the temperature range between 300 and 773 K. By modeling these pulse-responses it is possible to simultaneously determine the equilibrium constant for adsorption and the diffusivity. The pulse-response measurements prove to be very reproducible and the calculated parameters are in good agreement with values reported in literature. A unique characteristic of this method is the possibility to accurately determine both the equilibrium constant for adsorption and the diffusivity from a single measurement. Furthermore, this macroscopic method is the first to yield diffusivity values which are in good agreement with those determined using microscopic methods, such as Pulse-Field-Gradient NMR.

A full and a simplified model are presented for the description of the transient adsorption behavior of gases on and into microporous materials. The full model describes the adsorption behavior, including the concentration profiles within the sorbent particles. For fast diffusing gases, it is shown that the simplified model yields the same information on the adsorption and diffusion behavior in far less computing time.
Transient Adsorption Measurements

Introduction

The usual procedure to determine gas-phase adsorption parameters of a sorbent material is by studying the rate of adsorption using gravimetric, volumetric or barometric techniques. By a gravimetric technique the mass changes of a sorbent sample are measured as a function of the sorbent gas partial pressure. Volumetric and barometric techniques measure the adsorbed amount of gas from the change in gas volume or pressure, respectively. The disadvantage of these methods is that they are time consuming, as it is necessary to reach adsorption equilibrium with the surrounding gas phase, which is often reached only after a prolonged time.

The diffusion coefficient in microporous materials can be determined by a number of different techniques. These methods are for example NMR relaxation, tracer desorption, chromatographic methods, measurement of diffusional fluxes through a membrane, and determination of the uptake rate in adsorption measurements. The disadvantage of all of those methods is that they are elaborate. Furthermore, these methods produce diffusion coefficients, which can differ over two orders in magnitude [1]. Especially the NMR techniques yield values for the diffusion coefficient that are usually up to an order of two higher than the values determined by other techniques, although the NMR techniques are the most direct method for determining a diffusion coefficient inside a microporous material. A satisfactory explanation for these differences is, however, not yet available.

An entirely different method for determining both the diffusion coefficient inside a porous particle and the adsorption behavior of that sorbent particle, is the application of a transient pulse-response technique. This can be carried out by pulsing a small amount of gas over the sorbent material and measuring the pulse response of the gas. By modeling these pulse responses, the rate constants of adsorption and desorption can be determined. In the modeling the absence of a steady-state situation is incorporated. The advantage of this transient method is that it is very fast and reproducible. The application of the Multitrack system in the determination of adsorption parameters is described in this chapter. Multitrack is an apparatus for performing transient measurements in the ultra-high vacuum (Knudsen) regime, using very small gas pulses. An advantage of operating in ultra-high vacuum is that external mass transfer limitations are completely absent. A limitation of this technique is that experiments can only be performed at low partial pressures of the gases used.

The objective of this study was to investigate the possibility of applying fast pulse-response experiments for the determination of rate constants for adsorption and desorption, as well as the determination of the diffusion coefficient inside a microporous material. This was accomplished by modeling the adsorption, desorption and diffusion behavior of adsorbing gases, using the pulse responses measured of non-adsorbing gases as a reference. This method was applied to the zeolites silicalite-1 and ZSM-5, with adsorbing gases methane, ethene, propane, n-butane, iso-butane, carbon dioxide, and xenon.
Experimental

An extensive description of the Multitrack system is available elsewhere [2]. Multitrack is inspired by the TAP system, developed by Gleaves [3], and can be described as follows. A small (7 mm internal diameter) reactor is located in an ultra-high vacuum system. This reactor contains the sorbent material. To the bottom of this reactor either small gas pulses ($10^9$-$10^{10}$ molecules) or a small gas stream (0-20 ml/min) can be fed. At the reactor exit at the top, the bulk of the gas is removed using a set of skimmers. A small amount of gas travels as a molecular beam to the analysis section, consisting of three mass spectrometers, which are placed in-line with the molecular beam. Each of these mass spectrometers is able to measure one of the components in the molecular beam with a maximum sampling frequency of 1 MHz.

The adsorption experiments were performed with silicalite-1 and ZSM-5 (Si/Al=130) zeolitic material, both having a very regular shape with crystal size of about 50 μm diameter and 100 μm length. A SEM micrograph of the silicalite-1 crystals used is given in Figure 1. The measurements with silicalite-1 were performed using calcined silicalite-1, not calcined (as synthesized) silicalite-1, and silicalite-1 (as synthesized) calcined in-situ in the Multitrack reactor. The reactor content consisted of about 200 mg of SiC (carborundum) at the bottom on the support grid of the reactor, in the middle about 200 mg of zeolite, and on top a second layer of about 300 mg of SiC, with a second stainless steel grid on top to prevent movement of the particles in the reactor. The resulting total bed height in the reactor was always kept in between 10 and 10.5 mm. Some experiments have been performed using only

![SEM micrograph of calcined silicalite-1 used for the adsorption experiments.](image)

Figure 1.
SEM micrograph of calcined silicalite-1 used for the adsorption experiments.
Transient Adsorption Measurements

13 mg of zeolite material. Since it is difficult to distribute such a small amount of material evenly over the reactor diameter, the (calcined) zeolite was diluted in 200 mg of uncalcined zeolite material of the same batch. The implications for the measurements performed with this reactor loading will be discussed later.

The temperature range for this study was from ambient temperature up to 773 K. The upper temperature for the adsorption experiments was set by the maximum allowable temperatures before thermal degradation of the zeolites can occur. The gas pulse size used was approximately $10^{17}$ molecules. The gases measured were neon and argon (non-adsorbing in this temperature range), and adsorbing gases, namely: methane, ethene, propane, n-butane, iso-butane, xenon, and carbon dioxide. The data-acquisition time of the measurement was set for each of the experiments to measure the entire pulse response, two seconds for pulse-responses of non-adsorbing components, and up to twenty seconds for pulse-responses of adsorbing components.

Modeling the pulse responses

When modeling gas pulse responses through a packed bed in Multitrack, one can assume that the transport occurs exclusively via Knudsen diffusion, provided the gas pulses are sufficiently small. It had been determined by performing experiments with different pulse sizes, that this assumption is valid for pulses smaller than $2 \times 10^{17}$ molecules. Since all experiments performed in this study used gas pulses of $10^{17}$ molecules or smaller, it is permitted to model the pulse responses using Knudsen diffusion only. Convection is not a relevant process in the Knudsen diffusion regime as the mean free path of the molecules is set by the reactor size and content and not by collisions between molecules. Equation 1 can be used to calculate the Knudsen diffusion coefficient.

$$D_{Kn} = \frac{\varepsilon_b}{\tau_b} \frac{2\bar{r}}{3} \sqrt{\frac{8RT}{\pi M}}$$  \hspace{1cm} (1)

with $D_{Kn}$ Knudsen diffusion coefficient, $\varepsilon_b$ bed porosity, $\bar{r}$ average interparticle distance, $\tau_b$ bed tortuosity, R gas constant, T temperature, and M gas molar mass. If the particles are assumed to be spherical, the average interparticle distance can $\bar{r}$ be calculated from the average particle radius $r_p$ using:

$$\bar{r} = \frac{2\varepsilon_b}{3(1 - \varepsilon_b)} r_p$$  \hspace{1cm} (2)

All parameters necessary to calculate the Knudsen diffusion coefficient can be easily determined experimentally, except for the tortuosity. Each of the other parameters
was, therefore, measured separately. The tortuosity can be obtained from a fitting procedure used in the modeling of the measured pulse responses.

Figure 2 shows a schematic representation of the contents of the Multitrack reactor. As can be seen the reactor can be divided into four zones. An empty space between the reactor bed and the gas pulsing valves, an inert SiC zone, the sorbent containing zone, and a second inert SiC zone. When modeling these zones, each zone has its own set of differential equations. As mass transport takes place by diffusion only, the following differential equation can be used for the gas transport through the reactor:

$$\varepsilon_s \frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial z^2}$$  \hspace{1cm} (3)

with $C_z$ concentration at axial position $z$, $D$ diffusion coefficient, $z$ axial position, and $t$ time.

Since no particles are present in the first empty zone in the reactor, the average characteristic distance in this zone is equal to the inner diameter of the reactor. Since this inner diameter, ranging from 2 mm at the bottom to 7 mm immediately under the catalyst bed, is much larger than the particle diameter in the other zones (50 and 230 $\mu$m), the diffusion coefficient in this zone is large compared to the diffusion coefficients in the other zones. It is, therefore, allowed to simplify the model by assuming that this zone is ideally mixed. The validity of this simplification is discussed in more detail by Zou et al.[4]. The concentration in this mixed zone will be set by the gas pulses entering and the flux going into the first SiC zone. The gas pulses given by the high speed gas pulsing valves have a width at half height of about 100 $\mu$s, the width of the pulse response at the reactor exit was in this study always at least 0.1 s at half height. If the modeling of the pulse responses is done with time steps larger than 100 $\mu$s, a very small step size when modeling such ‘wide’ pulse responses, the entering (primary) gas pulse can be seen as a Dirac pulse. Such a Dirac pulse is incorporated in the model by simply increasing the value of the concentration of the mixed volume with the gas pulse size, at the time the gas pulse is given. The differential equation describing the first mixed zone then becomes:

$$h_{eq} \frac{\partial C_m}{\partial t} = D \left. \frac{\partial C_z}{\partial z} \right|_{z=0}$$  \hspace{1cm} (4)
with \( C_m \) the concentration in the mixed volume, \( C_z \) the concentration in the filled reactor zone at position \( z \), and \( h_{eq} \) equivalent length (height) of the empty volume (calculated by dividing the volume of the zone by the reactor cross sectional area). This equation can be interpreted as the concentration of the gas in the empty mixed volume section decreasing by the amount of gas diffusion through the very first section of the packed bed. To fulfill the mass balance of the system the flux out of the empty volume should be equal to the flux into the packed bed.

The first of the SiC zones can be described by using differential equation 3. As an inlet condition the following equation was chosen:

\[
C_z|_{z=0} = f_c \cdot C_m
\]

with \( f_c \) introduced as a friction factor describing the influence of the steel grid supporting the bed. This friction factor is used as a fitting parameter. Although it might be more accurate to derive differential equations across the support grid, it was decided to use this simplification, because the parameters for the diffusion through the grid are unknown. These parameters include the diffusion length due the varying thickness of the woven material, and the available cross-sectional area for diffusion, because the open space in the grid will be partly unavailable for diffusion, due to the presence of SiC particles. The value of this friction factor was found to vary from 0.3 to 0.7. These values were seen as realistic, in view of the very steep concentration gradient at the start of the packed bed, and the lower available porosity for diffusion. The friction factor was introduced, as it proved to describe the measured inert pulse-responses better than in the absence of this parameter. As the aim of this study was to determine the adsorption parameters, the exact origin of the entrance resistance was not investigated. At the reactor exit, the concentration profile is generally very flat and the concentrations are extremely low. Therefore, there is no need for the introduction of a similar friction factor at the reactor exit, as this will not improve the model significantly.

The zone in the middle of the packed bed contains the sorbent material. Differential equation 3 has, therefore, to be extended with adsorption and desorption terms. In the modeling adsorption is assumed to occur at the outside of the zeolite particles (or at the end of the zeolite pores), followed by diffusion into the interior. For the assumption of a spherical particle, the differential equations are in this case:

\[
\varepsilon_b \frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial z^2} - k_a \cdot N_a \cdot C_z \cdot (1 - \theta_{zR}) + k_d \cdot N_d \cdot \theta_{zR}
\]

\[
\frac{\partial \theta_{zR}}{\partial t} = D_{pore} \left( \frac{\partial^2 \theta_{zR}}{\partial r^2} + \frac{2}{r} \frac{\partial \theta_{zR}}{\partial r} \right)
\]

with boundary conditions:
\[-D_{\text{pore}} \frac{3}{R_p} \frac{\partial \theta_{z,R}}{\partial r} = k_a C_z (1 - \theta_{z,R}) - k_d \theta_{z,R} \quad (8)\]
\[\frac{\partial \theta_{z,0}}{\partial r} = 0 \quad (9)\]

with $\theta_{z,r}$ the surface coverage at axial position $z$ and position $r$ relative to the particle center, $k_a$ the rate constant for adsorption, $k_d$ the rate constant for desorption, $N_t$ the total amount of sites for adsorption (adsorption capacity) per sorbent bed volume, and $D_{\text{pore}}$ the diffusion coefficient of the adsorbed phase in the zeolite pores. Equation 6 represents the gas phase between the particles with adsorption occurring on the outside of the zeolite pores and is identical to equation 3 with additional adsorption and desorption terms. Equation 7 describes the diffusion in the zeolite particles. Boundary condition 8 represents the adsorption and desorption of gas, which has to be equal to the amount of gas that diffuses from or to the outside of the zeolite pores. Using the simplification of spherical particles, equation 9 stands for the symmetry of the concentration profile at the particle center. In these equations it is assumed there is no interaction between the adsorbed species. The pore diffusion coefficient can be made a function of the zeolite occupancy, as is often done. In this study the introduction of such a function was not necessary, in view of the very low zeolite occupancies ($< 0.01$) throughout all experiments performed. The parameters $k_a$, $k_d$, $D_{\text{pore}}$, and $N_t$ are treated as fitting parameters in the modeling. The gas concentration at the start of the sorbent zone has to be equal to the concentration at the end of the first inert zone.

The third packed bed zone, also containing SiC, can again be described by differential equation 3. The concentration at the start of this zone is equal to the concentration at the end of the sorbent zone. The concentration at the end of the reactor is set to zero. This boundary condition is described in more detail by Zou et al. [4]. The effect of setting this boundary condition is that no gas leaving the reactor will re-enter the reactor. This is a realistic assumption, considering the low pressure in the main vacuum chamber (and, therefore, at the reactor exit), and the very large pumping capacity, maintaining the ultra-high vacuum. Consequences of setting this boundary condition are that numerically 'matter' disappears from the model, and that it is impossible to use the concentration at the reactor exit as the modeled pulse response. The effect of this boundary condition is solved by not using the concentration at the reactor exit, but the flux (the first derivative in the axial position). Since this flux is actually measured by the mass spectrometers in the Multitrack system, this mathematical problem is then solved.

The boundary conditions in time for all equations are that all gas and surface concentrations at the starting time (t=0) are set to zero. At the time the gas pulse to the system is given, this is simulated by increasing the concentration in the mixed volume by the gas pulse size divided by the volume of the pre-reactor volume instantaneously.
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Solving the differential equations

The differential equations are fitted to the experimental data using a FORTRAN 77 program. The procedure used for the modeling is described in the next subsection. The method used for solving differential equations and fitting the equations to the experimental data is described in detail by van der Linde et al. [5]. The differential equations were entered in the FORTRAN program. In this program the set of partial differential equations was discretized using the ‘numerical method of lines’ by the DSS/2 libraries to a set of coupled ordinary differential equations. These equations were integrated using the backward differential formulas method with the LSODES library. Both the DSS/2 and LSODES libraries are described by Schiesser [6]. The amount of gridpoints used for describing the reactor was 101, which were evenly distributed over the three packed bed zones according to the height of the three zones in the reactor. The parameters to be estimated, \( f_\nu \), \( \tau_\nu \), \( D_{\text{per}} \), \( k_\nu \), \( k_{\nu'} \), and \( N_\nu \) were fitted using the Levenberg-Marquardt method. Using this method the Sum of Squared Residuals (SSRes) (squared differences between measured and modeled values for each time-step of the pulse response) was minimized by changing the parameter values.

A scaling factor was applied to the calculated pulse response to make the measured and calculated pulse responses have an equal area under the pulse response curve. The advantage of applying this scaling factor is, that it is not necessary to calibrate the mass spectrometers for the sensitivity of each component measured. This usage of a scaling factor instead of using calibration factors, of course, is only valid if one is sure that the entire gas pulse given has left the reactor exit, and no reaction has taken place. This was verified by using a measuring time that always exceeded the visible pulse response. A second check was done by repeatedly measuring the same pulse response. If a part of the gas pulse given would remain on the sorbent material, one would expect the consecutive gas pulses to have different pulse responses, since “missing” gas should be present on the sorbent material, and increasing the sorbent loading would result in changing pulse responses.

Modeling procedure

For each of the experimental series, the modeling of the actually measured pulse responses was separated into two parts: modeling of the diffusion through the reactor, followed by the determination of the adsorption parameters. All parameters, except for the 6 fitting parameters, \( f_\nu \), \( \tau_\nu \), \( D_{\text{per}} \), \( k_\nu \), \( k_{\nu'} \), and \( N_\nu \), were entered into the fitting program input file for the applied experimental conditions.

The two transport parameters, the friction-factor and the tortuosity, were determined by measuring the pulse-responses for a non-adsorbing gas. This was performed with neon and argon over the entire temperature range of the adsorption
experiments. The adsorption and desorption rate constant were set to zero and the friction-factor and tortuosity were fitted. The friction-factor was then fixed at the average value for neon and argon, and the fitting procedure was repeated per gas for the tortuosity only. The resulting two values were again averaged, and the tortuosity was then fixed at this average value. For all adsorption experiments with the same reactor content these two fixed parameters were used. These averaged friction-factor and tortuosity provided a good description of the diffusion through the reactor bed. Figure 3 demonstrates a predicted pulse response using these values, together with the corresponding measurement.

The adsorption capacities of the zeolites used are in the order of 1.4-1.5 mmol/g zeolite (propane) [7]. Therefore, the amount of gas pulsed is far below the adsorption capacity. This makes it difficult to determine the adsorption capacity \( N_0 \) from the pulse responses. It was decided to set \( N_0 \) at a fixed value for all experiments with the same zeolite loading in the reactor. This was done by fitting simultaneously three pulse responses for the same component at different temperatures. The temperatures were chosen in the range, where the adsorption was strong, moderate, and weak. These three pulse responses used a single \( N_0 \) parameter as fitting parameter, together with for each of the pulse-responses a \( k_s \) and \( k_p \) value. The error in this value of \( N_0 \), supplied by the fitting program, proved to be very large, and the correlation between \( N_0 \) and the rate constants was also strong. As a varying \( N_0 \) will directly influence the values of the \( k \)-parameters and, therefore, will make it impossible to compare these values, the \( N_0 \) parameter was then fixed at this value. After this procedure both tortuosity and the number of adsorption sites parameter

![Figure 3](image_url)

*Figure 3.*
Measured (gray) and modeled (black) pulse responses for an Argon pulse through a bed of in-situ calcined silicalite-1 (473 K).
Transient Adsorption Measurements

were kept constant for the complete experimental series with the same reactor content. The rate constants for adsorption and desorption were then determined by fitting the pulse responses measured at other temperatures and with other gases. Although the adsorption capacity is dependent on the adsorbing gas and on temperature, it was decided not to compensate for these influences, because they will only change the adsorption capacity by up to a factor of two, which is small compared to the fitting error in $N_c$.

Results

Table 1 contains the values of the tortuosity and friction factor as determined using non-adsorbing gas pulses for each of the six experimental series. The numbers of adsorption sites determined by fitting adsorbing gas pulse-responses are also given in this table. The experiments with the uncalcined silicalite showed no measurable amount of adsorption. By using the fitted values of the friction factor and the tortuosity, it should be noted that these values might deviate from the actual values, as these values were fitted to optimally describe the diffusional behavior through the reactor. If any of the parameters like particle size, porosity etc. deviate from the values entered into the model, this will result in the fitting routines changing the fit-parameters to achieve a best fit of the experimental data. Since the objective is, however, to determine the adsorption parameters, an accurate representation of the transport parameters of the gas through the bed is less important, as long as the model matches the actual gas pulse in the best possible manner. The measured and modeled pulse-responses for a non-adsorbing argon pulse with these averaged friction factor and tortuosity are shown in Figure 3. In this figure it can be seen that the model describes the measurement well.

<table>
<thead>
<tr>
<th>Amount</th>
<th>$\tau$</th>
<th>$f_c$</th>
<th>$N_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg</td>
<td>(-)</td>
<td>(-)</td>
<td>(mol/m$^3$)bed)</td>
</tr>
<tr>
<td>Silicalite-1 (calcined)</td>
<td>209</td>
<td>8.75</td>
<td>0.395</td>
</tr>
<tr>
<td>Silicalite-1 (calcined)</td>
<td>202</td>
<td>8.10</td>
<td>0.652</td>
</tr>
<tr>
<td>Silicalite-1 (calcined)</td>
<td>13.2</td>
<td>5.45</td>
<td>0.447</td>
</tr>
<tr>
<td>Uncalcined silicalite-1</td>
<td>244</td>
<td>4.79</td>
<td>0.395</td>
</tr>
<tr>
<td>In-situ calcined silicalite-1</td>
<td>244</td>
<td>4.28</td>
<td>0.290</td>
</tr>
<tr>
<td>ZSM-5(calcined)</td>
<td>190</td>
<td>4.19</td>
<td>0.403</td>
</tr>
</tbody>
</table>

*: weight before calcination
Figure 4 shows the pulse-responses of some experiments at different temperatures, in which n-butane is pulsed over in-situ calcined silicalite-1, together with the results for the corresponding fits. As can be seen, the model describes the pulse responses very accurately. When describing adsorption, one commonly uses an equilibrium constant for adsorption [8]. This constant corresponds to the adsorbed concentration divided by the gas concentration at equilibrium, i.e., equal rates of adsorption and desorption. Hence, it is easily seen that this equilibrium constant corresponds to the rate constant of adsorption divided by the rate constant of desorption:

\[ K_{eq} = \frac{k_a}{k_d} \]  \hspace{1cm} (10)

In Figure 5 van 't Hoff- and Arrhenius-plots are given for the diffusion coefficients, equilibrium constants for adsorption, and the desorption rate constants determined in a single experimental series for the adsorption of n-butane on silicalite-1. Plots are given for \( K_{eq} \) and \( k_d \) instead of \( k_a \) and \( k_d' \), as there is a lot of scatter in both the values of \( k_a \) and \( K_{eq} \). However, when the equilibrium constant for adsorption is calculated from these parameters, the errors in the parameters compensate for each other. The plot of \( K_{eq} \) therefore, shows an accurately determined rate constant for adsorption, whereas the plot of \( k_d' \) (a plot of \( k_a \) could

Figure 4.
Measured (gray) and modeled pulse responses (black) for n-butane pulses over a bed of in-situ calcined silicalite-1 at 473, 527, and 623 K.
also be used), should be seen as an indication for the rate at which the occupancy at the outside of the sorbent particle progresses to the equilibrium composition.

Figure 5.
Van 't Hoff- and Arrhenius-plots for the equilibrium constant for adsorption (A), pore diffusion coefficient (B), and rate constant of desorption (C) of n-butane on (ex-situ) calcined silicalite-1.
Figure 5 shows large values for $k_\mu$, indicating that the outside of the sorbent particle reaches the equilibrium composition in a very short time. A problem in the modeling is its sensitivity to the starting values used for the fitting procedure. If the starting values for the iteration process differ over approximately one order in magnitude from the ultimately obtained best fit, the fitting procedure will most of the times not be successful. As one attempt for a fit will usually take over 1 hour on a Pentium Pro 200 computer, it was decided to first fit the data with a simplified model to get good starting estimates. This model is described in the next paragraph.

**Model simplification**

To simplify the adsorption model, it is necessary to reduce the number of differential equations and fitted parameters as much as possible. The simplified model chosen to fit the measurements is based on the two following assumptions:

- The outside of the particle (the end of the zeolite pores) is in equilibrium with the gas phase surrounding the particle;
- The radial concentration profile into the particles decreases linearly.

The first assumption reduces the number of parameters by one, since the absolute rates for adsorption and desorption have no longer to be used. Instead, only the equilibrium constant for adsorption can be used. Considering the relatively large values of both $k_\nu$ and $k_\sigma$, this assumption is realistic. Using Langmuir's theory for adsorption, the equilibrium zeolite occupancy on the outside of the particle can now be calculated from:

$$\theta = \frac{K_{eq} \cdot C}{1 + K_{eq} \cdot C}$$

(11)

The second assumption drastically reduces the number of differential equations to be solved, as for each axial position now only one occupancy is used, the occupancy in the center of the particle. The full model uses 26 gridpoints into the particles, the simplification, therefore, reduces the number of differential equations to be solved by a factor of 13.

The simplified model with a uniform concentration profile across the sorbent particles leads to the following differential equations instead of equations 6 to 9 (for the assumption of a spherical particle):

$$\varepsilon_b \frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial z^2} - N_s \cdot K_{eq} \cdot D_{pore} \cdot \frac{3}{R_p^2} \cdot C_z + N_s \cdot D_{pore} \cdot \frac{3}{R_p^2} \cdot \theta_z$$

(12)

$$\frac{\partial \theta_z}{\partial t} = K_{eq} \cdot D_{pore} \cdot \frac{3}{R_p^2} \cdot C_z - D_{pore} \cdot \frac{3}{R_p^2} \cdot \theta_z$$

(13)
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Complete model

\[ K_{\text{eq}} = 0.00262 \]

\[ D_{\text{pore}} = 1.52 \times 10^{-9} \text{ m}^2/\text{s} \]

Simplified model

\[ K_{\text{eq}} = 0.00286 \]

\[ D_{\text{pore}} = 1.88 \times 10^{-9} \text{ m}^2/\text{s} \]

Figure 6.
Comparison between simplified and complete model for the adsorption of n-butane on silicalite-1 (513 K).

When a comparison is made between this simplified model, and the Linear-Driving-Force (LDF) model, first introduced by Glueckauf [9], it can be seen that our simplified model is a Multitrack-specific adaptation of this widely used LDF-model.

For one of the n-butane adsorption experiments in Figure 6 the measurement is shown, together with the results of the fits of both the complete and the simplified model.

Figure 7.
Comparison between simplified and complete model for the adsorption of iso-butane on silicalite-1 (415 K).
model. As can be seen both fits differ very little. By comparing the sums of squared residuals (SSRes) of both models, it is clear that the complete model does produce a better fit, since the SSRes of the complete model usually is about 10% lower. This allows for the possibility to use the simplified model for quick estimations of both $K_{eq}$ and $D_{per}$. The only exception in the measurements performed is the iso-butane adsorption. For iso-butane the simplified model is not able to produce adequate fits of the measured pulse responses, which is caused by the significantly lower pore diffusion coefficient of iso-butane. This is clearly visible in Figure 7, where the best fitted lines are shown for both models. Therefore, the use of the simplified model for slow-diffusing gases is not allowed, whereas the model produces a good description for the fast diffusing gases. This can easily be explained by the fact that in case of a slow diffusion process the simplification of a linear concentration profile across the sorbent particle is no longer valid.

Heat of adsorption

Figure 8 shows the van 't Hoff-plots of these equilibrium constants for all experiments performed with the in-situ calcined silicalite-1. The activation energy found in such a van 't Hoff-plot is defined as the 'heat of adsorption'. A number of different definitions are used for 'the' heat of adsorption. The definition as used in this chapter for the 'heat of adsorption' is 'the isothermal heat of adsorption at zero zeolite occupation', given by the slope of the equilibrium constant for adsorption. The heat of adsorption is a so-called 'isothermal heat of adsorption', since the heat effect due to adsorption can be neglected because of the very small gas pulses (heat effect < 0.01 J/pulse). The heat of adsorption is defined at zero zeolite occupation

![Figure 8](image_url)

*Figure 8.* Van 't Hoff-plot of the equilibrium constant for adsorption of measurements on in-situ calcined silicalite-1, constructed by calculating the equilibrium constant from the rate constants for adsorption and desorption.
Transient Adsorption Measurements

because the occupation will remain smaller than 0.01, as can be calculated from equation 11. The activation energies calculated from all constructed van 't Hoff plots as shown in Figure 8 are given in Table 2, together with the $K_{eq}^0$ value from the fitted line (pre-exponential factor), as given by equation 14.

$$K_{eq} = K_{eq}^0 \cdot e^{-\frac{E_{ads}}{RT}}$$

(14)

with $E_{ads}$ the heat of adsorption. As no measurable amount of adsorption was found to take place on the uncalcined silicalite-1, the results of these experiments are omitted from this table. The absolute values of the rate constants $k_s$ and $k_d$ are also omitted from this table, since the values varied significantly, even in a single experimental series. The only useful information these fits produced is that the values are usually very large (>10<sup>6</sup>), indicating that the outside concentration on the particle is close to equilibrium, as was assumed in the simplified model.

Although it is possible to calculate the adsorption-entropy ($\Delta S$) from the $K_{eq}^0$ values in Table 2 using equation 15, these values are not given, since the errors in these values are large. This large error is the result of a small error in the slope of the line in the van 't Hoff plot (in the adsorption enthalpy) causing a large deviation in

Table 2.
Heat of adsorption for all adsorption experiments, together with $K_{eq}^0$ values from the van 't Hoff-plots.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sorbent</th>
<th>$K_{eq}^0$ (10&lt;sup&gt;6&lt;/sup&gt; m&lt;sup&gt;2&lt;/sup&gt;/mol)</th>
<th>Heat of adsorption (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Silicalite-1'</td>
<td>4160</td>
<td>18.1</td>
</tr>
<tr>
<td>Ethene</td>
<td>Silicalite-1'</td>
<td>416</td>
<td>32.7</td>
</tr>
<tr>
<td>Propane</td>
<td>Silicalite-1</td>
<td>321</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1''</td>
<td>155</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>793</td>
<td>35.4</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Silicalite-1</td>
<td>108</td>
<td>43.2</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1''</td>
<td>17.0</td>
<td>48.9</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>397</td>
<td>42.5</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>Silicalite-1</td>
<td>61.1</td>
<td>43.8</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Silicalite-1''</td>
<td>1242</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>4148</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>Na-ZSM-5 (130)</td>
<td>50.0</td>
<td>40.4</td>
</tr>
<tr>
<td>Xenon</td>
<td>Silicalite-1</td>
<td>803</td>
<td>25.5</td>
</tr>
</tbody>
</table>

*: in-situ calcined

**: experiment with 13 mg sample

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the intercept of the line (the adsorption entropy). However, the order of magnitude of an entropy calculated in this manner is correct (ca. 100 J/mol, reported values (e.g. [12]) vary from 40-80 J/mol depending on the study and the adsorbing gas).

\[ \Delta S_{\text{ads}}^0 = -R \cdot \ln(K^0_{\text{eq}}) \]  

(15)

**Diffusion coefficient in zeolite pores**

Figure 9 shows the Arrhenius-plot constructed for the diffusion coefficient for all experiments performed using the *in-situ* calcined silicalite-1. The following equation is fitted to the data in the constructed Arrhenius-plots:

\[ D_{\text{pore}} = D_{\text{pore}}^0 \cdot e^{\frac{-E_{\text{diff}}}{R \cdot T}} \]  

(16)

with \( D_{\text{pore}}^0 \) the pre-exponential factor for the pore diffusion coefficient and \( E_{\text{diff}} \) the activation energy for pore diffusion. The values for the activation energies for diffusion and the corresponding pre-exponential factors obtained by the fitting of equation 16 to the experimental data are given in Table 3.

![Arrhenius-plot](image)

**Figure 9.**

Arrhenius-plot of the pore diffusion coefficient of measurements on *in-situ* calcined silicalite-1.
Transient Adsorption Measurements

Table 3.
Activation energies for diffusion and corresponding pre-exponential factors.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sorbent</th>
<th>$D_{pre}^0$  (10^-6 m^2/s)</th>
<th>$E_{diff}$  (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Silicalite-1</td>
<td>4.03</td>
<td>3.1</td>
</tr>
<tr>
<td>Ethene</td>
<td>Silicalite-1</td>
<td>9.72</td>
<td>7.5</td>
</tr>
<tr>
<td>Propane</td>
<td>Silicalite-1</td>
<td>4.87</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1''</td>
<td>30.7</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>8.07</td>
<td>8.7</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Silicalite-1</td>
<td>9.01</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1''</td>
<td>13.1</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>4.56</td>
<td>7.4</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>Silicalite-1</td>
<td>61.1</td>
<td>28.9</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Silicalite-1''</td>
<td>531</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Silicalite-1'</td>
<td>285</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>Na-ZSM-5 (130)</td>
<td>458</td>
<td>21.8</td>
</tr>
<tr>
<td>Xenon</td>
<td>Silicalite-1</td>
<td>228</td>
<td>14.4</td>
</tr>
</tbody>
</table>

*: in-situ calcined
**: experiment with 13 mg sample

Discussion

Validity of the experiments and modeling

*Diffusional transport parameters*

Before the validity of the activation energies and heats of adsorption can be discussed, the modeling procedure should be evaluated first. If the values of the tortuosity and friction factor for the same silicalite content in the reactor, before and after calcination, are compared, it can be seen that these are not the same (Table 1). Since the calcination procedure should only influence the inside of the zeolite and not the diffusion through the reactor bed, one would have expected that these values should be equal. The pulse responses for a non-adsorbing argon pulse under the same conditions with this zeolite, before and after calcination, are shown in Figure 10. In this figure it can be seen that there is no significant difference between these pulse responses. Both sets of tortuosity in combination with a friction factor ($f_t$) are able to describe these pulse responses. This can be explained by the pulse broadening effect of a higher tortuosity in case of the uncalcined silicalite is compensated by the higher friction factor, causing a narrower pulse response. This is in agreement with the correlation coefficients obtained during the fitting of these parameters. When the tortuosity and friction factor are fitted to a data set, correlation coefficients between these parameters vary from 0.96 to 0.98, indicating a strong interaction between these parameters. The exact average values of these parameters for each of the reactor
Figure 10.
Pulse responses of an argon pulse over the same bed of silicalite-1 in reactor (423 K). Pulses shown are the pulse response before and after the in-situ calcination procedure.

Figure 11.
Pulse responses of a propane pulse over the same bed of silicalite-1 in reactor (423 K). Pulses shown are the pulse response before and after the in-situ calcination procedure.
Transient Adsorption Measurements

Adsorption in zeolite pores

As shown in Table 1, the number of adsorption sites found did not vary much from the starting value of 3500 mol/m³ of the fitting procedure. This can be explained by the insensitivity of the model for the adsorbed amount of gas as a result of the very large excess of available adsorption sites compared to the amount of gas pulsed (1000 fold excess). This large excess of adsorption sites resulted in the adsorbed molecules having no influence on each other and always having free adsorption sites available. This is in agreement with the very large error in the number of sites parameter as given by the fitting program (in the order of 200 % of the parameter). This inconvenience leads to an inaccurate determination of the amount of adsorption sites. The apparently large amount of available adsorption sites does, however, indicate that the entire zeolite particle is used for the adsorption process.

A check was made to ensure the adsorption measured was indeed taking place in the pores of the zeolite, and that the better modeling of gradients into the particle was only caused by the introduction of an extra fitting parameter. This was done by pulsing the adsorbing gas over the uncalcined zeolite. In Figure 11 the pulse responses of propane over calcined and uncalcined silicalite are shown. It can clearly be seen that the pulse response over the calcined silicalite is much broader obviously due to adsorption. If adsorption were to occur predominately on the outside of the silicalite particles, on the silicon carbide filler, or on the reactor wall, the pulse response of propane over uncalcined silicalite should have been broader. This pulse response, however, can be modeled adequately by neglecting adsorption.

In the experiments with a very small amount of calcined silicalite-1 (13 mg) usage was made of the absence of adsorption on uncalcined silicalite. Because it is virtually impossible to create an even distribution of 13 mg in such a ‘large’ reactor, as used in Multititrack, it was decided to dilute this small amount of silicalite by pre-mixing it with 200 mg of uncalcined silicalite. This dilution allows for the opportunity to study adsorption on a small zeolite sample, provided that the temperature is kept low enough during the adsorption experiments to prevent calcination of the uncalcined zeolite. The advantage of performing experiments with such a small sample is that the influence of the diffusion into the particle will be stronger, as a greater part of the particle has to be utilized for a same total amount of adsorbed gas. Furthermore, the use of a small sample allows for the possibility to perform measurements at lower temperatures. This is the case, as the temperature range for the experiments is not only set by the hardware of the system (allowable temperatures of both Multititrack and sorbent material), but also by the value of $K_a^1N$. If this value is too low, no measurable adsorption is visible, if it is too high, the pulse response will be too broad to measure and model accurately. Since $K_a^1$ cannot be controlled, the only way of influencing the possible temperature range for the measurements, is by choosing $N_1$ by adapting the sample size.
Heats of adsorption

In Table 4 the reported heats of adsorption of some of the components measured are given. When the values calculated from the present measurements are compared to the reported values, it can be seen that they are in good agreement. Furthermore, when the values of the duplo experiments of carbon dioxide, propane and butane are compared, it can be seen that the variations are very small. If one looks at the Van 't Hoff plot in Figure 5, it can also be seen that almost all points are very close to the line of the best fit. This was not only the case for this Van 't Hoff plot shown, but for all constructed Van 't Hoff plots for the heats of adsorption. Only the data-points at the highest and lowest temperatures deviate somewhat. At those temperatures the adsorption is either very small or very large, respectively, and small variations in the adsorption equilibrium constant do not result in large changes in the pulse response. This is in agreement with the errors in the parameters as they are calculated by the modeling program. The relative errors in the estimated parameters are typically smaller than 5% in the middle of the temperature range and up to 25% at the lower and upper limit of the measurement range. Furthermore, at conditions where almost no measurable adsorption occurred, the equilibrium constants for adsorption are too high in comparison to the fitted lines. This deviation is caused by a small imperfection in the Multitrack system. If the flux into the analysis chamber is large (i.e. for narrow pulse responses), the removal of gases by the vacuum pumps cannot keep up with the amount of gas entering, resulting to some extent of tailing of the measured pulse-response. When a non-adsorbing gas is measured and subsequently modeled, this results in a less than perfect fit, as the model does not

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sorbent</th>
<th>This study</th>
<th>Literature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
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<td>18.6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.4</td>
<td>11</td>
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<td>12</td>
<td></td>
</tr>
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<td>20.5</td>
<td>13</td>
<td></td>
</tr>
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<td>Silicalite-1</td>
<td>32.7</td>
<td>26.5</td>
<td>11</td>
</tr>
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<td>Silicalite-1</td>
<td>35.4-36.5</td>
<td>37.8</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40.5</td>
<td>13</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Silicalite-1</td>
<td>42.5-48.9</td>
<td>49.4</td>
<td>13</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>Silicalite-1</td>
<td>43.8</td>
<td>48.5</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42</td>
<td>15</td>
</tr>
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<td>Silicalite-1</td>
<td>22.6-24.1</td>
<td>24.0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21.7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24.6</td>
<td>12</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Na-ZSM-5 (Si/Al=30)</td>
<td>40.4</td>
<td>42.0</td>
<td>11</td>
</tr>
</tbody>
</table>
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compensate for this phenomenon. If adsorption is modeled, the model is able to
describe the small amount of tailing by adding a small amount of extra adsorption.
As a consequence, all $K_q$-values in the constructed Arrhenius-plots have a lower
limit value of approximately $\ln(K_q) = -7.5$. Although it is possible to extend the model
to include this system imperfection, this was not done, as this would complicate the
modeling even more, and possibly have a negative influence on the error in the fitted
parameters. This error was taken into account when fitting lines through the points
in the Arrhenius-plots, by not using the clearly deviating points at the higher
temperatures. To facilitate the assessment of the results no data have been selectively
left out in the figures presented. The figures, therefore, include all experiments,
including the ones that were not used for fitting the lines in Arrhenius-plots.

Diffusion in zeolite pores

In Figure 9 it can be seen that the diffusion coefficients found at higher
temperatures deviate from the trends visible at lower temperatures. An explanation
for this observation can be found, because at high temperatures a higher amount of
adsorption is calculated by the model due to a system imperfection, as is discussed
above. As a result, any parameter relating to the adsorbed phase will be inaccurate,
since the model overestimates the adsorbed amount of gas. Therefore, it was decided
that, if in the Arrhenius-plots for the equilibrium constant for adsorption data points
were not used for the fitting of the activation energy due to the adsorption
overestimate, the corresponding measurements were also excluded in the fitting of the
activation energy for the pore diffusion coefficient.

In Figure 12 a summary is given for reported diffusivities of n-butane in
silicalite, together with the values obtained in this study. In this figure, it is clearly
visible that there is a large discrepancy between the reported values. Microscopic
methods, such as Pulse-Field-Gradient NMR (PFG-NMR) and Quasi Elastic Neutron
Scattering (QENS), generally yield the highest diffusivity values, with the lowest
activation energies for diffusion, whereas macroscopic methods, such as membrane
methods (MBR), chromatographic pulse methods (CPC), and frequency response
methods (FR), produce the lowest diffusivities with the highest activation energies
for diffusion. The cause of these differences is a subject of discussion in literature
[1,16]. Suggestions have been made that the lower diffusivities of the macroscopic
methods can be attributed to external diffusion limitations, influences of the carrier
gas in use, or imperfections of the zeolite crystals. The microscopic methods would
not have any of these problems, since the diffusion of molecules is measured while
they already are inside the zeolite crystal. Multitrack adsorption measurements
should also be grouped among the macroscopic methods, as the entire diffusion
process is examined from the gas phase into the zeolite crystals. Yet, quite
surprisingly, in Figure 12 it can be seen that the Multitrack diffusivities are in good
agreement with diffusivities obtained using microscopic methods, both in the
absolute value of the diffusion coefficient and in its temperature dependence. In
Figure 12.
Reported diffusivities of n-butane in silicalite-1 determined using different methods and diffusivities determined in this study. (◊: this method; - [18], ● [15]: CPC; □ [19], ○ [20], x [21]: single crystal membrane; + [22]: membrane; ▲ [23]; Δ [24]: frequency response; ■ [25]: PFG-NMR; * [26]: QENS; line: trend demonstrated by NMR diffusivities and Multitrack diffusivities).

Table 5 a comparison is made between activation energies for diffusion as calculated from the present experiments, together with those reported in literature for microscopic methods. As can be seen in this table, the activation energies for diffusion in the zeolite pores as determined by the present method agree well with the values reported in literature. The high diffusivity values of the measurements with a zeolite membrane at high temperatures is accounted by the author to the existence of a different diffusing regime at high temperatures [22].

Table 5.
Comparison between activation energies for diffusion found in literature determined using microscopic methods and calculated activation energies for diffusion (kJ/mol).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sorbent</th>
<th>Literature</th>
<th>Reference</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Silicalite-1</td>
<td>4.0</td>
<td>17</td>
<td>3.1</td>
</tr>
<tr>
<td>Propane</td>
<td>Silicalite-1</td>
<td>6.7-21</td>
<td>17</td>
<td>7.2-10.5</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Silicalite-1</td>
<td>8.1-13.7</td>
<td>17</td>
<td>7.3-8.2</td>
</tr>
</tbody>
</table>
Transient Adsorption Measurements

An explanation for the agreement between Multitrack and microscopic diffusivities can be found in the fact that both measure the actual unhindered diffusion of molecules inside the zeolite crystals. Since no carrier gas is used in Multitrack experiments and external diffusion limitations are by definition not possible in the Knudsen diffusion regime, the existence of these influences in other macroscopic techniques is most likely the cause for the lower diffusivities found. Imperfections in the crystals in macroscopic measurements can be ruled out as a possible cause for lower diffusivities, as in this study also imperfect, twinned crystals were used for the measurements, as is visible in Figure 1. Therefore, it can be concluded that Multitrack is an excellent method for the determination of the intrinsic diffusion properties of gases in zeolites.

Rate constants for adsorption and desorption

The modeling used for the description of the pulse responses produces the two parameters $k_a$ and $k_d$. The absolute values of these parameters were not used in this study to obtain an additional amount of extra information on the adsorption-desorption process. For example, the rate constant for adsorption could produce a sticking coefficient for adsorption, if the absolute rate of adsorption of this rate constant is related to the amount of collisions between gas molecules and sorbent calculated using the kinetic gas theory. The absolute rate constant for desorption can be used as an alternative in the determination of the heat of adsorption by using the temperature dependence of this parameter. A problem is, however, that the model used is very insensitive to these parameters, as can be seen in the scattering of the measured points in Figure 5 for the rate constant for desorption. This large amount of scattering causes lines fitted through this cloud of data-points to easily have incorrect slopes. For example, if the rate of desorption in Figure 5 were to be used for the determination of the heat of adsorption for n-butane, a value of 29 kJ/mol would be found, while this value should have been close to the heat of adsorption (43 kJ/mol). The only solution to this problem would be to increase the number of measurements significantly and thus remove most of the effects of the error in the individual data points. This is, however, beyond the scope of this study to demonstrate the possibilities of applying a fast pulse-response technique in the determination of adsorption parameters.

The order of magnitude obtained for the rate constant for adsorption can be checked. Using the kinetic gas theory it is possible to calculate the number of collisions between gas molecules and a surface [17]. Especially at low occupancies each collision will result in an adsorbing molecule (i.e. sticking coefficient equals 1). If one assumes all adsorption occurs on the outside of the zeolite particles, after which the diffusion inwards occurs, the theoretical rate of adsorption $r_a$ can then be calculated from equation 17:
\[ r_s = C \cdot \sqrt{\frac{R \cdot T}{2\pi \cdot M}} \cdot \frac{5}{2 \cdot R_p} \cdot (1 - \varepsilon_b) \] (17)

When this adsorption rate is compared to the rate of adsorption in equations 6 and 8, it can be seen that the rate constant for adsorption, as used in the presented model, should according to the kinetic gas theory [17] be equal to:

\[ k_a = \frac{1}{N_s} \cdot \sqrt{\frac{R \cdot T}{2\pi \cdot M}} \cdot \frac{5}{2 \cdot R_p} \cdot (1 - \varepsilon_b) \] (18)

When the values for the rate constant for adsorption calculated using this equation are compared to the values from the model fitted to the experiments, these values are within the cloud of data points from the measurements. This indicates the calculated values are realistic. The only exception is in this case again iso-butane, for which the modeled values for the rate constant for adsorption are about a factor of ten lower. A possible explanation for this behavior is that the sticking-coefficient for iso-butane is low. A possible explanation for a lower sticking coefficient might be a kind of steric hindrance in the adsorption of iso-butane.

Conclusions

A new procedure has been found to determine the dynamic adsorption behavior of gases on zeolites using fast transient pulse-response measurements in ultra-high vacuum. The measurement of the adsorption behavior using pulse-response experiments produces adsorption parameters in a short timeframe and in good agreement with values reported in literature. The parameters that can accurately be determined are the equilibrium constant for adsorption and the pore diffusion coefficient. For the number of adsorption sites and the absolute rate constants for adsorption and desorption approximate values can be found. The range in which the pulse response experiments can be carried out to determine the mentioned parameters is limited by the equilibrium constant for adsorption multiplied by the number of adsorption sites per reactor volume. If this factor is in between 1 and 100 successful adsorption measurements can be carried out.

The Multitrack method for the determination of the diffusivity of gases in macroporous materials is the first macroscopic method to yield diffusivity values in good agreement with those determined using microscopic methods, such as Pulse-Field-Gradient NMR. An explanation for lower diffusivity values obtained using other macroscopic methods can be found in the influence of a carrier gas on the diffusion or the existence of external transport limitations.

When the adsorption behavior of fast diffusing compounds in microporous materials is modeled, it is often not necessary to calculate the concentration gradients.
in the particles. This possibility gives the opportunity for the use of a simplified model for describing transient pulse-response adsorption experiments. This results in calculated parameters very close to those from calculations using a complete model in less than thirty times the computing time necessary.

### Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>gas concentration</td>
<td>mol/m³</td>
</tr>
<tr>
<td>C_m</td>
<td>gas concentration in pre-bed empty volume</td>
<td>mol/m³</td>
</tr>
<tr>
<td>C_z</td>
<td>gas concentration at axial position z</td>
<td>mol/m³</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>D_Kn</td>
<td>Knudsen diffusion coefficient</td>
<td>m²/s</td>
</tr>
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<td>diffusion coefficient in zeolite pore</td>
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<td>equivalent height of empty pre-bed volume</td>
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</tr>
<tr>
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<td>rate constant for adsorption</td>
<td>m³/mol/s</td>
</tr>
<tr>
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<td>rate constant for desorption</td>
<td>1/s</td>
</tr>
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</tr>
<tr>
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<td>m³/mol</td>
</tr>
<tr>
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<td>diffusion length</td>
<td>m</td>
</tr>
<tr>
<td>N_s</td>
<td>number of adsorption sites</td>
<td>mol/m³_bed</td>
</tr>
<tr>
<td>M</td>
<td>molecular mass of molecule</td>
<td>kg/mol</td>
</tr>
<tr>
<td>\bar{r}</td>
<td>average interparticle distance</td>
<td>m</td>
</tr>
<tr>
<td>r_s</td>
<td>rate of adsorption</td>
<td>mol/m³/s</td>
</tr>
<tr>
<td>r_p</td>
<td>average particle size (radius)</td>
<td>m</td>
</tr>
<tr>
<td>R</td>
<td>gas constant = 8.314</td>
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<tr>
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<td>particle radius</td>
<td>m</td>
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<tr>
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<td>time</td>
<td>s</td>
</tr>
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<td>t_diff</td>
<td>characteristic time for diffusion</td>
<td>s</td>
</tr>
<tr>
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<td>temperature</td>
<td>K</td>
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<tr>
<td>z</td>
<td>axial position</td>
<td>m</td>
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<tr>
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<td>diffusion length for diffusion in zeolite pore</td>
<td>m³/m³_bed</td>
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<td>catalyst bed porosity</td>
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<td>adsorbate occupancy</td>
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<td>adsorbate occupancy at axial position z</td>
<td>sites_occupied/sites_tot</td>
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<td>x</td>
<td>adsorbate occupancy at axial pos. z and radial pos. r</td>
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<tr>
<td>\tau_b</td>
<td>catalyst bed tortuosity</td>
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References

2. Chapter 1 of this thesis.
Chapter 5

Propene Oxide:
Processes and Possibilities

Summary

This chapter discusses the two processes currently in use for the production of propene oxide, the chlorohydrin process and de hydroperoxide process, together with new propene oxide production processes under development. Both currently applied processes have disadvantages. The chlorohydrin process has the environmental disadvantage of producing large amounts of waste, whereas the hydroperoxide process has the main disadvantage of producing a co-product in equimolar amounts.

Although a major research effort has been made in the development of a direct propene epoxidation process, all attempts so far have been unsuccessful. The silver-catalyst in use for the direct epoxidation of ethene is discussed extensively in respect to the problems in the application of this catalyst for the epoxidation of propene. By studying the mechanism of the reactions of both ethene and propene on this catalyst, a suggestion is made on how this catalyst theoretically should be modified to (selectively) epoxidize propene.

Of the other propene epoxidation processes under development that are discussed, one process shows the potential for short-term realization: the hydrogen peroxide combination process. This process produces in-situ hydrogen peroxide, which is then immediately used for the epoxidation of propene using a titanium-silicalite-1 catalyst.
Propene Oxide: Processes and Possibilities

Introduction

Propene oxide, also known as propylene oxide, methyloxirane, or 1,2-epoxypropane, is one of the more important starting materials in the chemical industry. The production of propene oxide consumes over 10% of all propene produced [1]. In 1995 the total market for propene oxide amounted to approximately 4.4 million tons/year. This market is annually growing by approximately 3% [2]. The major application of propene oxide is in the production of polyether polyols (65%), which are mainly used for the production of (polyurethane) foams. The second and third largest applications are in the production of propene glycol (30%) and propene glycol ethers (4%), respectively [3]. Propene glycols are mainly used in the production of polyesters, whereas propene glycol ethers are primarily used as solvents.

Propene oxide is currently produced using two different commercial processes, the chlorohydrin process and the hydroperoxide process. In 1995 the production capacity was distributed evenly between these two processes, but because of the environmental impacts of the chlorohydrin process, the most recently built plants are all using hydroperoxide process technologies. A disadvantage of the hydroperoxide processes is, however, the production of equimolar amounts of a coproduct, either styrene or t-butanol, depending on which variant of the hydroperoxide process is applied. A major research effort has been made in the development of alternative direct epoxidation processes for the production of propene oxide. The aim was to develop a process for the direct gas-phase oxidation, similar to the direct epoxidation of ethene. The selectivity of the catalysts developed so far, however, is by far insufficient to result in a viable process (usually lower than 30%, with the remaining part of the propene converted to carbon dioxide). Olin developed a process for the direct epoxidation of propene using molten salt ‘catalysis’, claiming promising results of 65% selectivity to propene oxide at 15% propene conversion [4]. This process is, however, not yet commercially applied. An alternative for the use of alkyl-hydroperoxides, used in de hydroperoxide processes, is hydrogen peroxide. Especially, when TS-1 (Titanium-Silicalite-1) is used as a catalyst, this allows for the possibility of a very selective (95%) and hydrogen peroxide efficient production of propene oxide [5]. The major problem for the commercialization for this process is, however, the fact that on a molar basis propene oxide and hydrogen peroxide have the same market value is making it impossible to profitably run the process at this time. This disadvantage can be solved by the in-situ production of the hydrogen peroxide.

The next paragraphs of this chapter will discuss the above mentioned propene epoxidation processes and examine possibilities for alternative epoxidation routes.
Current processes

Chlorohydrin process

The synthesis of ethene- and propene oxide using the chlorohydrin route was first described in 1859 by Wurtz [6]. In this reaction the alkene reacts with hypochlorous acid (HOCl) to produce the chlorohydrin. The hypochlorous acid is produced in-situ by an equilibrium reaction of the acid with water and chlorine. The chlorohydrin is thereafter dehydrochlorinated using aqueous potassium hydroxide to produce the epoxide. The conversion of chlorohydrins to epoxides is performed by an adaptation of the Wilkinson synthesis for ethers [7]. This route has long been the main process for producing both ethene- and propene oxide. In the 1940s the process started to be phased out for the ethene epoxidation because of the development of a more efficient direct epoxidation process using a silver catalyst. After that introduction many ethene-epoxidation plants using the chlorohydrin process were converted for the epoxidation of propene. The process is still applied for the propene epoxidation, however, at the moment it is gradually being replaced by the more environmentally friendly hydroperoxide processes.

Figure 1 schematically demonstrates the chlorohydrin process. The two reaction steps in the production of propene chlorohydrin in the first reactor

![Diagram of the chlorohydrin process]

Figure 1.
Schematic representation of the chlorohydrin process for the production of propene oxide.
Propene Oxide: Processes and Possibilities

(chlorohydrination) are production of the propene chloronium complex (1) in the first reaction step, followed by a reaction with water to produce two propene chlorohydrin isomers (2).

\[
\begin{align*}
\text{CH}_3\text{CH} &= \text{CH}_2 + \text{Cl}_2 & \xrightarrow{\text{H}_2\text{O}} & \text{CH}_3\text{CH} &= \text{CH}_2 \\
\text{Cl}^+ & \quad \text{Cl}^- \\
\text{CH}_3\text{CH} &= \text{CH}_2 + \text{H}_2\text{O} & \rightarrow & \text{CH}_3\text{CH} - \text{CH}_2 + \text{CH}_3\text{CH} - \text{CH}_2 + \text{HCl} \\
\text{Cl}^+ & \quad \text{Cl}^- & \text{OH} & \text{Cl} & \text{Cl} & \text{OH} \quad 90\% & 10\%
\end{align*}
\]

The selectivity of these reactions to the chlorohydrin isomers is approximately 90%. By-products formed are 1,2-dichloropropane (8%) (from the gas-phase reaction of propene with chlorine), dichloropropanols (1%) (produced from allyl chloride, also formed in the gas phase from the reaction between propene and chlorine), and dichloroisopropyl ethers (1%) (from the reaction of the chloronium complex with propene chlorohydrin). The chlorohydrination is usually carried out in a bubble column reactor at 1.5 bar and 323 K. Due to the corrosive nature of the reaction mixture, the use of rubber, plastic, or brick lined equipment is necessary.

In the epoxidation reactor, the dehydrochlorination of propene chlorohydrin occurs using a base (usually calcium hydroxyde) (3).

\[
\text{CH}_3\text{CH} - \text{CH}_2 \\
\text{OH} & \text{Cl} \\
2 & + \text{Ca(OH)}_2 & \rightarrow & 2 \text{CH}_3\text{CH} - \text{CH}_2 + \text{CaCl}_2 + 2 \text{H}_2\text{O} \\
\text{Cl} & \text{OH}
\]

The propene oxide is steam stripped from this reactor to prevent base catalyzed hydrolysis of the product. The dehydrochlorination is carried out in the same column where the products are stripped from the wastewater stream (1 bar, 373 K). The chlorinated hydrocarbons produced end up with the propene oxide stream and have to be removed. The brine leaving the bottom of the reactor contains some propene glycols, since hydrolysis of propene oxide cannot be completely avoided. These glycols and small amounts of other hydrocarbons present have to be biologically removed. Subsequently the brine is discharged, as the calcium chloride in the stream has no commercial value. This is one of the major disadvantages of the chlorohydrin process, since the amount of brine (5% CaCl₂) produced is usually about 40 times
larger than the amount of propene oxide produced and it is extremely difficult to remove all hydrocarbons from this waste-water stream. Re-use of the calcium chloride is not economically feasible, because of its low commercial value. Alternatively sodium hydroxide can be used instead of calcium hydroxide. This has the advantage that the sodium chloride produced can then be used in the production of chlorine, which can be recycled in the first step of the process. Although sodium hydroxide is used in some plants, the recycling step has so far never been applied because of a number of technical problems [3].

The raw propene oxide stream has to be purified by distillation from the water and chlorinated hydrocarbons. In this separation again care has to be taken that the propene oxide is not hydrolyzed to propene glycol. The relatively large amount (up to 10 %) of 1,2-dichloropropane is obtained as a second 'product' from the separation section. As this compound has very little usage, it not only causes a loss in yield, but also creates a disposal problem [6].

The two disposal problems (brine and chlorinated by-products) are the main reason that no new chlorohydrin plants are built and old plants are closed down instead of being modernized. Only the large scale plants (> 100,000 tons/year) are expected to remain operational for a longer period, as they are often integrated with chlorine production plants and have the potential of recycling the sodium chloride brine to the chlorine plant, when the technical problems have been overcome.

Hydroperoxide processes

Hydroperoxide processes are based on the peroxidation of an alkane to an alkyl-hydroperoxide. These alkyl-hydroperoxides then react with propene producing propene oxide and an alcohol. A characteristic of these processes is that apart from propene oxide a co-product is produced in equimolar amounts. At the moment two variants of this process are applied commercially. The first is the propene oxide - styrene monomer (PO-SM) process. In this process ethylene is oxidized to ethylene oxide hydroperoxide, which reacts with propene to produce propene oxide and α-phenylethanol. The α-phenylethanol is then dehydrated to produce styrene. The second process in use is the propene oxide – tert-butylalcohol (PO-TBA) process. In this process iso-butane is oxidized to tert-butylhydroperoxide (TBHP), which reacts with propene to produce propene oxide and tert-butylalcohol. This can be dehydrated to iso-butene or converted directly with methanol to methyl-tert-butyl ether (MTBE). Although other combination processes are possible, no others have been applied so far. Other possibilities are for example acetalddehyde to acetic acid, 2-propanol to acetone, iso-pentane via tert-pentyl alcohol to isoprene, cumene via dimethylphenylmethanol to α-methylstyrene, and cyclohexene via cyclohexanol to cyclohexanone. Characteristics of the hydroperoxide processes are that they are selective and produce far less waste than the chlorohydrin process. The major disadvantage of the hydroperoxide processes, however, is that always a fixed amount of coproduct is produced. As the markets for propene oxide and the
coproducts are not linked, a problem could arise should the demand for one of the products collapse.

Figure 2 schematically demonstrates the PO-SM process. The PO-TBA process differs only on details from the PO-SM process, so both processes are discussed simultaneously. The first reactor converts the ethylbenzene or iso-butane non-catalytically to its corresponding hydroperoxide by direct liquid-phase oxidation using oxygen or air. The oxidation is usually performed in a bubble column at 423 K and 30 bar when iso-butane is used, or 423 K and 3 bar in the case of ethylbenzene. The reaction equation of this reaction in the PO-SM process is given below (4).

\[
\begin{array}{c}
\text{CH}_2\text{CH} - \text{CH}_3 + \text{O}_2 \\
\rightarrow \\
\text{CH} - \text{CH}_3 \\
\text{OOH}
\end{array}
\]

A disadvantage of the processes using iso-butane is that approximately half the TBHP produced, immediately decomposes to TBA, thus lowering the propene oxide to coproduct ratio. The unreacted hydrocarbons are then removed and recycled. The hydroperoxide stream is sent to a second reactor, where it catalytically reacts with

---

**Figure 2.**
Schematic representation of the propene oxide – styrene monomer (PO-SM) process for the production of propene oxide.
propene to produce propene oxide and an alcohol. The temperature in this reactor is approximately 373 K at 30 bar pressure. The reactor used for the epoxidation is ideally mixed. Usually up to 5 reactors in series are being used of which the final reactor has a slightly elevated (10-20 K) temperature to obtain an optimal hydroperoxide efficiency. The total conversion in the reactors is larger than 95 % (of the hydroperoxide) at over 95 % selectivity to propene oxide, the only by-product produced is acetone. Equation (5) gives the epoxidation reaction in the PO-SM process.

\[
\text{CH}_2\text{CH}=\text{CH}_2 + \text{CH}_3\text{OH} \xrightarrow{\text{catalyst}} \text{CH}_2\text{CH}=(\text{CH}_2\text{OH} + \text{CH}_3\text{CH}=\text{CH}_2
\]

Most processes use either a homogeneous molybdenum catalyst or a heterogeneous titanium based catalyst to catalyze the epoxidation reaction. The disposal of the used homogeneous molybdenum catalyst causes a waste problem. After the reactor the propene and propene oxide are removed consecutively from the liquid stream. In case of the PO-SM process the remaining stream still contains some unreacted ethylbenzene, which then is removed and recycled. The alcohol stream can then be dehydrated to produce styrene or iso-butene, or with the PO-TBA process sold directly after purification as tert-butyl alcohol.

**Ethene-epoxidation type silver catalysts**

*Ethene epoxidation process*

Since the 1940s all newly built plants for the production of ethene oxide are based on a direct oxidation process using a silver-catalyst [8]. A fixed bed reactor is used to epoxidize ethene at 500 K and 30 bar. A typical conversion in the reactor is about 10 %, to prevent a further oxidation of the ethene oxide produced and simplify the problems caused by the exothermicity of the reaction. This relatively low conversion explains why the use of pure oxygen is usually preferred instead of air, since this simplifies the separations necessary for the recycle stream. The catalyst used in the process is a 10 w% silver catalyst supported on low surface area (< 1 m²/g) α-alumina containing several promoters. The selectivity of the reaction is usually about 80 - 90 %, the remainder of the ethene being converted to carbon dioxide.

*Silver catalyst*

The silver catalyst used for the ethene epoxidation has a high metal loading on a low surface area support. The high metal loading is more than sufficient to cover the entire support material, which can be seen as a means of only acting as a filler...
within the silver. The use of unsupported silver as a catalyst is also possible, however, this has a tendency to sinter at the reaction temperature. Other support materials are inert materials such as silicon carbide (also used commercially), glass wool, and quartz. All support materials have a low surface area, as microporous materials generally yield poor results because of the occurrence of heat problems inside the particles and further oxidation of ethene oxide produced in the pores [8].

Promoters used for the catalyst are alkali metals present on the catalyst and chlorine, which is continuously added to the system using a chlorinated hydrocarbon. The exact effect of the promoters so far has not yet been clarified. It is generally suggested that both the alkali metals and chlorine block sites, which are able to abstract hydrogen from ethene [9]. This hydrogen abstraction is suspected to occur on different sites than those, which activate the double bond and produce ethene oxide. This two-site mechanism is confirmed by the fact that the addition of promoters hardly has any influence on the ethene oxide production rate. A second explanation for the role of the alkali promoters is the enhancement of the alkene adsorption rate [9].

Originally, the idea existed that the epoxidation of ethene over silver occurred by molecular oxygen, producing ethene oxide and atomic oxygen on the catalyst. The atomic oxygen then could only be removed from the catalyst by complete oxidation of ethene. This model resulted in a maximum obtainable selectivity of 86 %. This seemed to be confirmed by the fact that higher selectivities had never been reached. However, during the last 20 years this idea started to change and atomic oxygen has now been confirmed to be the active species in all recent studies. One of the first studies to clearly identify atomic oxygen as the active species was by van Santen and de Groot [10], who studied the initial reaction rates for silver surfaces precovered by either atomic or molecular oxygen. In that study the surfaces precovered with atomic oxygen had significantly higher ethene oxide production rates than the surfaces precovered with molecular oxygen.

An explanation for the unique characteristics of silver in the epoxidation of ethene is found in its ability to dissociatively adsorb oxygen, which is weakly bound at high coverages [11]. If oxygen is unable to dissociate, the epoxidation will not occur. When the oxygen-metal bond is too strong, the formation of an epoxide is thermodynamically impossible. Oxygen adsorbed on silver is able to activate the C-H bond of ethene, explaining the selectivities lower than 100 %. This reaction is, however, slower than the epoxidation reaction and the sites most active for this reaction can be blocked using promoters.

The generally accepted reaction scheme for the epoxidation of ethene over a silver catalyst is represented in Figure 3. This

![Figure 3. Reaction scheme for the epoxidation and combustion of ethene.](image-url)
reaction scheme indicates that the complete oxidation occurs as both parallel and sequential reactions. The oxidation rate of the epoxide \( k_r \) is very small compared to reactions 1 and 2 [12]. The reactions are zero order in oxygen and first order in ethene, within the operating window of the process. When the same silver catalyst is applied in the epoxidation of propene, the reaction scheme in Figure 3 is also found to be valid and identical reaction orders are found, the selectivity towards propene oxide, however, is very low (usually less than 10 %). The rate constant for the complete oxidation of propene oxide is again extremely low and negligible. The low selectivity for propene oxide is primarily caused by the high rate of the complete oxidation of propene, which is almost a factor of 10 faster than the complete oxidation of ethene. On the other hand, the epoxidation reaction of propene is almost a factor of 10 slower than the epoxidation reaction of ethene. The next paragraph discusses the differences in reactivity of propene and ethene on a molecular scale to explain these differences in reactivity.

Reaction mechanism in the ethene and propene epoxidation

Carter and Goddard [9] presented a comprehensive oxyradical mechanism to explain the differences in reactivity of ethene and propene in both the epoxidation and the complete combustion. This mechanism is based on valence bond calculations on the thermodynamics of the different reaction steps and is verified by experimental results. The active species is assumed to be a surface atomic oxyradical, which is

---

**Figure 4.**

Reaction scheme for the epoxidation and total oxidation reaction pathways for ethene over a silver catalyst [9].
adsorbed atomic oxygen with its unpaired electron pointing away from the catalyst surface. This is in contrast to the di-σ oxide type oxygen, which has both electrons bonded to the silver surface. The thermodynamic calculations suggest that the oxyradical type oxygen will only form at higher oxygen surface coverages. This is consistent with reported higher epoxidation selectivities at higher oxygen surface coverages [11].

Figure 4 demonstrates the calculated energy levels for both the epoxidation and combustion of ethene over atomic oxygen on a silver surface. When ethene reacts with oxygen, the reaction can proceed in two ways. The first possibility is the abstraction of a hydrogen atom. This reaction has a relatively high activation energy (184 kJ/mol), and once this reaction step has occurred, the only possible subsequent reaction steps result in the complete combustion of ethene. On the other hand, the oxyradical attack on the double bond is able to proceed without a significant activation to produce an oxygenated reaction intermediate. This intermediate can subsequently produce adsorbed ethene oxide, with the desorption of the epoxide only having a small barrier energy (42 kJ/mol). This scheme is consistent with a drop in epoxidation selectivity at higher temperatures [10], since the initial barrier for the combustion-precursor will then be less of a problem.

When the scheme for the reaction of ethene is compared to that of propene in Figure 5, it can be seen that these are largely analogous. For propene the abstraction

Figure 5.
Reaction scheme for the epoxidation and total oxidation reaction pathways for propene over a silver catalyst [9].
of a hydrogen atom is more favorable than for ethene, as propene is able to produce an allylic intermediate. This allylic intermediate results in a significantly lower barrier energy (67 kJ/mol) for the direct combustion step, which can partly explain the lower epoxidation selectivity for propene. The initial reaction of the oxyradical with propene to produce the epoxide precursor is thermodynamically somewhat more favorable for propene than for ethene (ethene 21 kJ/mol, propene 29 kJ/mol), which could partly compensate for this drop in selectivity. A bigger problem is the propene epoxide precursor. It has an alternative reaction pathway available in addition to the epoxidation reaction, as in the case for ethene epoxide precursor. The γ-hydrogen atoms of the propene oxide reaction intermediate extend approximately 0.27 nm across the surface from the location where the reaction with the first oxygen atom occurred. The distance between the different oxygen atoms on the surface is approximately 0.29 nm, which is close enough for the γ-hydrogen atoms to reach. The abstraction of one of these hydrogen atoms is favorable and the intermediate formed can only result in a complete combustion of the molecule. This same reaction intermediate will probably also be produced, when the allyl-intermediate produced from the direct hydrogen abstraction of propene, is completely oxidized. The reaction step, in which the epoxide precursor reacts with a neighboring oxygen atom, does not occur with ethene, since it has no γ-hydrogen atoms and abstraction of a β-hydrogen atom would result in the production of an unstable carbene, which would have a high energy barrier.

A check on this mechanism can be made by comparing the reactivity of compounds with and without γ-hydrogen atoms. Under identical conditions the reactivity and selectivity towards the epoxidation of ethene, propene, and 3,3-dimethyl-1-butene were determined. The results of these experiments are given in Table 1. The details on the experiments given in this table can be found in chapter 6 of this thesis.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conversion (%)</th>
<th>Epoxidation selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>17.8</td>
<td>47.4</td>
</tr>
<tr>
<td>Propene</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>3,3-dimethyl-1-butene</td>
<td>4.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>
In Table 1 it can be seen that the selectivity for epoxidation of ethene and dimethylbutene is significantly higher than the propene epoxidation selectivity. No conclusions can be drawn from the conversions on the reactivities of the different gases, since in the experiments the conversion was limited by the amount of oxygen present. Higher epoxidation selectivities can, therefore, result in a higher conversion, and combustion of longer hydrocarbons naturally results in lower conversions. These measurements are in agreement with reported selectivities on other alkenes without γ-hydrogen atoms, such as norbornene [13] and styrene [14]. It is, however, difficult to distinguish whether the higher selectivities for dimethylbutene, norbornene, and styrene are caused by a lower direct hydrogen abstraction rate or because of a lower hydrogen abstraction rate of the oxygenated intermediate on the catalyst surface. These tested compounds all lack the allylic stabilization of the intermediate that is formed after the direct hydrogen abstraction. However, as these components possess a significantly larger amount of hydrogen atoms, it would be expected that the direct hydrogen abstraction rate would be relatively higher. Furthermore, in case of the propene oxidation, it would be expected that the direct hydrogen abstraction would play a dominant role in the combustion route. As a consequence, it would then be possible to achieve high epoxidation selectivities for propene at low temperatures, since the direct combustion has a higher energy barrier than the epoxidation route. High propene epoxidation selectivities at low temperatures over silver-type catalysts have neither been found nor reported, which also suggests that hydrogen abstraction of the oxygenated intermediate is most important.

Assuming that high selectivities over a silver catalysts can be obtained for the propene epoxidation if one were able to block the hydrogen abstraction of the oxygenated surface intermediate, it naturally comes to mind that this might be achieved by increasing the distance between the oxygen atoms on the silver surface. The easiest way to establish this would be to lower the oxygen surface occupancy on the catalyst. However, as the active oxyradical is only present at surface occupancies higher than 0.5, this will not stimulate the epoxidation reaction. A second possibility is to increase the distance between the silver sites on the catalyst. Creating such a catalyst by impregnating a very small amount of silver on a support is not realistic, as this would require an extremely low loading. A catalyst with silver particles of only a few atoms large would, however, be extremely sensitive towards sintering and probably possesses different chemical and/or physical properties. A better alternative is to create the catalyst by alloying the silver with an inert material.

An isolated site silver catalyst can easily be created by alloying gold with silver. Silver and gold are able to form stable alloys (exothermally) in every composition, and gold is totally inactive in either propene epoxidation or combustion in the temperature range used for epoxidation. This type of alloy catalysts were investigated by Toreis and Verykios [15] for the epoxidation of ethene. In their study they reported an increase in reaction rate with an increasing gold content at unchanged epoxidation selectivity (up to 200 % increase at 10 atom % gold). Gold contents in the alloy of over 10 %, yielded both lower reaction rates and epoxidation
selectivities. Silver-gold alloys with over 30 % of gold on the surface showed no conversion of ethene at all. When studying the catalysts using oxygen TPD, they found that above this amount of gold only one type of oxygen desorbed, whereas two desorption peaks were observed at lower gold contents. The lower temperature desorption peak of the catalysts with a low gold content is found at approximately the same temperature as the single desorption peak in case of the higher gold-content catalysts. Which of the oxygen desorption peaks corresponds to the active oxyradical species was not clarified. The single oxygen desorption peak at higher gold contents cannot be explained by adsorption of oxygen in molecular form, since molecular oxygen desorbs at much lower temperatures (200 K) compared to the temperature of this desorption peak (420 K). The adsorption of oxygen in molecular form, however, could explain why the catalysts with a gold content of over 30 % are inactive in the epoxidation. Alternatively this inactivity could be possible that at higher gold contents all oxygen is bound stronger to the silver, since the silver then is not able to relocate electrons, when oxygen is adsorbed. This relocation will be blocked by the intermediate gold atoms. A further explanation for the absence of any ethene conversion at gold contents of over 30 % is given by the impossibility for ethene to adsorb on a silver site next to oxygen, since only small silver clusters are present in the alloy.

A second study by Geenen et al. [12] examined both the epoxidation of ethene and propene over supported silver-gold alloy catalysts. In their study they still found epoxidation activities for both ethene and propene at gold surface contents of up to 50 %. However, the epoxidation selectivity dropped with an increasing gold content. No changes in the reaction rate were reported as a function of the gold content. In the case of the oxidation of propene, the catalyst starts making an increasing amount of acrolein, when more gold is added (no acrolein production is detected in the absence of gold). This selectivity towards acrolein reaches almost 100 % at a gold content on the surface higher than 75 %. This is explained by the presence of isolated silver sites at the catalyst. These sites are unable to dissociate oxygen, and oxygen, therefore, only adsorbs in molecular form. This molecular adsorbed oxygen can react with propene according to the mechanism in Figure 6, producing acrolein.

Figure 6.
Reaction scheme for conversion of propene to acrolein over an isolated site silver catalyst [12].
Propene Oxide: Processes and Possibilities

Outlook towards the possibility of a propene-epoxidizing silver-catalyst

If one summarizes the models mentioned in the previous paragraphs, two important points remain, which are:

- A significant part of the combustion of propene is caused by the reaction of γ-hydrogen atoms of an adsorbed oxygenated propene oxide precursor with a neighboring adsorbed oxygen atom;
- Propene oxide is formed from atomic oxygen only. The active oxygen species exists only at relatively high oxygen coverages.

By combining these points it can be concluded that if one is able to create a silver catalyst with isolated active sites and put atomic oxygen on these sites, this catalyst should be able to make selectively propene oxide, provided that it is not necessary for propene to adsorb on the catalyst next to the oxygen. The calculations by Carter and Goddard [9] confirm that a separate propene adsorption is not necessary. A relatively simple way to create the catalyst is to use a silver-gold alloy. Since it is necessary to create atomic oxygen on this catalyst and (di)oxygen does not dissociate on the isolated sites, an alternative way of providing atomic oxygen has to be found. A possibility could be the use of nitrous oxide (N₂O), since silver is a good catalyst for the decomposition of nitrous oxide. However, two prerequisites have to be fulfilled, namely the decomposition should be performed on isolated sites and the atomic oxygen should be relatively stable on this site. This oxygen can be used to produce propene oxide. One problem remains for this concept of epoxidizing propene using nitrous oxide: the decomposition of nitrous oxide on the silver catalyst requires a temperature of at least 520 K[12], while the epoxidation is more selective at somewhat lower temperature (preferably 470 K). Propene is able to directly abstract a hydrogen atom, producing the allylic intermediate, which will lead to complete combustion (Figure 5). As a consequence, even atomic oxygen on an isolated site silver catalyst will cause some propene combustion. Since this combustion route has a relatively high barrier energy (67 kJ/mol), it would be beneficial to carry out this reaction step at a lower temperature than is necessary for the nitrous oxide decomposition. A solution to this problem can be found in the use of a two step process in which both reactions can be carried out at different temperatures, such as in the riser-regenerator reactor of the maleic anhydride process or in a rotating monolith reactor [16].

Although this concept should in theory work for the production of propene oxide, attempts to prepare a working catalyst have so far been unsuccessful. The silver-gold alloy catalysts prepared had, similar to those prepared by Toreis and Verykios [15], neither epoxidation nor combustion activity for both ethene and propene at high gold contents, the activity dropping with the gold content in the low content range. The oxygen TPD profiles measured supported the similarity between the catalysts of Toreis and Verykios and ones synthesized in this study. The alloy catalysts produced acrolein from propene and molecular oxygen only in trace amounts, whereas a significant acrolein producing activity for this type of catalyst was found by Geenen et al. [12]. An explanation for these differences in performance
is not available, as the synthesis used for both groups of catalysts is similar. Although the absence of acrolein producing capability was a negative sign, the catalysts were tested using nitrous oxide as oxidant. However, this did also not result in any propene oxide production in the high-gold content catalysts. The lower gold content catalyst showed lower epoxidation selectivities, similar to the results of Yong and Cant [17]. More information on this type of silver-gold catalysts is given in chapter 6.

Hydrogen peroxide combination process

A recent development in the production of propene oxide is the production of propene oxide using hydrogen peroxide produced in integrated process [20-22]. Although commercially available hydrogen peroxide is no alternative as an oxidizing agent for the epoxidation of propene, because of its high cost, this process is viable if the hydrogen peroxide is produced in-situ. The most expensive step in many chemical processes is the separation of the products, which is also the case for the production of hydrogen peroxide. Most hydrogen peroxide is nowadays produced using the anthrahydroquinone autoxidation process [18]. In this process the hydrogen peroxide is produced in diluted form in a water-methanol mixture. The zeolite Titanium-Silicalite-1 (TS-1) is able to very selectively epoxidize propene using diluted hydrogen peroxide [5, 19]. Instead of separating the hydrogen peroxide produced, it can be used directly in the epoxidation of propene using TS-1. The separation of the propene and propene oxide from the water-methanol mixture can easily be accomplished, allowing an excellent integration of a hydrogen peroxide process and a propene epoxidizing process. This integrated process is currently under development by Enichem [21, 22].

Because of the very promising possibilities of this combination process a technical and economical evaluation has been made on this type of process [20]. A simplified representation of this process is given in Figure 7. The two reactors in the left part of this figure depict the hydrogen peroxide synthesis out of hydrogen and oxygen using anthrahydroquinones, the reactor in the center is the epoxidation reactor.

When the quinones used in this process are alternately oxidized and reduced they produce hydrogen peroxide. The oxidation and reduction are performed in two separate reactors. A bubble column is applied for the oxidation of the quinones, during which the hydrogen peroxide is produced. For the palladium catalyzed hydrogenation of the quinones a slurry, fixed bed, or monolith reactor can be used. Both hydrogenation and oxidation are carried out at around 320 K and 1.2 bar. Equations (6) and (7) show the hydrogen peroxide producing reactions of the quinones for the most commonly used 2-ethylanthrahydroquinone.
The hydrogen peroxide synthesis is carried out in mixture of a hydrophobic (e.g., xylene) and a hydrophilic (water + methanol) phase. These phases are separated using a settler after which a hydrogen peroxide containing water/methanol stream is obtained. The hydrogen peroxide in this stream is used to epoxidize propene (at close to 100% conversion) using TS-1 as a catalyst (8).

\[
\text{H}_2\text{O}_2 + \text{CH}_3\text{CH}═\text{CH}_2 \xrightarrow{\text{TS-1}} \text{H}_2\text{O} + \text{CH}_3═\text{CH}═\text{CH}_2
\]

The epoxidation reaction using TS-1 is carried out in a fixed bed reactor at 313 K and atmospheric pressure. After some relatively simple separation steps the propene oxide is obtained and the water-methanol mixture is sent back to the hydrogen peroxide synthesis.

Although it is possible to use other catalysts such as molybdenum oxide or tungsten oxide to epoxidize propene with hydrogen peroxide, these catalysts are all extremely sensitive to the presence of water [23, 24]. Even though the water in the feed stream could be removed, removal of water produced in the epoxidation process is more difficult. Furthermore, all other catalytic systems consist of homogeneous catalysts, resulting in an extra separation step being necessary. This makes TS-1 at this time to be the only economically possible catalyst to be applied in this process.

When an economic evaluation is made for a 400,000 tons/year propene oxide production facility using this process, this relatively large scale plant would require an investment of approximately 250 million dollars. The pay-out time for the investment would, however, be less than 1.5 years based on the current price levels of propene, hydrogen, oxygen, and propene oxide, indicating this type of process could be extremely profitable. An explanation to why this type of plant has not yet been built, despite of its clear profit making potential can be found in the fact that it consists of very new technology. Especially the TS-1 catalyst could be the cause of unexpected additional costs, in particular it might deactivate faster than expected on
Figure 7.
Flow scheme for a new propene epoxidation process by integrating a anthrahydroquinone hydrogen peroxide production process with a propene epoxidation reaction catalyzed by TS-1 [20].

the basis of lab scale experiments. Furthermore, the increasing demand for oxygen containing fuel additives such as the octane number booster MTBE (methyl-tert-butyl ether) results in an extra incentive on the application of the PO-TBA process. As the MTBE demand (and, therefore, TBA demand) rises, this might bring the cost of propene oxide down as under those circumstances it can be considered as the by-product of TBA production. However, it can be expected that if new propene oxide-only plants are needed, this process will be on top of the list of processes, especially since Enichem is gathering experience on the lifetime of the TS-1 catalyst in a pilot plant reactor for this process [25].

A different approach in this epoxidation route, also under development by Enichem, is to carry out all three reactions (the oxidation and reduction of the quinones and the epoxidation) in the same reactor [25]. This process was demonstrated on lab scale, however, the practical application of the process will be complicated by the explosive nature of a hydrogen-oxygen mixture. Furthermore, the production of hydrogen peroxide using quinones in a single reactor has not yet been applied, making the single reactor approach more precarious than the split reactor process. Therefore, the actual application of the process shown in Figure 7 is more likely, as this process can easily be integrated with an existing hydrogen peroxide
production facility and is more flexible, since it can also be applied for other TS-1 catalyzed oxidations using hydrogen peroxide.

Other processes

Epoxidation using nitrous oxide

An alternative oxidizing agent for the epoxidation of propene, which has been extensively investigated is nitrous oxide \((N_2O)\) \([26, 27]\). The underlying thought for the choice of nitrous oxide as an oxidant is that atomic oxygen is produced on the catalyst from the decomposition of the oxide. After the discussion in literature ended whether atomic or molecular oxygen was acting as active species in the silver catalyzed epoxidation reaction, the idea emerged that molecular oxygen might be causing the complete oxidation. The supply of atomic oxygen by decomposing nitrous oxide on a silver catalyst would then result in a more selective epoxidation. The mechanism proposed by Carter and Goddard \([9]\), however, does not support this view. On the other hand, nitrous oxide would be an excellent oxidant in the isolated site catalyst discussed earlier.

Despite the fact that there are only some indications that epoxidation using nitrous oxide might be successful, it makes sense to have a closer look into the feasibility of such a process. A major disadvantage for this kind of process is that nitrous oxide is not commercially available in large quantities. Virtually all nitrous oxide currently produced is produced as a by-product of the adipic acid production using the nitric oxide production of cyclohexanol \([28]\). If one were to produce propene oxide using nitrous oxide, it would be necessary to place the production facility close to a adipic acid plant. The largest scale adipic acid plants currently in use, produce about 300,000 tons of adipic acid/year. Although these adipic acid processes can produce nitrous oxide in equimolar amounts, the amount of propene oxide produced as a co-product next to adipic acid could by estimate only be 30,000 tons/year \([29]\). If one was to see this process as a way of disposing of the harmful (greenhouse gas) nitrous oxide, this could be a moderately profitable process \([29]\). To produce propene oxide, however, in large amounts from an epoxidation process using nitrous oxide, not only the isolated site catalyst had to be created, but a process to directly produce nitrous oxide has to be developed, as the large scale production (400,000 tons/year) of propene oxide as a co-product next to adipic acid would result in an adipic acid production of more than twice the total 1987 adipic acid demand \([28]\). The profitability of this production route is, therefore, uncertain since it is not guaranteed both the isolated site catalyst and independent nitrous oxide production process can be developed and the costs of both can only be roughly estimated.
Epoxidation using molten salts

A conceptual process for the epoxidation of propene using molted alkali-nitrate salts had been developed by Olin. Olin has filed a large number of patents on this process, of which the latest dates back to 1991 [30]. In this process a at pressure of 20 bar and a temperature of 473 K a propene oxide selectivity of 65 % at 15 % propene conversion is reported when a propene – air mixture is flowed through a molten alkali-nitrate salt mixture. The major by-products are aldehydes, carbon monoxide, and carbon dioxide. Recirculation of the aldehydes resulted in an increased selectivity. Higher selectivities have been reported when a supported palladium co-catalyst is used [31] or when sodium hydroxide is added to the molten salt [32]. Using the same molten salt systems, it has also been reported that propane can be directly epoxidized to propene oxide [33]. However, the reported selectivities for the epoxidation of propane are low (< 15 %). It should be noted that the reported high epoxidation selectivity of 65 % with a propene conversion of 15 % should be sufficiently high to run a profitable direct epoxidation process. However, so far no plants for this process have been built. The epoxidation of propene using molten salts is discussed in detail in chapter 8 of this thesis.

Homogeneous catalysts

Although a large number of homogeneous catalytic systems [34] are available to epoxidize alkenes, almost all of these catalysts only use hydroperoxides as oxidant [24]. Using these hydroperoxides, high selectivities (> 90 %) at moderate propene conversions (10 %) can be obtained [35]. When (di)xygen is used as oxidant, on the other hand, the epoxidation selectivities are usually much lower (< 15 %)[36], although higher selectivities (up to 50 % at 12 % conversion) are also reported [13]. A major problem of more selective homogeneous catalysts is that the catalyst is being consumed during the reaction [37]. This consumption can usually be explained by one of the following two reasons. First, when the 'catalyst' oxidizes propene, it cannot be re-oxidized by molecular oxygen. Second, when the 'catalyst' takes up an oxygen molecule, it epoxidizes propene and loses one oxygen atom. The second oxygen atom remains bonded to the 'catalyst'. This oxygen atom bonded to the catalyst is not active in the epoxidation reaction and the catalyst is deactivated. The catalyst could in this case be reactivated by reduction in a second reactor.

Although some of the homogeneous catalysts found so far are performing better than most heterogeneous systems, no processes based on these homogeneous catalysts are applied. An explanation can be found in the general disadvantages of homogeneous catalysts: the necessity of an extra separation of the catalyst from the liquid stream leaving the reactor and the loss of catalyst and/or ligand(s). Since propene has a high vapor pressure, the use of a solvent for the reaction will also be necessary, unless one is prepared to operate the process at a high pressure. As propene oxide is a cheap bulk chemical these extra costs (separation and pressure) can make a homogeneous process a costly one. Nevertheless, it might be worthwhile to consider homogeneous processes, as they are successfully applied in other
selective oxidation processes, e.g. the production of terephthalic acid and the Wacker oxidation of ethene.

Other processes

Apart from the processes mentioned earlier, a large number of other routes for the epoxidation of propene have been described. One of these routes, the low temperature epoxidation of propene over a gold on titania catalyst in the presence of both hydrogen and oxygen. This catalyst is able to produce propene oxide at 100 % selectivity, at a low conversion of 1 %. The mechanism of this type of catalyst is most likely the creation of a hydrogen peroxide – like compound on titania sites by the gold. The titania at these sites probably exists in the same configuration as in the TS-1 epoxidation catalyst. More details on this reaction will be discussed in chapter 7.

The non-catalytic gas-phase oxidation of propene is also reported to produce relatively large amounts of propene oxide (65 % selective at 7 % conversion [38]). Because of some similarities in the results of the non-catalytic oxidation and the ‘catalytic’ oxidation in molten salts, these two processes will be discussed simultaneously in chapter 8.

Other propene epoxidation processes, that have been described in literature are epoxidation of propene using photochemically activated oxygen [39], electrochemical processes [2], peracid processes [1], and biocatalytic systems (enzymes and/or microorganism)[1]. None of these alternative approaches, however, are able to compete with the processes currently available.

Conclusions

From the two processes currently in use for the epoxidation of propene, the chlorohydrin and the hydroperoxide process, it is expected that only the hydroperoxide process will survive because of the environmental impacts connected to the chlorohydrin process. Alternative processes for the propene epoxidation are under development. The only one of these processes that might actually be applied within the next ten years is the hydrogen peroxide combination process under development by Enichem, as this is a clean, selective, and economically viable process. However, as long as the demand for both oxygenated fuel additives and styrene keep growing, it is more likely that new propene oxide plants will use one of the two hydroperoxide processes. Alternatives for the propene epoxidation processes that might be realized on a longer timescale are: an isolated site – ethene epoxidation type catalyst in a two-stage split-reactor design and a dispersed gold on titania catalyst, which creates a hydrogen peroxide alike component in-situ from hydrogen and oxygen.
References

Chapter 6

Propene Epoxidation

using Silver Catalysts

Summary

The epoxidation of ethene and propene has been investigated using a type of silver catalyst that is commonly used in ethene-epoxidation processes. The oxidation has been carried out using both oxygen and nitrous oxide as oxidizing media. The higher epoxidation selectivity of ethene in comparison to propene was confirmed to be the cause of the reactivity of the γ-hydrogen atoms of propene. Both the transient Multitrack experiments and the steady-state flow experiments using nitrous oxide confirm an oxyradical mechanism to be responsible for the epoxidation reaction. Attempts to create active propene epoxidizing isolated-site silver-catalysts by alloying silver with gold have been unsuccessful, although the production of some acrolein by these catalysts confirmed the presence of some isolated silver sites.
Propene Epoxidation using Silver Catalysts

Introduction

In the search for a catalyst for the direct epoxidation of propene, one of the first possible catalysts that naturally comes to mind is the silver catalyst that is commonly used in processes for the direct epoxidation of ethene. Therefore, it is self-evident to investigate the possibilities for this catalyst in the propene epoxidation. The cause of the bad performance of a silver catalyst in the epoxidation of propene is extensively discussed in chapter 5 of this thesis. The principal conclusion in that discussion was that only if one was able to create an isolated site silver catalyst and put atomic oxygen on those isolated sites (for example using nitrous oxide), one might be able to selectively produce propene oxide. Some experiments briefly mentioned in chapter 5 are discussed in more detail in this chapter. The experiments discussed in this chapter were mainly performed to confirm the model proposed in chapter 5 for the mode of operation in the case of a silver catalyst.

The performance of an ethene epoxidation catalyst will be examined in the epoxidation of both ethene and propene, using both oxygen and nitrous oxide as oxidizing agents. The catalyst is examined in a flow-reactor system as well as in the Multitrack system in order to gain insight in both the general catalyst performance and the reaction mechanism. Besides the 'standard' silver on alumina catalyst, also attempts to prepare an isolated site silver catalyst by alloying the silver with gold will be discussed.

Experimental

Steady-state catalyst testing

The steady-state epoxidation experiments were performed in a flow set-up. In this set-up the reactant gases, nitrogen, oxidant (oxygen or nitrous oxide), and alkene (ethene or propene), were continuously fed by means of mass flow controllers (maximum flow 100 Nml/min) with the possibility to add a fourth gas or to saturate the gas with a liquid (e.g. 3,3-dimethyl-1-butene). The reactor used was a 10 ml stainless-steel fixed bed reactor, placed in an fluidized-bed oven (773 K maximum temperature).

The catalyst used for the epoxidation experiments was a reduced 18 w% silver on low surface area α-Al₂O₃ (2 m²/g). This catalyst could be prepared by incipient wetness impregnation of silver nitrate on the alumina, followed by decomposition of the nitrates in boiling dioctyl-sebacic acid.

The analysis of the reaction products was performed using an automated sampling gas chromatograph equipped with a flame ionization detector (FID), analyzing a gas sample every 10 minutes. The column used for the analysis was a Rescom FFAP 0.312 mm diameter, 25 m length capillary column, operated at 323 K with helium as a carrier gas. This configuration was able to separate all oxygenated organic components relevant in this study, hydrocarbons could not be separated,
since they all had the same residence time as the carrier gas. The sensitivity of the gas chromatograph towards propene and the major reaction products was determined using calibration mixtures. Since the complete combustion products (CO and CO₂) could not be identified using the gas chromatograph, a non-dispersive infrared (NDIR) detector was used downstream of the sample valve of the gas chromatograph, measuring both the concentrations of carbon dioxide and carbon monoxide. The two signals from the NDIR and the temperature in the reactor were continuously recorded using a personal computer. Since water is also present as a combustion product and water will disturb the operation of the NDIR, a Permapure membrane drier was used to remove the water from the gas stream before it reached the NDIR. To prevent condensation in the tubing of the set-up of reaction products, all tubing up to the NDIR detector was heated to 373 K. After the NDIR detector the gas was either directly vented or sent into a gas sampling cylinder, to allow for a more detailed post-run analysis, for example using GC-MS.

**Multitrack experiments**

The Multitrack system and the type of experiments that can be performed using this set-up are discussed in chapter 1. The epoxidation of ethene and propene was investigated using Multitrack in the temperature range from 423 to 873 K. The experiments performed were single pulse experiment, in which the steady-state situation was examined, when ethene or propene was alternately pulsed with oxygen. The experiments were performed using ¹⁸O₂ to facilitate the interpretation of the measurements. Especially the interpretation of the epoxidation experiments with ethene using ¹⁸O₂ would be difficult, since the main m/e signals of ethene oxide would coincide with the signals from CO₂ (m/e=44) or ethene (m/e=29). Although ethene has a molecule mass of only 28, it does produce a signal on the mass spectrometer at m/e=29, as a result of hydrogen ions (protons) from one ionized molecule reacting with (and ionizing) a second ethene molecule.

The experiments were performed using the same batch of silver on alumina catalyst as used in the flow-experiments. The amount of catalyst used was 416 mg, with the catalyst crushed to a particle size in between 300 and 423 μm. The reactor used had a 7 mm inner diameter, the bed height was 10 mm. The gas-pulse sizes for all gases were approximately 1×10⁻⁷ molecules.

**Silver-gold alloy catalysts**

Silver-gold alloy catalysts have been prepared in an attempt to create an isolated site silver catalyst. The preparation of the catalysts was performed according to the method applied by Geenen et al. [1] and Toreis and Verykios [2]. This type of preparation should result in homogeneous silver-gold alloys, even more since these two metals have the natural tendency to alloy in any silver-gold ratio.

The catalysts were prepared by incipient wetness impregnation of the metals on the alumina support. Both the silver and gold precursors (AgCN and AuCN) were dissolved in the appropriate amount of aqueous 1,2-diaminoethane (volume
Propene Epoxidation using Silver Catalysts

ratio water : 1,2diaminoethane = 1 : 3). The amount of metal cyanides used was set to obtain a total metal loading on the α-Al₂O₃ (2 m²/g) of 8 w%, the gold content in the alloy was varied from 0 to 50 w%. The alumina was dried at 453 K prior to impregnation. After impregnation the catalyst was dried in air at 363 K for at least 24 hours, after which it was calcined at 523 K for 24 hours.

The activity of the catalyst was tested in steady state using the flow set-up discussed above. The catalysts were analyzed using a home made oxygen TPD (temperature programmed desorption) to examine the effect of the gold in the alloy on the adsorption-desorption behavior of oxygen on silver, as well as with SEM (Scanning Electron Microscopy) equipped with EDX-analysis (Energy Dispersive X-ray).

Results

Steady-state activity for epoxidation of different alkenes and oxidants

The results of steady-state activity measurements for the epoxidation of different alkenes over the standard silver catalyst used are given in Table 1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conversion (%)</th>
<th>Epoxidation selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>17.8</td>
<td>47.4</td>
</tr>
<tr>
<td>Propene</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>3,3-dimethyl-1-butene</td>
<td>4.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

In Table 1 two observations can be made: higher alkenes have a lower conversion and the epoxidation selectivity for propene is significantly lower than the selectivities for ethene and 3,3-dimethyl-1-butene.

A comparison between the epoxidation selectivity of ethene for oxidation using oxygen and nitrous oxide is made in Table 2.
Table 2.
Comparison between measured conversions and selectivities for the epoxidation of ethene using oxygen or nitrous oxide as oxidant (10.2 g of silver catalyst (18 w% on \(\alpha\)-Al\(_2\)O\(_3\)), 1.0 bar, 523 K, total flow rate 40 Nml/min, 12.5 vol.% O\(_2\) or 25 vol.% N\(_2\)O, 25 vol.% alkene, balance N\(_2\)).

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Conversion (%)</th>
<th>Epoxidation selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>27.4</td>
<td>30.2</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>12.4</td>
<td>12.0</td>
</tr>
</tbody>
</table>

In Table 2 it can be seen the use of nitrous oxide as oxidant instead of oxygen results in both a lower epoxidation selectivity and conversion.

**Multitrack Experiments**

The steady-state situation was examined for both ethene and propene when alternately the alkene and \(^{18}\)O\(_2\) were pulsed over the ethene epoxidation silver catalyst. Since the Multitrack experiments were performed to gain insight in the reaction mechanism of the epoxidation reaction on the catalyst surface, no calibrations were performed for the sensitivity of the system for the various reaction products. The discussion of the experiments will, therefore, only be qualitatively.

At low temperature (up to 523 K), the conversion of ethene was very low. Only the different carbon dioxide isotopes (C\(^{13}\)O\(_2\), C\(^{13}\)O\(^{17}\)O, and C\(^{15}\)O\(_2\)) were visible as products in trace amounts (<<0.1%). In the products \(^{18}\)O was also present, instead of only the \(^{18}\)O pulsed, which can be ascribed to the large amount of oxygen present in both the silver and the support from the catalyst. At 573 K, besides the combustion products also ethene oxide was observed. The pulse responses of products and feed gases are given in Figure 1. At a temperature of 623 K the amount of ethene oxide produced is slightly higher (20%), the combustion products on the other hand decrease by approximately by 20%. At a temperature of 673 K both the epoxidation rate and the combustion rate drop rapidly (epoxidation 50% of rate at 573 K, combustion 30%), even higher temperatures result in only trace amounts of ethene oxide and a combustion rate slowly decreasing with temperature.

A similar epoxidation experiment in Multitrack using propene, only yielded a very small amount of propene oxide at 573 K (Figure 2) and 623 K. Experiments at higher temperatures yielded extremely small amounts of propene oxide, which were nearly the same order of magnitude as the noise in the mass-spectrometer signal. The amount of propene oxide produced, however, was significant and could not be attributed to electronic noise or fragmentation of other compounds. The rate of combustion of propene remained more or less constant despite of the increasing temperature.
**Figure 1.**
Epoxidation of ethene over a silver catalyst using $^{18}$O$_2$ in the Multitrack system at 573 K. Steady-state situation when oxygen and ethene are alternately pulsed (oxygen t=0, ethene t=1 s, cycle time 2 s). Pulse sizes $1.0*10^{17}$ molecules, 416 mg of 18 w% silver on $\alpha$-Al$_2$O$_3$ catalyst.

**Silver-Gold catalysts**

The propene oxidation activity of the silver-gold alloy catalysts prepared was very low (conversion << 0.1 % at 523 K), making it extremely difficult to determine the influence of the gold content on the catalytic behavior. However, the production of trace amounts of acrolein was detected, whereas those traces were absent when a similar catalyst without gold is used. The oxygen-TPD profiles measured confirmed the alloying of the silver and gold in the catalyst. The alloying was also confirmed after EDX (Energy Dispersive X-ray) analysis of a number of metal particles visible on the alumina support under a SEM (Scanning Electron Microscope), which showed the particles to contain both silver and gold in the approximate ratio used in the synthesis.
Figure 2.
Epoxidation of propene over a silver catalyst using $^{18}$O$_2$ in the Multitrack system at 573 K. Steady-state situation when oxygen and propene are alternately pulsed (oxygen t=0, propene t=1 s, cycle time 2 s). Pulse sizes $1.0 \times 10^{17}$ molecules, 416 mg of 18 w% silver on α-alumina catalyst.

Discussion

Steady-state experiments

The higher epoxidation selectivity in Table 1 for ethene and 3,3-dimethyl-1-butene compared to propene can be explained by the reactivity of the γ-hydrogen atoms of propene, confirming the mechanism for the epoxidation over a silver catalyst proposed in chapter 5. The lower epoxidation selectivity of 3,3-dimethyl-1-butene compared to ethene, can be explained by the larger number of hydrogen atoms in 3,3-dimethyl-1-butene, and, therefore, higher likelihood of a hydrogen
abstraction. The differences in conversion for the three components can be explained by the fact that the oxygen conversion in all experiments was 100%. Therefore, a lower epoxidation selectivity and a larger number of carbon atoms in the alkene naturally lead to a lower overall conversion.

The lower epoxidation selectivity in Table 2, when nitrous oxide is used as oxidant, is also in agreement with the oxyradical mechanism in chapter 5. The oxyradical being responsible for the epoxidation in this mechanism, is only present at high oxygen surface coverages. When nitrous oxide is used for the epoxidation, the total surface coverage of oxygen is lower than is possible when (di)oxygen is used for the epoxidation. This lower oxygen coverage is caused by the fact that when nitrous oxide decomposes on the silver surface, nitrogen is produced, which also occupies surface sites. When the nitrogen desorbs, an empty site on the surface is created, naturally resulting in a lower oxygen surface coverage. As a result, the maximum obtainable oxygen surface coverage is lower (resulting in a lower conversion) when nitrous oxide is used as an oxidant instead of (di)oxygen and as a result of the lower oxygen coverage the fraction of active oxyradicals in the total amount of adsorbed oxygen is also lower, which results in a lower epoxidation selectivity.

An explanation for the extremely low activity for the silver-gold alloy catalysts was not found. The production of trace amounts of acrolein by these catalysts, however, confirms that isolated silver-sites were present on the silver-gold catalysts. This conclusion can be drawn since, as demonstrated by Geenen et al. [1], molecular oxygen adsorbed on an isolated silver-site produces acrolein instead of propene oxide. To accurately study the potential of this type of catalyst, it will, however, be necessary to create catalysts with a higher activity.

**Transient experiments**

Both ethene and propene produce only trace amounts of epoxide when the epoxidation is carried out in the Multitrack system. The low selectivity can be explained by the oxyradical mechanism [chapter 5, Carter and Goddard [3]]. The oxygen surface coverage on the catalyst in the Multitrack system is low, and as a result very few active oxyradical species will be present. This is in agreement with the ethene- and propene oxide in Figures 1 and 2 being produced before the bulk of the carbon dioxide is produced. Similar experiments with ethene by Gleaves et al. [4] in the TAP system also showed ethene oxide being produced before carbon dioxide. The production of epoxide in advance to the combustion products can be easily explained. When the alkene pulse arrives at the catalyst bed, initially the oxygen surface coverage on the silver catalyst is relatively high, therefore, producing some epoxide. When some reaction has occurred the oxygen surface coverage drops and, therefore, also the number of oxyradicals drops. As a result the primary reaction product is the epoxide and the secondary product carbon dioxide. A conclusion that can be drawn from this, is that it is important to have sufficient oxygen present in the gas stream, when ethene (or propene) is epoxidized, since only in that case a large number of oxyradicals will be present on the catalyst. As in most experiments
performed in the flow reactor set-up, a 100% oxygen conversion was reached, the oxygen coverage on the catalyst (at least near the exit of the reactor) is relatively low. The number of oxyradicals on the catalyst will, therefore, be relatively low and the selectivity as a result less than optimal. An increase in oxygen concentration in the reactor feed, however, is not attractive, since this will result in the reactor operating within the explosion limits of the gas mixture, which is, of course, not recommended. A suggestion for a more selective use of the same catalyst, can be found in the use of a two stage reactor concept. In one reactor the catalyst then is fully loaded with oxygen, to obtain a maximum number of active oxyradicals on the catalyst. In the second reactor (or reactor section) the alkene feed is sent to the catalyst, and the epoxide is produced. In this reactor care should be taken that only a small portion of the oxygen is removed from the catalyst, since in that case the active oxyradicals can produce the epoxide, whereas the other (non-selective) oxygen atoms remain behind on the catalyst. It should be noted, however, that in commercial ethene epoxidation the process is usually operated at low ethene conversions (10%) and that the oxygen conversion is less than 100%. As a result the oxygen coverage on the catalyst will be higher than in the flow experiments performed in this study, and as a result more (selective) oxyradicals will be present. The economic advantage of operating a more complex two-stage process to possibly obtain a higher selectivity is, therefore, a priori not clear.

In the Multitrack experiments no epoxide could be detected during the oxygen pulses in the continuous cycles of alternate oxygen and alkene pulses. This is also in agreement with the oxyradical mechanism, since this involves the reaction of the alkene with an adsorbed oxyradical: when the oxygen pulse is given, the catalyst only contains adsorbed alkene and a reaction using the oxyradical mechanism is impossible. The only visible reaction product after the oxygen pulse is given, therefore, is carbon dioxide. The small pulse pulse-response of m/e=28 during the oxygen pulse in the ethene epoxidation (Figure 1), most likely is a small amount of ethene being driven from the surface by oxygen.

Although during the epoxidation experiments ¹⁸O₂ was used, the oxidation products contained relatively large amounts of ¹⁶O. This amount is more than can be explained by leaks in the vacuum system or by ¹⁶O contamination of the ¹⁸O₂ used. The most likely explanation is an exchange within the catalyst between freshly added ¹⁸O and silver-subsurface ¹⁶O and/or oxygen exchange with the alumina support material. Since the amount of catalyst is extremely large compared to the gas pulse size, this exchange can occur over an extremely long period (over 100000 pulses, assuming a 1% oxygen consumption per pulse). Since the total amount of gas pulses given to the catalyst during the complete range of epoxidation experiments is approximately 1000, it can be concluded that the composition of the bulk of subsurface oxygen did not change significantly during the experiments. The ¹⁶O visible in the reaction products can be used to get an impression of the rate of oxygen exchange between surface and subsurface oxygen. The exchange appears to be fast considering the relatively large amounts of C⁶O⁴O and C⁵O₂ produced. Epoxides
containing $^{18}$O could not be detected. However, the formation of $^{18}$O-containing epoxides cannot be ruled out completely, since measurement of the most sensitive m/e ratio for a $^{18}$O-containing epoxide (29) was not possible, because this ratio contains a secondary signal of the large amount of ethene or propene present.

Conclusions

Both the steady-state flow experiments and the transient Multitrack experiments confirm the oxyradical mechanism for the epoxidation of alkenes over a silver catalyst. This oxyradical mechanism is able to explain the lower epoxidation selectivity when nitrous oxide is used as an oxidant and the order in which the reaction products are produced in Multitrack experiments (first epoxide then carbon dioxide). Although Multitrack could be used to gain some information on the epoxidation over a silver catalyst, to accurately investigate this reaction the sensitivity of the Multitrack system will have to be improved, for example by moving the mass spectrometers closer to the reactor exit.

The low epoxidation selectivity over a silver catalyst of propene compared to ethene can be explained by the reactivity of the $\gamma$-hydrogen atoms of propene. Substitution of these hydrogen atoms by methyl-groups results in a higher epoxidation selectivity.

Although the silver-gold alloy catalysts prepared had an extremely low activity, the creation of isolated silver sites in these catalysts could be confirmed by the production of trace amounts of acrolein in the partial oxidation of propene by these catalysts.

References

Chapter 7

Propene Epoxidation

using Dispersed Gold on Titania Catalysts

Summary

Highly dispersed gold catalysts on a titanium containing support can be used for the low-temperature direct epoxidation of propene. These catalysts are able to very selectively (>99 %) epoxidize propene using an hydrogen-oxygen mixture, however, the propene conversion remains low (<2 %). The mode of operation of the catalyst, based on the close cooperation between gold and support material, is discussed. Major challenges for the catalysts developed so far remain to be solved: firstly, the efficiency with which the catalyst utilizes hydrogen has to be improved, since a high hydrogen efficiency is crucial for the process economics, and secondly, the adsorption strength and subsequent polymerization of propene oxide has to be reduced for a successful application of this type of catalyst.
Propene Epoxidation using Dispersed Gold on Titania Catalysts

Introduction

Highly disperse gold-on-titania catalysts have been the focus of many recent studies on the low temperature CO oxidation [1]. The catalytic low temperature CO oxidation is mainly of interest for maintaining habitable conditions in spacecraft. The same gold-on-titania catalysts have more recently been used to very selectively epoxidize propene using a mixture of hydrogen and oxygen [2]. In this chapter an attempt will be made to clarify the mode of operation of this type of catalyst and to improve the low conversions (maximum 2%) reported so far.

Gold is almost never used as a catalyst, since it is inert in most reactions. In the CO oxidation reaction, gold by itself is inactive [3]. However, when gold is deposited in the form of small particles (typically < 20 nm) on a number of (by themselves also inert) metal oxide support materials (e.g. α-Fe₂O₃, Co₃O₄, NiO, ZrO₂, or TiO₂) a very active CO oxidation catalyst is created [4,5]. Some of these catalysts are even able to obtain relatively high CO combustion rates at temperatures as low as 200 K [4]. The deposition of the same metal oxides on gold powder also results in an active CO oxidation catalyst [3].

At a temperature of 300 K no measurable adsorption of oxygen on gold occurs, whereas carbon monoxide only adsorbs weakly. On the other hand, on titania (or one of the other active supports) both oxygen and carbon monoxide adsorb [3]. The mechanism for the reaction, which has most recently been proposed, is the adsorption of CO at the gold particles, with the adsorption of oxygen at the titania, followed by the reaction at the gold-titania interface [3,6]. Considering the low oxygen adsorption on gold and the fact this catalyst is active, probably due to a phase cooperation between titania and gold, this mechanism is most likely.

The mechanism of the epoxidation of propene over gold on titania has not been solved. Based on the CO-oxidation mechanism on this type of catalyst, it, however, is to be expected that the oxygen will be adsorbing on titanium sites. The phase cooperation suggests that then either propene or hydrogen adsorbs on the gold. The presence of both hydrogen and oxygen next to propene in the reaction mixture is an indication for two possible mechanisms. The first possibility is that part of the catalyst reacts with molecular oxygen, followed by a reaction with propene to produce propene oxide plus the catalyst, still having an excess of one oxygen atom. This excess oxygen atom is subsequently removed by hydrogen to produce water plus the catalyst in its initial state. The second possibility for a reaction mechanism of this type of catalyst for the epoxidation of propene is that in some manner a hydroperoxide-like compound is produced by the gold on the catalyst. Titanium silicalite-1 (TS-1) is an excellent propene epoxidation catalyst, when hydrogen peroxide is used as oxidant [7]. The active species in the TS-1 zeolite is titanium [8]. In fact titanium can also be used as a catalyst in epoxidation reactions without the TS-1 structure, both in homogeneous [9] and heterogeneous catalysis [10]. A likely suggestion for the mechanism then is that (di)oxyg en adsorbs non-dissociatively on the titanium, whereas hydrogen adsorbs dissociatively on gold. Via a spillover
mechanism single hydrogen atoms are transferred from the gold to the oxygen molecule on titanium, creating a hydroperoxide-like compound, similar to the active titanium hydroperoxo species in the epoxidation of lower alkenes over TS-1 using hydrogen peroxide [8]. This hydroperoxide is able to react with propene, producing propene oxide, plus a hydroxyl-group on the titanium. A second hydrogen atom subsequently is transferred from the gold to this hydroxyl-group, producing water and so completing the catalytic cycle. The two suggested reaction mechanisms are schematically shown in Figure 1.

![Diagram](image)

**Figure 1.**
Two possible mechanism for the dispersed gold on titania catalysts. A: first mechanism possible, B: second possible mechanism

The crucial aspect of gold in both proposed mechanisms is its inability to dissociate (di)oxygen, while gold is able to dissociatively adsorb (di)hydrogen. The ability to dissociate (di)oxygen would catalyze the undesired combustion of hydrogen (and possibly of propene and propene oxide).

The aim in this study is to investigate the mode of operation of gold-on-titania catalysts and to try to improve their performance. Since the catalyst is based on the cooperation between gold and titanium an important aspect can be the gold dispersion on the support, since a higher gold dispersion results in a larger contact area between gold and titanium. Because the support material is suggested to be an active part of the catalyst, an attempt will be made to find a more active support material. A promising support material could be titanium silicalite-1, especially in view of the possibility of a peroxide intermediate taking part in the reaction and the high activity of TS-1 in the epoxidation of propene using hydrogen peroxide.
Propene Epoxidation using Dispersed Gold on Titania Catalysts

Experimental

Catalyst performance testing

Propene epoxidation

The steady-state epoxidation experiments were performed in a flow set-up. In this setup the reactant gases, nitrogen (70 vol.%), oxygen (10 vol.%), hydrogen (10 vol.%), and propene (10 vol.%), were continuously fed by means of mass flow controllers (maximum flow rate 100 Nmol/min). The fixed-bed reactor used was a 10 ml stainless-steel reactor, placed in an oven (773 K maximum temperature).

The analysis of the reaction products was performed using an automated sampling gas chromatograph, analyzing a gas sample every 10 minutes. The column used for the analysis was a Rescom FFAP 0.312 mm diameter, 25 m length capillary column, operated at 323 K with helium as carrier-gas. A flame ionization detector (FID) was used for the analysis. This configuration was able to separate all oxygenated organic components relevant in this study, hydrocarbons were not separable since they all had the same residence time as the carrier gas. The sensitivity of the gas chromatograph towards propene and the major reaction products was determined using calibration mixtures. Since the complex combustion products (CO and CO$_2$) could not be identified using the gas chromatograph, a non-dispersive infrared (NDIR) detector was used after the sample valve of the chromatograph, measuring both the concentrations of carbon dioxide and carbon monoxide. The two signals from the NDIR and the temperature in the reactor were continuously recorded using a personal computer. Since water is also present as a combustion product and water will disturb the operation of the NDIR, a Permapure membrane drier was used to remove the water from the gas stream in front of the NDIR. To prevent condensation in the tubing of the set-up of reaction products, all tubing up to the NDIR detector was heated to 373 K. After the NDIR detector the gas was either directly vented or sent into a gas sampling cylinder, to allow for a post-run more detailed analysis, for example using GC-MS. To determine the hydrogen and oxygen consumption in the reactor, gas samples were taken with a gas syringe through a septum located immediately after the reactor. These samples were then injected into a different gas chromatograph with a 13X column and a TCD (Thermal Conductivity) detector to determine the hydrogen : oxygen : nitrogen ratio, from which the hydrogen and oxygen consumption could be calculated.

The propene-epoxidation performance of one of the catalysts was tested at a longer gas space velocity in a stirred-batch reactor. A gas mixture of an identical composition as used in the flow experiments was put into this reactor (a 300 ml autoclave) at a slightly elevated pressure (1.5 bara). Into the autoclave 1 gram of catalyst was placed. The gas in the autoclave was well mixed and brought in good contact with the catalyst using an impeller (600 rpm mixing rate). Periodically gas samples were taken through a septum using a gas syringe for analysis in the same gas chromatographs used for the steady-state flow experiments.
CO oxidation

The performance of some of the dispersed gold catalysts was tested for the oxidation of carbon monoxide. The reason for conducting these experiments was to establish if a link exists between the CO oxidation activity and the propene epoxidation activity. Since in both reactions the catalyst activity is possibly set by the spillover rate (of CO for the CO oxidation, or of hydrogen-atoms for the epoxidation of propene), the existence of a link in activity between the two reactions in principle might be possible. If this relation would be found, then this would mean that the large amount of research into low temperature CO oxidation catalysts based on dispersed gold systems could be utilized directly for improving the direct propene-epoxidation catalyst.

The CO oxidation performance tests were carried out using a six-flow reactor system, in which the reaction is examined simultaneously for five catalysts and one blank under identical conditions. The analysis section switches automatically between the six reactors in the system. The CO oxidation was measured from 300 to 800 K for 60 mg catalyst samples in a 300 Nml/min gas stream of 1000 ppm CO with 20 % O₂ in argon. The CO and CO₂ concentrations were measured using an NDIR infrared detector.

Synthesis of Titanium Silicalite-1

Two different syntheses were used successfully (and reproducibly) for the preparation of TS-1. Both were aimed to obtain TS-1 with a Si/Ti ratio of 33. Since it is crucial for the synthesis to have no alkali metals present, both syntheses were performed in PE containers, the water used in the syntheses was doubly distilled.

In the first synthesis 1.75 g of 1,6-diaminohexane (Fluka >99 %) was dissolved in 40 ml of water, to which 3 g of silica (Degussa A 200 Aerosil) was added [11]. The mixture was stirred vigorously. 510 µl of tetrabutyl-orthotitanate (TBOT, Aldrich 97 %) was dissolved in 10 ml of dry isopropanol (Fluka, <0.005 % H₂O), which was slowly added to the silica, after which the mixture was stirred for another 30 minutes. Subsequently 1.33 g of TPA-Br (tetrapropylammoniumbromide, Fluka >98 %) in 25 ml of water was slowly added, producing a gel-like substance. The mixture was heated for 3 hours to 353 K to evaporate the alcohol. The mixture was then placed into a rotating Teflon-lined autoclave to crystallize at 453 K for 5 days. The solid from the autoclave was filtrated and washed 3 times with distilled water and dried for 2 hours at 393 K. The solid was calcined for 10 hours at 803 K. The TS-1 from this synthesis will be called TS-1a.

In the second synthesis (producing sample TS-1b) 23 g of tetraethylorthosilicate (TEOS, Aldrich 98 %) was stirred, while 12.8 g of TPA-OH (tetrapropylammoniumhydroxide, Aldrich 40 w% solution) was added [12]. 1.1 g of TBOT was dissolved in 5 gram of dry isopropanol and added slowly to the TEOS mixture, producing a white mixture. After 15 minutes of mixing, another 4.7 g of TPA-OH solution was slowly added. The isopropanol was removed by heating the solution to 353 K for 3 hours. To the gel obtained 35 ml of water was added and the
mixture was transferred into a Teflon-lined autoclave. The autoclave was heated to 443 K for 1 day to facilitate the crystallization process. The crystals obtained were filtrated and washed with distilled water. The crystals were dried in air for 5 hours at 373 K, followed by calcination at 773 K for 5 hours.

Apart from the two TS-1 samples synthesized, two other samples of TS-1 were used for the preparation of the catalysts. These samples were obtained from the Department of Organic Chemistry and Catalysis of the Delft University of Technology. These TS-1 samples contained 1.4 and 2.0 w% of Ti, the zeolitic structure of these samples was confirmed by XRD. These samples will be referred to as TS-1c and TS-1d.

As a comparison for the TS-1 catalyst as support, also a dispersed titania on silica support material for the gold was prepared. The aim of this catalyst was to determine whether a change in catalytic performance of a TS-1 based catalyst compared to an amorphous titania based catalyst would be the cause of the zeolite structure or by a interaction between silica-titania and gold. Since the aim was to prepare a dispersed titania on silica, it was decided to deposit 0.1 monolayer of titania on the silica support, according to the method described by Rajadyaksha et al. [14]. 220 μl of TEOT (tert-eaethyl-orthotitanate) was dissolved in 90 ml of dry isopropanol, to which the silica support (Aldrich Davisl 646, 290 m²/g) was added. The isopropanol was evaporated in a rotating vacuum evaporator at 333 K. The catalyst support was dried in air for 2 hours, after which it was calcined at 873 K for 2 hours.

**Catalyst preparation**

The gold-on-titania catalysts were prepared by a number of different impregnation methods on different titanium containing supports. The standard support material for the catalysts was Degussa P-25 titania (primarily anatase, surface area approximately 50 m²/g). Other catalysts were prepared on different samples of TS-1 (titanium silicalite-1 zeolite), titania supported on silica, and, as references for the function of titanium, on silica (Aldrich Davisl 646, 290 m²/g) and on γ-alumina (Akzo Ketjen 000-3E, 270 m²/g). The preparation of the titania on silica and TS-1 samples is discussed in a separate paragraph.

The gold precursors used for the impregnations were gold(III)chloride (Aldrich 99.99 %) and hydrochloroauric acid (Aldrich HAuCl₃·3 H₂O >49 % Au). The amount of gold impregnated on the supports was kept constant at 1 w%. The impregnation of the gold on the support was done in a number of different manners:

1. Incipient wetness impregnation of hydrochloroauric acid, followed by drying at 363 K;
2. ‘Wet’ impregnation with hydrochloroauric acid in water (approximately 10 ml per gram of support) of which the pH was raised to a value of 10 using ammonia, followed by evaporation of the water using a rotating vacuum evaporator [1];
3. Sodium hydroxide was added to a hydrochloroauric acid solution (approximately 10 ml per gram of support) until a pH value of 9 was reached, after which the
support was added. The slurry obtained was stirred at 343 K for 1 hour, after which it was filtered and dried at 363 K [13];
4. The support is dispersed in water (approximately 10 ml per gram of support) to which ammonia is added to raise the pH to a value between 9 and 10. Over a period of two hours the required amount of gold (in the form of AuCl₃ dissolved in water) is added dropwise to the support under vigorous stirring. The mixture is stirred for another half an hour after which it is filtrated and washed two times with distilled water. The catalyst is dried over calcium chloride in a dissiccator (atmospheric) [1].

The thus obtained catalysts were activated in a variety of manners:
a. Calcination for 4 hours at 673 K;
b. Heat treatment in vacuum for 4 hours at 673 K;
c. Calcination for 3 hours at 673 K, followed by reduction in 40 vol.% hydrogen in nitrogen at 573 K for 3 hours;
d. Calcination for 4 hours at 773 K;
e. Dried only in vacuum for 2 hours.

In this chapter the manner in which a specific catalyst has been prepared will be referred to by using the number + letter for impregnation + activation (e.g. gold on titania 1a for a gold on titania catalyst prepared by incipient wetness impregnation calcined for 4 hours at 673 K). The catalysts prepared and their colors are given in Table 1.

<table>
<thead>
<tr>
<th>Support</th>
<th>Preparation method</th>
<th>Activation</th>
<th>Color</th>
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</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>4</td>
<td>a</td>
<td>Grayish blue</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1</td>
<td>c</td>
<td>Light blue</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2</td>
<td>c</td>
<td>Pinkish blue</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3</td>
<td>a</td>
<td>Dark blue</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3</td>
<td>b</td>
<td>Purplish blue</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3</td>
<td>e</td>
<td>gray</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4</td>
<td>a</td>
<td>purplish blue</td>
</tr>
<tr>
<td>TS-1a</td>
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<td>a</td>
<td>purplish pink</td>
</tr>
<tr>
<td>TS-1b</td>
<td>4</td>
<td>d</td>
<td>purple</td>
</tr>
<tr>
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<td>a</td>
<td>pinkish purple</td>
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<tr>
<td>TS-1d</td>
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<td>grayish pink</td>
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<tr>
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<td>reddish brown</td>
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<td>TiO₂ supported on SiO₂</td>
<td>4</td>
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<td>Bordeaux red</td>
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Propene Epoxidation using Dispersed Gold on Titania Catalysts

Catalyst Analysis

The catalysts and supports used have been analyzed in a variety of different manners. These methods will not be discussed in detail. only the technique and the aim of the analysis will be mentioned.

TS-1 samples and supported gold catalyst were examined using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) to determine the dispersion of the gold on the catalysts and identify whether the zeolites prepared were crystalline. With the SEM analysis gold particles could not be identified directly due to the low resolution of the system. By creating an image of the backscattered electrons, the gold particles could be identified. EDX (Energy Dispersive analysis of X-rays) was used with both SEM and TEM to identify the presence of gold on the catalysts and the presence of titanium in the TS-1 samples prepared.

The nature of the TS-1 samples prepared was also checked using XRD (X-ray diffraction) to examine the bulk crystals prepared, using DRIFT (Diffuse Reflection Infra-red Fourier Transform) spectroscopy to identify the nature of the titanium in the zeolite, and using DREAS (Diffuse Reflection Adsorption Spectroscopy) to check whether the titanium in the zeolite had a tetrahedral surrounding (compared to the octahedral surrounding in amorphous titania). DREAS was also used for the supported gold catalysts in an attempt to establish a link between the color of the catalyst and its visible-light adsorption (and the gold particle size determined using SEM/TEM). The Si:Ti ratio of TS-1 was determined using ICP-AAS (Inductive Coupled Plasma – Atom Adsorption Spectroscopy).

The presence of adsorbed components on a spent catalyst was determined using thermogravimmetrical analysis (TGA) on the catalyst in air.

Results

Propene epoxidation

In the flow experiments a number of catalysts proved to be completely inactive in the epoxidation of propene. These catalysts were gold supported on γ-alumina, silica, TS-1a, and gold on titania synthesized using methods 1c, 2c, 3a and 3e. Only at temperatures above 473 K, these catalysts showed some propene conversion, the products being CO, CO₂, ethanal, acetone, propanal, and acrolein. At 473 K none of these catalysts showed a propene conversion higher than 1%.

Some of the results obtained using active epoxidation catalysts are summarized in Table 2. The catalysts summarized in this table all have been prepared by method 4a. Gold on titania prepared by method 2c had an activity (and selectivity) compared to the same catalyst prepared by method 4a.
Table 2.
Overview performance of supported gold catalysts active in the epoxidation of propene. All catalysts prepared by synthesis method 4a.

<table>
<thead>
<tr>
<th>Support</th>
<th>Temperature (K)</th>
<th>Conversion (%)</th>
<th>Selectivity* (%)</th>
<th>Activity (mg(<em>{\text{propene}})/g(</em>{\text{cat}})/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>323</td>
<td>0.8</td>
<td>&gt;99</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>1.3</td>
<td>&gt;99</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>363</td>
<td>0.5</td>
<td>20</td>
<td>3.3</td>
</tr>
<tr>
<td>TS-1b</td>
<td>398</td>
<td>0.5</td>
<td>&gt;99</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>0.6</td>
<td>&gt;99</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>1.0</td>
<td>98</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>548</td>
<td>1.4</td>
<td>25</td>
<td>15.3</td>
</tr>
<tr>
<td>TS-1c</td>
<td>343</td>
<td>0.3</td>
<td>&gt;99</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.5</td>
<td>&gt;99</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>0.8</td>
<td>&gt;99</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>1.1</td>
<td>95</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>448</td>
<td>1.5</td>
<td>78</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>2.0</td>
<td>50</td>
<td>21.4</td>
</tr>
<tr>
<td>TS-1d</td>
<td>423</td>
<td>0.6</td>
<td>&gt;99</td>
<td>6.3</td>
</tr>
<tr>
<td>TiO(_2) on SiO(_2)</td>
<td>373</td>
<td>1.0</td>
<td>&gt;99</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>1.5</td>
<td>80</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>448</td>
<td>4.0</td>
<td>10</td>
<td>26.6</td>
</tr>
</tbody>
</table>

*In the discussion on the epoxidation yield limitation a note will be made on these selectivities.

In Table 2 it can be seen that it is possible to epoxidize propene selectively at low temperature. A modest increase in temperature results in a higher conversion without a decreasing selectivity, a further increase in temperature results in a loss in selectivity as well. At low temperature (<350 K) the activity of the TS-1 supported catalysts and the titania on silica catalyst (the dispersed titanium catalysts) is lower than the activity of titania supported catalysts. By increasing the temperature the dispersed titanium catalysts can obtain somewhat higher activities than is possible with the titania supported catalysts, without a loss in selectivity. The products produced at high temperatures, when the selectivity is lower than 100 %, are for all catalysts (similar to the product of the inactive catalysts) CO, CO\(_2\), ethanol, acetone, propanal, and acrolein.

A disadvantage of the titania supported catalysts, compared to the catalysts on a dispersed titanium support material such as TS-1, is the tendency to deactivate. An increase in reaction temperature above 360 K results in a rapid deactivation of the catalyst, as it can be observed from the low activity of the titania supported catalyst at 363 K in Table 2. Also at a low reaction temperature titania supported catalysts deactivate. At a reaction temperature of 323 K these catalysts lost approximately half
their activity in 2 hours reaction time. The dispersed titanium catalysts showed no deactivation whatsoever.

In Table 2 it can be also seen that the propene oxide yields in none of the experiments rose above 1.3 %. It is remarkable that an increase in temperature during an experiment momentarily resulted in higher propene oxide concentrations in the gas stream leaving the reactor, which is demonstrated in the experiment shown in Figure 2. These higher concentrations, however, are probably not caused by a short time higher activity of the catalyst, but by desorption of propene oxide from the catalyst as a result of lower equilibrium constant for adsorption at a higher temperature.

![Graph](image)

**Figure 2.**
Propene oxide yield over 1 wt.% gold on TS-1c catalyst during experiment with stepwise increases in reaction temperature. (0.3 g catalyst, 33 Nml/min flow, 10 vol.% propene, 10 vol. % \(H_2\), 10 vol. % \(O_2\), balance \(N_2\)).

Attempts to obtain higher propene oxide yields by using either larger amounts of catalyst or lower gas flows, were only partly successful. In Figure 3 the catalyst activity for a TS-1 supported catalyst is shown. The expected decreasing yield for a higher WHSV (weight hourly space velocity) value is clearly visible. It should be noted, that the decreasing propene oxide yield at a higher WHSV is a result of putting the yield as a percentage of the propene feed, the absolute amount of propene oxide produced does increase with the WHSV. The increasing propene oxide yield at low WHSV values allows for the possibility to reach a high propene oxide yield, if the contact time is made sufficiently long or the amount of catalyst is made large enough. Limitations in the amounts of catalyst available and to the flow set-up, however, did not allow for these experiments to be performed under steady-
Figure 3.
Propene oxide yield for the epoxidation of propene over gold supported on TS-1d as a function of the WHSV in steady-state flow experiments (423 K, 10 vol.% propene, 10 vol. H₂, 10 vol.% O₂, balance N₂).

state conditions. Therefore, these experiments have been performed batchwise in a stirred-autoclave reactor.

The propene epoxidation over gold on titania (4a) measured in a batch reactor did not result in higher propene oxide yields after longer reaction times (higher space velocity) than the reaction times used in the flow experiments. The first gas sample taken from the reactor after 10 minutes of reaction time (WHSV ca. 2) showed a propene oxide yield of approximately 1.2%. The amount of propene oxide in the autoclave remained constant for approximately 2 hours, after which the concentration started to drop slowly. To test the hypothesis the catalyst might be decomposing (or polymerizing) propene oxide, and thereby limiting the amount of propene oxide in the autoclave, experiments were performed in which approximately 50 μl of liquid propene oxide was injected into the autoclave reactor. The propene oxide concentrations measured in these experiments are shown in Figure 4. In this figure, it can be seen that propene oxide ‘disappears’. By measuring gas chromatograms for longer periods of time and at higher column temperatures, it was determined that small amounts of dioxanes and heavier hydrocarbons (> C₆) were being produced. These products could not be detected in the flow experiments. It cannot, however, be ruled out that these compounds were also produced in the flow experiments, but were below the detection limit of the gas chromatograph used, since the amount of propene oxide in the gas stream under reaction conditions was over 100 times less than the propene oxide concentration in the autoclave after the injection of liquid propene oxide.
Propene Oxide concentrations in stirred autoclave reactor after injection of 50 μl of propene oxide at different temperatures (1 g of 1 wt.% Au on TiO₂ catalyst type 4a, pressure: 1.7 bar, gas composition: 10 % propene, 10 % H₂, 10 % O₂ in nitrogen).

Table 3.
Overview of the oxygen and hydrogen efficiencies in the epoxidation reaction of propene over supported gold catalysts (based on a stoichiometric reaction to produce propene oxide and water).

<table>
<thead>
<tr>
<th>Catalyst Support</th>
<th>WHSV (g/g/h)</th>
<th>T (K)</th>
<th>propene conv. (%)</th>
<th>Epoxidn. Selec. (%)</th>
<th>Hydrogen eff. (%)</th>
<th>oxygen eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1d</td>
<td>1.2</td>
<td>423</td>
<td>1.1</td>
<td>&gt;99</td>
<td>5.0</td>
<td>7.9</td>
</tr>
<tr>
<td>TS-1d</td>
<td>7.9</td>
<td>423</td>
<td>0.6</td>
<td>&gt;99</td>
<td>5.5</td>
<td>12.8</td>
</tr>
<tr>
<td>TiO₂ (4a)</td>
<td>4.3</td>
<td>323</td>
<td>0.8</td>
<td>&gt;99</td>
<td>22.8</td>
<td>53.3</td>
</tr>
<tr>
<td>TiO₂ (4a)</td>
<td>4.3</td>
<td>343</td>
<td>0.5*</td>
<td>&gt;99</td>
<td>29.4</td>
<td>45.4</td>
</tr>
<tr>
<td>TiO₂ (4a)</td>
<td>4.3</td>
<td>348</td>
<td>0.9</td>
<td>&gt;99</td>
<td>26.2</td>
<td>41.0</td>
</tr>
</tbody>
</table>

*:catalyst was somewhat deactivated
Hydrogen and oxygen efficiency

For some measurements the hydrogen and oxygen consumption during the reaction was determined, since not only the epoxidation selectivity is an important factor, but also the hydrogen and oxygen efficiencies are just as important for the process economics. The results of these measurements are summarized in Table 3.

CO oxidation

The most important results of the CO oxidation experiments are given in Figure 5, in which the CO conversions for the different catalysts are shown as a function of the reaction temperature. The conversion measured in the blank reactor was small compared to the conversions of the catalysts (less than 1 % under 500 K, raising to 10 % at 800 K). The conversion that was observed in the blank experiments is most likely caused by a contamination on the quartz reactor or on the thermocouple in the reactor. A duplo experiment performed with one of the gold-on-TS-1 catalysts in a second run in a different reactor produced identical results for both experiments.

A remarkable observation that can be made in Figure 5 is the low activity of the TS-1 supported catalysts. Furthermore, a large difference in reactivity between comparable TS-1 samples is visible. It is also clear that catalysts inactive for the propene epoxidation can be active for the CO oxidation (such as in the case for gold-on-silica, gold-on-γ-alumina, and vacuum calcined gold-on-titania).

Figure 5.
CO conversion versus temperature for a selection of supported gold catalysts (supports mentioned in legend, 50 mg catalyst, gas flow rate 300 Nml/min containing 1000 ppm CO, 20 vol.% O₂, balance Ar).
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Catalyst characterization

Titanium silicalite-1

The TS-1 from both syntheses yielded crystals, which were visually very different. TS-1a consisted of large 35 μm coffin shape white crystals. TS-1b looked like a very fine white powder, which under a light microscope had no clear structure. SEM micrographs of both samples are given in Figure 6. TS-1b consisted of very small crystallites (10 nm) agglomerated to form 150 nm particles. The SEM micrographs of the samples TS-1c and TS-1d resembled those of TS-1b. Since the large coffin shaped crystals of sample TS-1a gave the suspicion that the crystals might be pure silicalite, the composition of this zeolite was analyzed by ICP-AAS. This analysis confirmed the presence of 0.95 w% of titanium in the crystals. Although this amount of titanium is less than the amount that was aimed at during the synthesis (2.3 w%), this amount does qualify the sample to be titanium silicalite-1. EDX measurements on the crystals confirmed the presence of titanium within the zeolitic structure in both the TS-1 samples synthesized.

![SEM micrographs of two samples of TS-1 synthesized. A: TS-1a, B: TS-1b](image)

Figure 6.
SEM micrographs of two samples of TS-1 synthesized. A: TS-1a, B: TS-1b

The XRD spectra of the two TS-1 samples prepared are given in Figure 7. As a reference the diffractogram of silicalite-1 is given in the same figure. A characteristic of TS-1 compared to silicalite-1, is the single peak (reflection) at 2θ=24.4 of TS-1, where silicalite-1 has a double reflection [15]. The single reflection in the X-ray refractogram in Figure 7 of both the TS-1 samples is clearly visible, indicating both samples are indeed TS-1.

The DRIFT spectra of TS-1a, TS-1b, and TS-1c are given in Figure 8. In this figure the absorption band at 960 cm<sup>-1</sup> is visible. This band is attributed to the presence of titanium in the zeolite framework [16]. Reference DRIFT spectra were measured for silicalite-1, amorphous silica, and amorphous titania. None of these spectra showed an absorbance band at 960 cm<sup>-1</sup>
Figure 7.
XRD spectra of TS-1 samples synthesized, together with a silicalite-1 reference sample.

Figure 8.
DRIFT spectra of TS-1 samples used for the synthesis of supported gold catalysts. The band at 960 cm\(^{-1}\) is a characteristic of TS-1.

The last analysis performed on the TS-1 samples is DREAS. The results of this analysis are shown in Figure 9, together with a measurement performed on amorphous titania. The presence of clustered (amorphous) titania in the zeolite sample would result in an absorbance below 30000 cm\(^{-1}\) [17, 18]. From Figure 9 it can be seen that no amorphous titania can be determined in any of the TS-1 samples.
Figure 9.
DREAS spectra of three TS-1 samples, compared to measurement of amorphous titania. Shown is the Kubelka-Munck function of the reflectance (correlated to absorbance).

Supported gold catalysts
A clear distinction could be made in the SEM micrographs of active gold on titania catalysts (e.g. 4a) and inactive catalysts (e.g. 1c). In active catalysts no gold particles were visible indicating that the gold particles present were below the detection limit of the system (< 20 nm), whereas relatively large (typically 100 nm, up to 500 nm) gold particles are visible in the inactive catalyst (Figure 10).

TEM micrographs were taken from the active catalyst, one of which is shown in Figure 11. The active catalyst was shown to be containing 3-10 nm large gold particles, homogeneously distributed across the titania surface. The micrographs did not show a difference in the size of the gold particles between a fresh and a spent catalyst, indicating that the catalyst deactivation is not caused by sintering of the gold particles.
Figure 10.
SEM micrograph of inactive gold supported on titania catalyst, synthesis type 1c. The small arrows point out 100 nm gold particles, the large arrow points out a 500 nm particle.

Figure 11.
TEM micrograph of gold supported on titania, synthesis type 4a.
Figure 12.
TEM micrograph of gold supported on TS-1c, synthesis type 4a. The gold particles are dark colored.

The size of the gold particles of the TS-1 with the very small crystals (TS-1b, c, and d) (3-15 nm) in the TEM micrographs shown in Figure 12 is not significantly larger than the size of the gold particles on titania. The gold particles on the large crystal TS-1a are 2-10 nm (Figure 13). A possible explanation for the inactivity of this type of TS-1 is visible in the same figure. The gold particles can be seen to be located only on the outside of the crystals, as can be clearly seen in this figure, since the micrograph is taken along one of the sides of the crystal, resulting in a large number of gold particles being visible along the right edge. The inactivity then could be explained by an inhomogeneous distribution of titania over the crystal. Since titania has a tendency to crystallize faster than silica, it is possible that the titanium is located more or less only inside the crystals, therefore, not being in contact with the gold particles. This hypothesis, however, could not be verified experimentally.

In Table 1 it can be seen that the colors of the catalysts synthesized varies significantly. Therefore, DREAS measurements have been performed with a number of these catalysts, in an attempt to establish a link between color and visible light reflectance (which obviously should be present), and the catalytic activity. The results of these measurements are given in Figure 14.
Figure 13.
TEM micrograph of gold supported on TS-1a crystals, the dark dots are gold particles.

Figure 14.
DREAS spectra of several dispersed gold catalysts. Shown is the reflection versus the visible light wavelength. The combination of the reflections can be related to the catalyst color.
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Thermogravimetrical analyses of spent and fresh gold on titania samples are given in Figure 15A. In the heat flux signal of the used catalyst two clear peaks are present, corresponding to an increased rate of mass loss. Since the peaks in the heat flux are positive, they correspond to a (exothermal) combustion of a residue (possibly polymerized propene oxide or coke) on the catalyst. The initial negative heat flux, with a decrease in sample mass, can be explained by desorption of water or other adsorbed components from the catalyst. The negative heat flux at high temperatures can be explained by sintering or recrystallization of the titania. A similar measurement performed with gold on TS-1 is shown in Figure 15B. In this case only the second of the two combustion peaks is present, indicating only one type of residue being present on this catalyst. Similar TGA measurements have been performed with gold on silica supported titania used in epoxidation experiments. These measurements also showed only one combustion peak, at the same temperature of approximately 600 K.

Discussion

Catalytic operation

In the introduction two possible mechanisms for the mode of operation of the dispersed gold on titania catalysts were mentioned: 1) the oxidation of propene by molecular oxygen adsorbed on titania, followed by the removal of a remaining oxygen atom on a titania site by hydrogen, most likely after adsorption of hydrogen on a gold particle; 2) adsorption of molecular oxygen on titania, after which via a spillover mechanism a gold particle donates a hydrogen atom to the adsorbed oxygen, to produce a peroxide-like compound, reacting with propene to produce propene oxide, after which a second hydrogen atom is donated to produce water.

Based on the experiments performed, it can be concluded that the second of these mechanisms (demonstrated in Figure 1B) is most likely, since the first mechanism should be able to produce propene oxide from a propene-oxygen only stream, although only for a short period of time. However, this behavior of the catalyst was not observed. Also the better performance of the TS-1 supported catalyst, compared to the titania supported catalysts is an indication that the second mechanism is more likely, since TS-1 is an excellent epoxidator when hydrogen peroxide is used as an oxidant.
Figure 15.
TGA profiles of fresh and spent samples of 1 wt.% Au on TiO₂ (A) and 1 wt.% Au on TS-1c (B). TGA analysis in air, heating rate 5 K/min, sample mass 30 mg.

Catalyst activity

Titanium is an essential factor in the use of a dispersed gold catalyst in the epoxidation of propene. Gold sponge and gold supported on silica or alumina had no epoxidation activity at all. Although in the CO oxidation using this type of catalysts the cooperation between gold and (titania) support is also important, the mode of operation of the catalyst is different for both reactions. This is clearly seen when the performance of gold on titania 3a is examined. This catalyst is very active
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in the CO oxidation, but almost inactive in the propene epoxidation. In general, vacuum heat treated catalysts (such as for gold on titania 3a) are reported to have a higher activity than (air) calcined catalysts [4], which is attributed to smaller gold particles as a result of the heat treatment in vacuum. A possible explanation for the inactivity of the vacuum heat-treated catalyst is that the catalyst undergoes a change in properties during calcination, for example in the surrounding of the titania. Tetrahedral surrounded titania is suggested to be the active species in the epoxidation reaction by peroxides [19], whereas octahedral titanium is inactive. Vacuum calcination might result in a decrease in tetrahedral titanium (or calcination in air might result in an increase), this can explain the difference in activity of similarly prepared, but differently calcined catalysts. The CO oxidation reaction then is less sensitive for the type of titanium, and, therefore, both catalysts are active for this reaction.

An explanation for the inactivity of the catalyst prepared by incipient wetness impregnation (1a) can be found, since the gold particle size of this catalyst is extremely large compared to the other catalysts. As a result the gold-titania contact surface is very small, and the catalyst, therefore, inactive, since contact between gold and titania is most likely essential for a spill-over mechanism.

Gold supported on TS-1 catalysts are active in the propene epoxidation, although the reaction temperature should be increased compared to gold on titania catalysts. A likely explanation for the need for a higher reaction temperature can be found in the significantly lower titanium content of the support material. Therefore, also the gold particles are in contact with far less titanium atoms. The smaller amounts of titanium atoms need a higher reaction temperature to reach an identical conversion. The same explanation also stands for the gold on silica supported titania catalyst. Also in this case the amount of titania is smaller, and each titanium atom has to be more active for a similar conversion. An explanation for the lower activities of the TS-1 supported catalysts in the CO oxidation reaction, compared to both the silica and titania supported catalysts, might be a lower adsorption of oxygen on the support material as a result of the zeolitic structure in which both titanium and silicon are incorporated. Diffusion limitations, which often slow down zeolite catalyzed reactions, are not likely to be the cause of the lower activity of the TS-1 supported catalysts, since the reaction probably takes place at (or near) the gold particles, which are located on the outside of the zeolite crystals.

The inactivity of TS-1a for the epoxidation of propene might be attributed to an inhomogeneous distribution of titanium across the zeolite crystals. Since titanium has the tendency to crystallize faster than silicon, it is possible that the large crystals consist only in the interior of TS-1, while the exterior is silicalite-1. As all gold particles are located on the outside of the crystals, this would result in the absence of an efficient phase cooperation between gold and titanium, and, therefore, result in an inactive catalyst. The fact that sample TS-1a is indeed TS-1 was, apart from the analyses performed, also checked by determining its propene epoxidizing activity in the liquid phase using hydrogen peroxide as oxidizing compound by the method

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described by Clerici et al. [7]. In these experiments sample TS-1a had a higher propene oxide production rate than sample TS-1c, indicating that the number of active titanium sites in sample TS-1a is higher, which supports the explanation of a low activity of the dispersed gold on TS-1a being caused by an inhomogeneous titanium distribution, since the active sites are definitely present.

The color of the supported gold catalysts (Table 1) is a result of the interaction between the small gold particles with the support. The intensity of the color is a measure for the size of gold particles, smaller particles result in a darker color. The absence of a color of the uncalcined catalyst can be explained by the gold on the support still being the precipitated gold oxide. Although the color of the catalysts matches the light reflection measured from these catalysts using DREAS (Figure 14), a relation between visible light reflection and catalytic activity was not found. The absence of such a relationship is most clear when the light reflection of either both titania (one active the other inactive in the epoxidation) supported catalysts or the active titania on silica supported gold and inactive silica supported gold are compared. Both pairs of catalysts have a similar light reflection and a very different catalytic behavior, making the color (except for the intensity as a measure of particle size) not useful to predict the catalyst performance.

Catalyst deactivation

Contrary to the TS-1 and titania on silica supported catalyst, the gold on titania catalysts deactivate significantly. This deactivation occurs slowly at a reaction temperature of 323 K, but fast above 350 K. An often occurring factor in deactivation is sintering of the active particles on a supported catalyst. The lack of activity for a catalyst with large gold particles, such as gold on titania 1c, seems to support the hypothesis of sintering being responsible for the deactivation of a titania supported catalyst. The change in particles size between a fresh and spent catalyst as observed from the TEM micrographs is, however, not of significance. Since the catalyst had prior to use been subjected to calcination at 673 K, it does not seem likely that deactivation would occur by sintering at a reaction temperature as low as 323 K.

A second explanation for the deactivation of the titania supported catalysts could be the deposition of a reaction product on the catalyst, either blocking the active gold sites, the titania sites, or the spillover pathway between these sites. The thermogravimetrical analysis of titania supported gold shows a combustion peak at 500 K. The TS-1 and silica supported titania subjected to identical TGA analyses, did not show this combustion peak. Since these catalysts do not deactivate, it is, therefore, likely that the deactivation of the titania supported catalysts is caused by the compound that is combusted at 500 K in TGA. This catalyst poisoning compound will probably be a polymer of either propene or propene oxide. It is not likely that the deactivation is caused by coke formation, since the combustion temperature is too low, and coke was not detected in the TEM (and linked EDX) analysis performed on the spent catalysts.
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The adsorbed components resulting in a combustion peak at 600 K in the TGA analysis are probably not the cause of any deactivation, since no deactivation was detected on the TS-1 and titania on silica catalysts. Furthermore, the size of this combustion peak is independent on the time-on-stream of the catalyst. Even the catalyst used in the stirred batch reactor, to which a large amount of propene oxide was added, did not show a larger combustion peak at 600 K. This indicates that the components that are combusted at this temperature, form rapidly when the catalyst is subjected to reaction conditions and do not hinder the catalyst operation. Possibly this peak can be attributed to adsorbed components on titanium sites not in contact with gold particles, which could explain the higher combustion temperature.

An explanation for the fact that the TS-1 and dispersed-Ti on silica catalyst do not show any significant deactivation might be that the deactivation occurs by a polymerization of a number of propene(oxide) molecules adsorbed on neighboring titanium-sites. Since the TS-1 and titania-on-silica supported catalyst have the titanium present in a dispersed form, polymerization between a large number of molecules is less likely. Some polymerization will also occur even on the dispersed titanium support materials (this was confirmed by the detection of small amounts of dioxanes in the batch-autoclave experiments), however, the smaller number of neighboring Ti-sites will result in smaller polymers (such as dioxane as propene oxide dimer), which are more likely to desorb from the catalyst than large polymers.

Apart from (polymerized) propene (oxide) being the cause of the deactivation of the catalysts, it could also be possible that the presence of water would have some influence on the catalyst. Therefore, experiments were performed in which water was added to the reaction mixture. In the first experiment water (10 vol.% in the gas phase) was added to the reaction mixture in a propene oxide decomposition experiment in the stirred autoclave reactor (similar to the experiments shown in Figure 4). The addition of water had no measurable influence on the propene oxide consumption rate in the reactor. In the second experiment a similar amount of water was added to the gas feed in a flow experiment. This experiment showed no measurable change in the propene oxide production after the water addition. From these experiments it can, therefore, be concluded the influence of water on catalyst or reaction is negligible.

Epoxidation yield limitation

The supported dispersed catalysts all had propene oxide yields of 1.5 % at maximum. Only a single report in literature shows a somewhat higher yield of 2 %, when a propene : hydrogen : oxygen : nitrogen mix of 5 : 40 : 10 : 45 is used [2]. Such a ‘high’ epoxide yield with this feed gas composition could not be reproduced, although identical conditions were aimed at. The fact that experiments performed in the stirred-autoclave reactor did not show higher epoxidation yields, is a key to the cause of the maximum obtainable yield of only 1-2 %. Two possible explanations come to mind for the limitation in the yield: product inhibition or product reactivity.
The experiments, in which propene oxide was injected into the stirred autoclave (Figure 4), clearly indicate that a sequential (polymerization) reaction of the propene oxide is the main cause of this limitation. This propene decomposition reaction is faster at a higher temperature, which indicates it is an activated process not only controlled by the propene oxide surface coverage, which is lower at a higher temperature. The polymerization of propene oxide was confirmed by the dioxanes and heavier hydrocarbons that were detected in the reaction mixture, after the propene oxide disappeared. Also the fact that the TGA analyses of the catalysts showed adsorbed hydrocarbons supports this view. This then could also imply that the selectivity of the catalysts might not be as high as it seems. Since an amount of (polymerized?) propene (oxide?) remains on the catalyst, the selectivity should be lower than 100 %. When only the gas stream leaving the reactor is analyzed, this might not be noticed. Since the propene consumption is small, it is impossible to determine the propene conversion accurately from the change in the propene area in the gas chromatograms.

From the difference in mass loss between the fresh and the used catalysts in the TGA analyses it can be estimated that the amount of the adsorbed components on the catalysts can be up to 1 % of the weight of the catalyst. From this amount, it can be estimated that this residue on the catalyst can be up to approximately 25 % of the propene conversion in a typical experiment. The selectivities given in Table 2, therefore, can be up to 25 % higher than the actual selectivities. On the other hand, if only propene oxide is adsorbed on the catalyst and if one is able to make this propene oxide desorb from the catalyst, both the propene oxide yield and selectivity would be somewhat higher.

Catalyst evaluation

Except for the epoxidation selectivity, one other very important aspect in the feasibility of application of the dispersed gold catalysts in the propene epoxidation is the efficiency of the catalyst for the use of hydrogen and oxygen. Low hydrogen (and to a lesser extent oxygen) efficiencies will make the application of this type of catalysts not realistic. In literature [2] relatively high hydrogen efficiencies of up to 30 % are reported. In this study a comparable hydrogen efficiency was found for the propene epoxidation over gold supported on titania. Experiments with gold supported on TS-1 yielded much lower (5 %) hydrogen efficiencies. An explanation for these lower efficiencies might be the higher reaction temperature used when epoxidizing with gold on TS-1, with as a result a higher rate of direct oxidation of hydrogen compared to the indirect oxidation in the epoxidation reaction. Since a high hydrogen efficiency is essential, it will, therefore, be necessary to prepare catalysts with an optimal titanium-gold interaction and active at a temperature as low as possible to minimize the direct oxidation of hydrogen.

Another cause for excess hydrogen consumption could be the hydrogenation of propene to propane. An analysis of the product gases using a gas chromatograph capable of separating propane and propene did not show any propane production.
This is in agreement with analyses reported by Haruta [20] which show that gold supported on titania is capable of hydrogenating propene to propane, but if the gold loading on the catalyst is smaller than 0.4 wt.%. Since all catalysts prepared in this study had a gold loading of 1 wt.%, no propene hydrogenation is expected to have occurred.

The aspect of a low conversion of the catalyst might not be solved straightforward, since the catalyst converts higher propene oxide concentrations into heavier compounds. Therefore, the application of this type of catalyst might have to depend on a technological solution to have the catalyst convert only small amounts of propene, and remove the product from the gas stream.

A possibility might lie in the observation that in the flow experiments performed a small (10 K) increase in temperature resulted in an increase in propene oxide concentration in the gas stream of up to a factor of 3, for approximately 10-15 minutes. This increase in propene oxide concentration was primarily caused by an increased rate of desorption of propene oxide from the catalyst as a result of the higher temperature. A strong propene oxide adsorption on the catalyst also explains the initially lower propene oxide concentration measured at the reactor exit, as is visible at the start of the experiment shown in Figure 2. Therefore, application of the catalyst in a two-stage reactor system (riser regenerator reactor, rotating monolith reactor, interconnected fluidized beds, etc.) might prove to produce good results. In one stage the propene oxide is produced (at low temperature) on the catalyst, while in the other stage the temperature is increased or pressure is decreased, and concentrated propene oxide is released. It could perhaps even be possible to separate the process into more steps, in which the formation of a peroxide-alike species on the catalyst is separated from the epoxidation reaction, or to separate the hydrogen and oxygen reaction with the catalyst in two reactors, to obtain safer operation conditions. A simpler reactor system in the form of a pressure- or temperature-swing reaction system might also be applied. In this situation the reactor is switched from propene oxide production to propene oxide release when the catalyst at the end of the reactor bed is 'saturated' with propene oxide (i.e. a breakthrough of propene oxide). Into these aspects, however, an additional research effort has to be made, as well as into the possibility that it might be possible to either block the propene oxide polymerization reaction on the catalyst or lower the propene oxide adsorption strength, and in that way design a catalyst that is able to obtain higher epoxidation yields.
Conclusions

Dispersed gold-on-titanium catalysts can be used to selectively epoxidize propene using a mixture of hydrogen and oxygen at low temperatures. Although this type of catalyst has many parallels to similar catalysts used for the low temperature CO oxidation, the activities for both reactions are not connected. The use of a dispersed titanium containing support material instead of pure titania results in a catalyst better resistant to deactivation and able to obtain slightly higher propene oxide yields, however, the reaction temperature for these catalysts needs to be higher.

The maximum propene oxide yields obtained with this type of catalysts remains low (less than 2 %). These low yields are a result of a polymerization of propene oxide occurring on the catalyst when the propene oxide partial pressure becomes to high. This problem might be overcome by the application of a multi-stage reactor system, such as a riser-regenerator, rotating monolith, or interconnected fluidized beds.

The presence of hydrogen is crucial for the activity of the catalyst, most likely because of a reaction mechanism, which creates a hydroperoxide-alike compound on the titanium atoms of the support. This hydroperoxide is expected to be the species reacting with propene to produce propene oxide. The efficiency for the hydrogen consumption at the moment is too low (< 30 %) for the profitable application of this type of catalyst. The development of a catalyst active at even lower temperatures will probably solve the problem of a low hydrogen (and oxygen) efficiency.

References

Chapter 8

Propene Epoxidation

using Molten Salts

Summary

The epoxidation of propene using molten salts has been investigated. The use of molten salts in the propene epoxidation has been developed by Olin, claiming propene oxide selectivities of up to 65% at 15% propene conversion. The propene epoxidation was studied in a number of different molten salt mixtures with a number of components added in an attempt to increase selectivity. By comparing the epoxidation results in the molten salts to experiments using the same, but empty reactors, an attempt was made to clarify the mode of operation of the salt. From a number of different possibilities in which the salt could be active, the most likely was found to be that the salt acts as a 'catalyst' in the formation of free radicals, necessary for the homogeneous gas-phase oxidation taking part in the gas bubbles in the salt. The salt, therefore, does not actually take part in the oxidation reaction, but only acts as an initiator to the radical reaction process.
Introduction

A conceptual process for the epoxidation of propene using molten salts was developed in the 1980's by Olin and is described in a number of patents that were published between 1988[1] and 1991[2]. The main differences between the processes discussed in these patents are in the use of different bubble column reactor geometries containing the salt through which a propene – air mixture was sent at a wide range of temperatures (473-773 K) and pressures (ambient to 5 MPa). The salts used in the reactors for the epoxidation are alkali nitrates, which might contain one of a number of co-catalysts to improve selectivity and/or conversion. Recycles of by-products are also claimed to enhance the selectivity of the reaction. The best results reported using this approach are 65 % selectivity towards propene oxide at 15 % propene conversion, which would be sufficient for the economical application of such a process. The major by-products reported are ethanal and carbon dioxide.

The mechanism at which a molten salt process could produce propene oxide, however, is still unknown. Considering the process conditions the following mechanisms producing propene oxide suggest themselves:

1. Propene is epoxidized by the nitrates in the molten salts, after which the reduced nitrates are re-oxidized by oxygen;
2. A kind of hydroperoxide mechanism is occurring, in which a part of the propene is oxidized to a hydroperoxide. This hydroperoxide reacts with a propene molecule to produce propene oxide and by-products;
3. The molten salt might not participate in the reaction and only act as a medium facilitating to quickly heat up the propene air mixture, after which a gas-phase radical reaction takes place in the gas bubbles;
4. A radical reaction might occur in the molten salt between propene and oxygen, both dissolved in the salt.

Although other possibilities for the activity of the molten salt could be suggested, such as for example the alkali metals being the catalytic species, the above mentioned options are most likely. Furthermore, it can be discussed whether the salt is indeed acting as some kind of catalyst, or only as a solvent or heat transfer medium, even if the reaction is actually taking place in the salt or at the gas-liquid interface. In this chapter different experiments will be discussed either to prove or rule out the above mentioned mechanistic possibilities. These experiments will, therefore, include the following:

- Epoxidation in molten salt mixtures in absence of nitrates to check the activity of the nitrates (1);
- Addition of catalysts, which are in used in the hydroperoxide propene-epoxidation processes, to the molten salt to check the occurrence of a hydroperoxide type-mechanism (2);
- Comparison between reaction in the molten salt and experiments using an empty reactor to check if the reaction occurs in the salt (3);
Experiments using different amounts of molten salt or with or without stirring of the salt in the reactor to change the contact time between gas and salt (3 and 4). From these experiments the comparison between blank experiments and experiments using molten salts is of course most important, since even if the molten salts are active in the epoxidation, it is necessary to take into account a possibly occurring homogeneous gas-phase reaction.

Experimental

The equipment used for the molten salt experiments is a basic type flow set-up. In this setup the reactant gases, nitrogen, oxygen, and alkene, were continuously fed by means of mass flow controllers with the possibility to add a fourth gas or to saturate the gas with a liquid. Unless stated otherwise, the composition of the gas used for the reaction had the volumetric ration for oxygen : propene : nitrogen of 1 : 2 : 4. All flow rates given are at standard conditions (298 K, 0.1 MPa). Residence times, however, are reported at the actual reaction conditions. The use of higher oxygen concentrations or lower nitrogen concentrations would result in experimenting within the explosion limits, and was, therefore, ruled out. A number of different reactor vessels were used, one 400 ml stainless steel reactor, and a variety of glass reactors, from 100 ml to 400 ml volume, some with an internal glass stirrer. The vessels all had porous gas inlets at the bottom, producing approximately 1 mm diameter gas bubbles. Most reactors contained a special insert to reduce the empty volume above the molten salt in the vessel, although there always was at least 10 ml of void space available above the salt, the possible influence of this volume will be discussed later. Further reducing this void could result in the possibility of entrainment of salt with the gas outlet stream, which then would solidify in the downstream tubing of the setup. The reactor temperature could be controlled in between ambient and 773 K, the reactor pressure was set by the pressure drop of the tubing and was slightly higher than atmospheric pressure (maximum 40 kPa, typically 20 kPa above atmospheric pressure).

The analysis of the reactor products was performed using an automated sampling gas chromatograph, analyzing a gas sample every 10 minutes. The column used for the analysis was a Rescom FFAP 0.312 mm diameter, 25 m length capillary column, operated at 323 K with helium as carrier gas. A flame ionization detector (FID) was used for the analysis. This configuration was able to separate all oxygenated organic components relevant in this study, hydrocarbons without oxygen were not separable, since they all had the same residence time as the carrier gas. The sensitivity of the gas chromatograph towards propene and the major reaction products was determined using calibration mixtures. Since the complete combustion products (CO and CO₂) could not identified using the gas chromatograph, a non-dispersive infrared (NDIR) detector was used after the sample valve of the chromatograph, measuring both the concentrations of carbon dioxide
and carbon monoxide. The two signals from the NDIR and the temperature in the reactor were continuously recorded using a personal computer. Since water is also present as a combustion product and water will disturb the operation of the NDIR, a Permapure membrane drier was used in order to remove the water from the gas stream in front of the NDIR. To prevent condensation in the tubing of the set-up of reaction products, all tubing up to the NDIR detector was heated to 373 K. After the NDIR detector the gas was either directly vented or sent into a gas sampling cylinder, to allow for a post-run more detailed analysis, for example using GC-MS.

The epoxidation experiments were performed mostly using low melting mixtures of potassium, sodium and lithium nitrates, but also low melting eutectic mixtures of other salts were investigated. Contrary to the experiments performed with molten alkali nitrates, the melting points of the individual salts used in these mixtures were higher than the experimental temperature. Therefore, it was necessary to pre-melt these salts to obtain the desired low-melting eutectic mixture.

Results and first Discussion

Comparison between molten salt catalysis and homogeneous gas phase reaction

The ‘standard’ salt mixture used for the epoxidation experiments described by Olin consisted of a eutectic mixture of sodium and potassium nitrate (55-45 w%). Table 1 shows the measured conversion of propene and the selectivity towards the different products for this salt mixture, compared to those obtained using blank experiments in the same reactor, together with the results of a comparable experiment in an Olin patent [1].

Other products, which are found to be produced in trace amounts in the oxidation experiments (both in the salt and the blank), are formaldehyde, 2-propanol, and several dioxanes. The alkanes and alkenes produced are mainly methane, ethene, butenes, and 1,5-hexadiene. The amounts of small alkanes produced (<C5) do not differ much between the blank and the salt experiments. The increase in alkane/alkene production in the blank experiment compared to the salts is primarily caused by an increase in the amount of 1,5-hexadiene produced and to a lesser extent by an extra amount of butenes. When the molten salt experiment is compared to the results of a similar experiment by Olin, it can be seen that the main difference is the observed conversion. This difference can partly be explained by the higher carbon dioxide production in the Olin experiment. A higher carbon dioxide production will lead to a lower conversion, since the conversion in the experiments is limited by the amount of oxygen, and the total combustion of propene used more oxygen than the partial oxidation. A complete explanation for the lower Olin conversion in the example in Table 1 cannot be given, however. The higher carbon dioxide production and absence of a carbon monoxide production reported by Olin might be explained, at least partly, by the lumping of these two gases.
Table 1.
Comparison between conversions (mol%) and selectivities (mol%) for the direct epoxidation of propene in molten salt (55 w% NaNO₃ + 45 w% KNO₃) and empty reactor. Reactor: material: glass, volume 250 ml, 250 g of salt, total flow rate 35 Nml/min, 673 K.

<table>
<thead>
<tr>
<th>Residence time (s): in salt</th>
<th>Molten Salt</th>
<th>Blank</th>
<th>Olin [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>in void</td>
<td>0.3</td>
<td>-</td>
<td>3'</td>
</tr>
<tr>
<td>Conversion</td>
<td>30</td>
<td>190</td>
<td>-</td>
</tr>
<tr>
<td>Selectivity to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propene oxide</td>
<td>36</td>
<td>31</td>
<td>16</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>28</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>4</td>
<td>8</td>
<td>n.r.</td>
</tr>
<tr>
<td>Ethanal</td>
<td>11</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>Methanol</td>
<td>30</td>
<td>28</td>
<td>24</td>
</tr>
<tr>
<td>Acrolein</td>
<td>8</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Propanal</td>
<td>11</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>Acetone</td>
<td>4</td>
<td>4</td>
<td>n.r.</td>
</tr>
<tr>
<td>Alkanes and Alkenes</td>
<td>4</td>
<td>5</td>
<td>n.r.</td>
</tr>
<tr>
<td>Others</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>4</td>
</tr>
</tbody>
</table>

n.r.: not registered; *: estimated

As can be seen from Table 1 there is a similarity in both the conversion and the product distribution between the results obtained using molten salts and the blank experiment. The similarity in conversion can be easily explained by a complete conversion of all oxygen present in the gas stream. The similarity in product composition is more difficult to explain. This similarity could either suggest a similarity in the reaction mechanism for the salt catalyzed reaction and the homogeneous gas phase reaction or indicate that the homogeneous gas-phase reaction is taking place in the gas bubbles in the molten salt and that the salt by itself has no activity at all. It should be noted, however, that the residence time for the blank experiments is significantly longer (over 1 minute) than the residence time of the gas in the salt (order of 0.3 seconds). On the other hand, it is inevitable that the gas in the presence of a salt has a relatively long residence time in the void space above the salt (order 20 seconds). When experiments are performed in a smaller glass reactor (50 ml), with a residence time closer to the total residence time of gas in the experiments with molten salts (including the residence time in the void space above the salt), it can be seen that the conversion in the empty reactor is significantly lower, indicating that the salt in some way does influence the reaction. This can be seen in Figure 1, where the conversion in an empty glass reactor is given for different residence times. In this figure it can be seen that in the experiments in which the flow was decreased slowly (i.e. from short to long residence times) at a given residence time (45 s) the conversion suddenly increases sharply. If the same experiment is
Figure 1.
Propene conversion in an empty 30 ml glass reactor as a function of residence time (723 K).

performed with a flow, which is gradually increased, the conversion drops drastically only with a residence time decreased to 15 s. The leveling of the propene conversion at a maximum value in the experiments with a residence time of over 50 seconds, can again be explained by a 100 % conversion of the oxygen in the reaction mixture. Performing the experiments in reactor with different sizes or length over diameter ratios but operated at equal residence times did not result in significantly different conversions or product distributions.

An explanation for the hysteresis behavior visible in Figure 1 is probably that once the amount of radicals in the reactor taking part in the homogeneous gas-phase reaction is sufficiently high, the reaction rate becomes that fast that long residence times are no longer necessary. Only if the gas flow is increased even further, the reaction can be ‘blown out’. To exclude the possibility of the hysteresis being caused by a change in the physical properties of the reactor (either the glass itself or a remaining reaction residue) as a result of the high temperatures, in one continuous experimental run the hysteresis loop was observed twice when the flow was gradually decreased and increased twice, thus ruling out the possibility of the hysteresis being caused by either changes in the glass of the reactor or by residual reaction products. An explanation for the somewhat lower maximum conversion in Figure 1, compared to the conversion in Table 1, can be found in the slightly increased selectivity towards combustion at a higher temperature. The occurrence of a similar type of hysteresis in the homogeneous gas-phase propene oxidation has been reported [5] to occur when the reaction is started when the reaction temperature is increased, and the high reaction rate is then maintained when the temperature is
lowered. In the presence of salt this type of hysteresis is not observed, and the reaction is always in the ‘active’ state. If 3 ml of the standard sodium-potassium nitrate salt mixture is added, while the reaction is in the inactive high flow state ($\tau = 12.5$ s), into the same empty 30 ml reactor used for the measurements showing the hysteresis, the reaction immediately lights off to its activated state. An increase of the gas flow to obtain the minimal residence time possible in this setup of 5 seconds still does not result in the reaction going to the non-activated reaction rate state. Clearly the presence of the salt provides and enhances the epoxidation activity.

A second indication for an active role of the salt in the propene conversion is found in experiments with an equilibrated (subjected to reaction condition until conversion and selectivities do no longer vary) stainless-steel reactor. In the absence of a salt, this equilibration procedure is important, as a fresh steel reactor produces the same results as the glass reactor in Table 1. The main products for this empty equilibrated steel reactor (723 K), however, only are carbon monoxide and carbon dioxide, indicating that the surface to which the gas is exposed to during the homogeneous gas-phase reaction strongly influences the product composition. The production of propene oxide is only in the order of 1 % (at a conversion of approximately 25 %). In the presence of a salt this steel produces the same conversion and product as given in Table 1 for the glass reactor. It can, therefore, be concluded that these products are produced while the gas resides within the salt for the short time it takes for a bubble to rise to the top of the liquid salt level, and not in the much longer residence time of the gas above the salt, where the gas is in contact with the steel. It is likely that the products are produced in the residence time of the bubble in the salt (0.3 s) as the uncatalyzed homogeneous reaction as presented in Figure 1 requires much longer reaction times to obtain a conversion of approximately 30 %. It is clear that the molten salt enhances the reaction rate drastically.

*Composition of the molten salt*

As indicated in the previous paragraph the molten salts influence the propene conversion. To investigate the role of the nitrate in the salt, experiments were performed using a eutectic mixture of alkali carbonates (34.2 w% $K_2CO_3$, 33.9 w% $Na_2CO_3$, 31.9 w% $Li_2CO_3$). The difference in conversion and selectivity between this mixture and the nitrate mixtures was, however, not significant. Therefore, it can be concluded that the nitrates by themselves are not the active species in the catalytic process. To determine the possible activity of the cations is more difficult. Experiments have been performed using different mixtures of sodium, potassium, and lithium nitrates, all leading to identical results. In these experiments it is possible to leave out any one or even two of these salts and still obtain a low melting salt. As the activity might be caused by any alkali metal, it would, therefore, be of interest to apply a low-melting mixture without alkali metals. The oxidation of propene was, therefore, performed in a eutectic mixture of calcium nitrate (52.4 w%) with barium chloride. The conversion and product distribution of this salt mixture again was very
similar to that of the carbonate salts. Since the presence of chlorides could have resulted in the production of chlorinated compounds, the use of a chloride salt would preferably have been avoided. Other stable low melting salt mixtures without alkali metals, however, were not found.

Since all salt mixtures used produce similar results, it seems likely that the molten salt is not actually a catalyst but either a solvent for reaction (e.g. radical reaction in liquid phase of some kind of hydroperoxide autoxidation mechanism), or that strong polarity of the ions of the molten salt act as an initiator for the homogeneous gas-phase reaction.

*Molten salt additives*

**Potassium hydroxide**

In the Olin patents the use of a number of different co-catalysts is suggested to improve the conversion and selectivity of the reaction. Since the basic (no additives) molten salt experiments indicate that it is more likely that the salt is acting as a reaction medium instead of as a catalyst, the term additive should be preferred instead of the use of co-catalyst. The first of these additives used is sodium hydroxide. Table 2 gives the conversion and selectivities when halfway during an experiment sodium hydroxide is added to the salt mixture.

<table>
<thead>
<tr>
<th></th>
<th>Before addition</th>
<th>After addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>33</td>
<td>20</td>
</tr>
<tr>
<td>Selectivity to</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propene oxide</td>
<td>22</td>
<td>27</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>7</td>
<td>2*</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Methanol</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Acrolein</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Others</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

*: based on the hydroxide consumption, the selectivity towards carbon dioxide would be approximately 20 %.

In Table 2 it can be seen that the addition of sodium hydroxide results in a change in the product distribution. However, since the sodium hydroxide will react with carbon dioxide produced, the low selectivity for carbon dioxide is virtual and the ‘disappearance’ of carbon dioxide is responsible for the lower than 100 % total
selectivity. The high efficiency for the hydroxide to capture the carbon dioxide from the gas phase is an extra indication that the oxidation process mainly occurs while the gas is in good contact with the salt (i.e. while the gas still travels upward in the form of bubbles), and not in the void space above the salt since in that case a larger amount of carbon dioxide should have been measured. Furthermore, it can be concluded from Table 2 that the hydroxide has an influence on the reaction mechanism as the product composition changes. From these results it could be concluded that the reaction occurs within the molten salt or at the gas-salt interface. An alternative conclusion could be that the presence of carbon dioxide influences the selectivities towards the other products, and since the hydroxide captures the carbon dioxide a different product distribution is found. To distinguish between these two possibilities an experiment was performed in which part of the nitrogen diluent was substituted for carbon dioxide (no hydroxide present).

In an epoxidation experiment using 59 w% NaNO₂ / 41 w% LiNO₃ at 673 K nitrogen was partly substituted by carbon dioxide. The addition of 10 % of carbon dioxide to the feed gas only had a minor influence on the oxidation reaction rate, resulting in a drop in conversion from 33 to 28 %, while the epoxidation selectivity rose from 22 to 27 %. An explanation for these changes was not found. However, it can be concluded that the selectivity enhancement with the addition of sodium hydroxide to the molten salt mixture is not caused by the removal of carbon dioxide, as this gas apparently has a positive influence on the selectivity. Therefore, it is clear that the salt plays an active part in the reaction, since the effect of the sodium hydroxide cannot be explained otherwise.

**Hydroperoxide catalyst**

One of the possibilities for the activity of the molten salt in the epoxidation of propene is that it might act as a solvent for a hydroperoxide autoxidation mechanism, in which part of the propene is oxidized to a hydroperoxide. This hydroperoxide is able to react with a propene molecule to produce propene oxide and a by-product. Since this reaction does not easily occur in the absence of a catalyst, and peroxides are unstable at higher temperatures, the addition of a catalyst for this reaction could drastically improve the selectivity, when this mechanism is significant in the propene oxide production. Molybdenum oxide is a homogeneous catalyst that can be used to epoxidize propene using a peroxide as oxidant [3][4]. Dissolving approximately 1 w% of molybdenum(VI)oxide in the salt, however, did not result in a measurable change in either the conversion or the selectivity of the reaction. Therefore, based on the current data it can be concluded that a hydroperoxide autoxidation mechanism is not likely.
Discussion

Although the direct epoxidation of propene oxide in a molten salt produces results very similar to direct epoxidation experiments with a homogeneous gas-phase reaction, the use of the salt does result in a higher conversion when the same residence time is used. This indicates that the salt does enhance the reaction rate. The similar conversion, which is found in most experiments, can be explained since the conversion was controlled by the available amount of oxygen in all experiments, except those with an empty reactor and a short residence time. The similarity in products indicates a comparable reaction mechanism.

The homogeneous gas-phase oxidation of propene has been a subject of several detailed studies [5-10]. An excellent review of this process has recently been given by Stark and Waddington [10], in which the possible radical reactions occurring are summarized, totaling up to 230. The product distribution in these studies is similar to that found in this study, the major products being propene oxide, ethanal, carbon monoxide, and carbon dioxide. The only discrepancy between the different studies is that some (e.g. [7]) report (similar to this study) the formation of relatively large amounts of methanol, whereas others (e.g. [10]) report the production of relatively large amounts of formaldehyde. In this study relatively large amounts of methanol were found with formaldehyde only being produced in trace amounts. A possible explanation for this difference in reported quantities of methanol and formaldehyde, is the stage of the radical reaction process at which the gases leave the reactor. Formaldehyde is produced early in the process and the amount reduces after longer reaction times, whereas methanol is produced as a sequential product [6].

The exact distribution of the different reaction products varies between the different studies. Small deviations in for example pressure [10], temperature [6], feed gas composition [7], or reaction time [8] can result in large differences in the product distribution. Also the use of a stainless-steel instead of Fyrex-glass reactor [10] has a significant influence on the products. The drop in yield of propene oxide yield in the study of Stark and Waddington (30 %), however, was not as large as in this study (90 %). An explanation for these changes can be the presence of catalytically active metals on the steel surface. The latter issue is the main reason for the use of well-cleaned glass reactors for the study of the homogeneous gas-phase propene oxidation.

In all the studies into this type of reaction, the propene oxide selectivities, however, never come close to the high selectivity of 65 % reported by Olin [2] in their molten salts and reaction conditions. Due to limitations in the experimental equipment, no experiments have been performed at the high pressure (2.5 MPa) and low temperature (500 K) used by Olin to obtain this selectivity. Although such a high propene oxide selectivity is never reported in any of the mechanistic studies for the homogeneous gas phase propene oxidation, it is quite possible this is the case since no high pressure experiments were performed in those studies. Another Olin patent [11] reports a 65 % propene oxide selectivity in the homogeneous gas-phase reaction.
(in the absence of molten salts) at 7% propene conversion (500 K). In this case the pressure necessary to obtain this result is 11 MPa. Although a propene epoxidation selectivity of 65% would be sufficient to run a propene epoxidation plant profitable, propene oxide has up to now never been produced in this manner. That this process is not applied can be explained by the extreme sensitivity of the process to a number of different (process) variables. For example, in an empty virgin stainless-steel reactor, it originally was possible to produce high quantities (30% selectivity) of propene oxide for a few hours, after which the propene oxide selectivity suddenly dropped (although no process variables were changed) and could not be restored in any way. The risk of a similar occurrence in a full-scale plant can be a major roadblock in the commercialization of this type of process.

An important aspect of both the homogeneous gas-phase and molten-salt propene epoxidation processes, is the exothermicity of the reactions occurring. Especially the combustion reaction can cause problems, with heat of reaction liberated of 2 MJ/mol. If the combustion reaction should become predominant, this would lead to an adiabatic temperature rise of approximately 1000 K. In the lab-scale experiments performed, this adiabatic temperature rise was of no importance because of the small gas flows used (the heat production with the typical flow of 35 ml/min would be approximately 1.5 W). For a full scale process, this could result in hazardous problems. For example, if the epoxidation selectivity would drop, resulting in a higher combustion 'selectivity' this would cause a temperature rise, resulting in an increase in CO₂ selectivity and a temperature runaway. The large advantage of the application of a molten salt, compared to a 'normal' homogeneous gas-phase reaction, therefore, is the easier control of the reaction temperature. The molten salt is acting as a buffer-capacity for an extra amount of heat produced, and allows for the possibility of an external cooling to the reactor by a salt circulation.

Since the epoxidation of propene using either molten salts or applying a homogeneous gas-phase reaction yield similar results, the molten salt process running either at lower pressures or shorter contact times, it seems likely that both processes involve the same reaction mechanism, i.e. a gas-phase radical reaction. The rate enhancement of the molten salt can then be explained by the ability of the salt to start-up the reaction by an easier production of the free radicals necessary for the reaction. An explanation for this might be the strong polarity of the salt. So far, other catalytic effects of the molten salt on the epoxidation reaction are not supported by any of the experimental results. The blank experiments were performed in Pyrex glass reactors and it cannot be ruled out that the glass has some influence on the reaction (i.e. assistance in the formation of radicals for the homogeneous gas-phase reaction). However, from the hysteresis behavior observed (Figure 1) and the high conversion at short residence times in the experiment using only a very small amount of salt, it can be concluded that for the homogeneous gas-phase reaction to sustain itself neither glass nor salt are necessary. In the initiation of the radical reaction the molten salts are very effective. The significantly longer residence times needed in an empty glass reactor for the reaction to 'light off' indicates that the
radical initiation by the glass surface or the spontaneous radical formation in the gas phase (which is less likely at the temperatures of the experiments performed) is much slower.

Conclusions

The use of molten salts to epoxidize propene yields similar results to the partial oxidation of propene by a homogeneous gas-phase reaction. The effect of the molten salts is a significant enhancement of the reaction rate, most likely by the production of radicals, allowing for either shorter reaction times or lower pressures. Although Olin reports propene oxide selectivities of up to 65% for both the molten salt propene oxidation and the homogeneous gas phase oxidation, such a high selectivity could not be reproduced. The possible commercialization of either a homogeneous gas phase propene oxidation or a molten salt propene oxidation will depend on finding a solution to the extreme sensitivity of the reaction to the process conditions. The mechanism for the production of propene oxide using both a homogeneous gas phase process and a molten salt process involve radical reactions and, therefore, have less potential for improvement than catalytic processes.

References

Summary and Evaluation

Multitrack

After a number of modifications had been made to the Multitrack system, a sensitive technique was available for the transient investigation of catalytic processes. The full potential of the system has been demonstrated using the model reaction ‘the transient CO oxidation over platinum’ (chapter 3) and by performing transient adsorption and diffusion measurements on (in) microporous materials (chapter 4). The CO oxidation study demonstrated that the use of this advanced technique can result in new insights into such an extensively studied reaction. The adsorption/diffusion study demonstrated that accurate modeling of measured pulse responses can yield rate constants in excellent agreement with reported values with a small number of very fast measurements. The Multitrack technique for determining these rate constants is the first macroscopic technique to yield results in agreement with those obtained using microscopic methods, such as Pulse-Field-Gradient NMR.
However, in case of a reaction of which both selectivity and conversion are low, such as for example is the case in chapter 6 for the propene epoxidation over a silver catalyst, the sensitivity of the system is insufficient to obtain workable pulse responses.

To improve the sensitivity of the Multitrack system it would be necessary to put an additional mass spectrometer into the main vacuum chamber, preferably within 1 cm of the reactor exit, which would result in a 300 fold increased sensitivity of the system. This mass spectrometer, however, would measure a signal that is somewhat disturbed by the residual gas in the main vacuum chamber and it might be necessary to numerically correct for this disturbance. A further improvement that would be recommended for the current system is the development of a modified reactor assembly. The current reactor assembly has a large empty volume in between the catalyst bed and the pulse valves. As is demonstrated in chapter 2, this empty volume determines the actual pulse shape given to the catalyst bed and thereby the time resolution of the system. A newly designed reactor assembly in which this volume in minimized would have a second advantage, apart from the increased time resolution. Since a smaller pre-bed volume results in a narrower pulse arriving at the catalyst bed, the height of the pulse would consequently be higher and narrower at an equal pulse size.

**Propene epoxidation**

Chapter 5 discusses a number of possibilities for new propene epoxidation processes. From these processes only one is at a stage in which it might be applied in the near future: a combination process in which hydrogen peroxide is produced and immediately consumed to produce propene oxide using TS-1 as a catalyst. Although this process, currently at the pilot-plant stage under development by Enichem, is not a direct epoxidation process, since the epoxidation is carried out by hydrogen peroxide rather than by oxygen. This process has the advantages of a clean and selective reaction without the production of a co-product. The use of commercially supplied hydrogen peroxide for the propene epoxidation using TS-1 is not feasible as on a molar basis propene oxide and hydrogen peroxide approximately have the same market value. The hydrogen peroxide combination process, on the other hand, is economically feasible, since it removes the need for a number of separation steps necessary in the hydrogen peroxide production. Furthermore, TS-1 is able to epoxidize propene oxide using diluted hydrogen peroxide.

Three catalytic systems have been examined for the direct epoxidation of propene oxide: silver based catalysts, highly disperse gold on titanium systems, and molten salt systems. The use of silver catalysts, which are commercially used for the direct epoxidation of ethene, for the propene epoxidation results in very poor selectivities. These low selectivities are primarily caused by the reactivity of the γ-hydrogen atoms of propene. Based on the acquired knowledge on the mode of
operation of a silver catalyst in both the epoxidation and combustion of propene it should theoretically be possible to create a catalyst based on silver that is able to selectively epoxidize propene, although attempts to prepare such a catalyst have not been successful. It is expected that if one would succeed in creating an isolated site (i.e. a cluster of four silver atoms) silver catalyst and one could put atomic oxygen on these sites, this catalyst should be able to perform the propene epoxidation selectively.

The second catalyst examined consists of highly disperse gold particles on a titanium containing support. This type of catalyst epoxidizes propene using oxygen and hydrogen. The mode of operation of this type of catalyst is based on the cooperation between gold and titanium. Most likely is that a kind of peroxide species is created on the titanium sites via a spill-over mechanism in which gold donates a hydrogen atom to an adsorbed oxygen molecule on titanium. This peroxide is able to epoxidize propene. The advantages of this system are the high epoxidation selectivity (up to 100 %) and the low reaction temperature (as low as 323 K). A number of challenges, however, remain in the development of this catalytic system. First of all the efficiency of the catalyst for the hydrogen consumption is a point of concern. Especially at higher temperatures (423 K) the hydrogen efficiency can drop to a value as low as probably 5 % making this process far from profitable. At lower temperatures (343 K) the hydrogen efficiency is about 30 %, and it is expected that even lower reaction temperatures will result in higher hydrogen efficiencies. A low reaction temperature, however, has the disadvantage of a strong propene oxide adsorption on the catalyst, which can result in polymerization of propene oxide on the catalyst, and thus result in deactivation of the catalyst. The use of a dispersed titanium support material (such as TS-1) does not have the problem of deactivation as a result of propene oxide polymerization, however, the lower titanium content necessitates a higher reaction temperature to reach an acceptable conversion, bringing back the problem of the hydrogen efficiency. A solution to these problems might be found in the use of a two (or more) stage reaction system, in which in one reactor propene oxide is produced at low temperature (high hydrogen efficiency), with the epoxide remaining adsorbed on the catalyst. In a second reaction the propene oxide is removed from the catalyst by a rise in temperature or a decrease in pressure, resulting in a concentrated propene oxide stream. This type of process can be carried out more or less batchwise using two (or more) reactors in a pressure (or temperature) swing operation in which propene or hydrogen is to be used as a sweep gas in the epoxide-desorption step. A more complex continuous operation for example can be carried out in a riser-regenerator process (temperature variation) or a rotation monolith (pressure variation).

The third and last 'catalytic' system examined is the epoxidation of propene oxide in molten salts. Based on a number of patents on these systems, the epoxidation of propene oxide in molten salts looked promising, with reported epoxidation selectivities of up to 65 % at 15 % propene conversion. The molten salts in these systems, however, were determined not to actually catalyze the epoxidation
reaction but merely initiate a homogeneous gas phase (radical) reaction. This reaction cannot be controlled and is instable towards many outside influences, such as small changes in temperature or pressure. Considering the complex nature of the homogeneous gas-phase reaction and the highest selectivity measured of only 30%, it is, therefore, recommended not to proceed this pathway in the propene epoxidation.
**Samenvatting**

**Inleiding**

Propeenoxide is een van de belangrijkste bulkgrondstoffen in gebruik in de chemische industrie. Circa 10% van de totale hoeveelheid geproduceerde propeen wordt omgezet naar propeenoxide. Op dit moment worden twee processen toegepast voor de produktie van propeenoxide. Het eerste en langst toegepaste proces is het chlorohydrin proces. Het belangrijkste nadeel van dit proces is dat het milieuvriendelijk is door de grote hoeveelheid zouten die ontstaan tijdens de propeenoxide produktie. Bovendien bevat het geproduceerde propeenoxide een aantal chloorhoudende verontreinigingen, welke verwijderd moeten worden. Vanwege milieuoverwegingen zal dit proces in het belangrijkste deel van de wereld dan ook niet meer (nieuw) toegepast mogen worden.

Het tweede proces voor de produktie van propeenoxide is het (relatief schone) hydroperoxide proces, waarvan het nadeel is dat in dit proces naast propeenoxide in een equimolare hoeveelheid een co-produkt wordt gevormd. Van dit proces worden twee varianten toegepast, te weten het PO-TBA proces (tert-butanol als co-produkt, wordt gebruikt voor de produktie van MTBE een octaangetalverhogend benzineadditief) en het PO-SM proces (styreen als co-produkt, gebruikt om
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polystyreen te maken). Het grote nadeel van de produktie van een co-produkt in een vaste hoeveelheid wordt duidelijk als gekeken wordt naar de op dit moment inzakkende markt voor MTBE, terwijl de vraag naar propeneoxide blijft stijgen.

Het doel van dit promotieonderzoek was de ontwikkeling van een nieuwe katalysator (proces) om propeneoxide direct te kunnen produceren. Het voordeel van een directe oxidatie met zuurstof (lucht) is de lage kostprijs van een oxidatiemiddel. Een goedkoop oxidatiemiddel is nodig gezien de relatief lage marktwaarde van propeneoxide. Zo is het bijvoorbeeld wel mogelijk om propaan schoon en selectief te epoxideren met waterstofperoxide, maar vertegenwoordigen waterstofperoxide en propeneoxide dezelfde marktprijs, zodat deze epoxidatie financieel niet aantrekkelijk is.

Een hulpmiddel om een geschikte katalysator te vinden voor de propeneepoxidatie, wat in het kader van dit promotieonderzoek is ontwikkeld, is de Multitrack opstelling waarmee katalysatoren op een zeer korte tijdschaal onderzocht kunnen worden. Gezien de complexiteit van deze techniek en de grote hoeveelheid tijd besteed aan de ontwikkeling ervan, bevat dit proefschrift voor de helft een beschrijving van deze techniek en een demonstratie van de mogelijkheden ervan. Het tweede deel bevat het onderzoek naar een nieuw propeneepoxidatieproces.

Multitrack

Multitrack is een opstelling ontworpen om katalysatoren op een zeer korte tijdschaal te onderzoeken, geïnspireerd op de TAP- (Temporal Analysis of Products) techniek ontwikkeld door Gleave. Het principe is gebaseerd op een kleine katalysatormateriaal bevattende reactor in een ultra-hoog vacuumsysteem, waaraan kleine (10^9 moleculen) gaspulsen worden gegeven. Door de gaspulsen zoals deze de reactor verlaat te onderzoeken, zowel wat vorm en samenstelling betreft, wordt informatie over de katalysator verkregen. Hoofdstuk 1 bevat een beschrijving van Multitrack, de experimenttypen en de ontwerpproblematiek.

Om uit de pulseresponsen gemeten met Multitrack snelheidsconstanten te berekenen van de verschillende processen welke plaatsvinden op de katalysator, is het noodzakelijk om de gemeten responsen te kunnen beschrijven met een numeriek model. Hoofdstuk 2 beschrijft de modellen die gebruikt kunnen worden voor de Multitrack experimenten.

Hoofdstukken 3 en 4 zijn bedoeld om de mogelijkheden van Multitrack te demonstreren. In hoofdstuk 3 wordt de platina-gekatalyseerde CO-oxidatie als modelreactie onderzocht. Hierin wordt aangetoond hoe met behulp van een nieuwe krachtige techniek zelfs bij een al uitgebreid onderzochte reactie als de CO-oxidatie nog nieuwe aspecten kunnen worden gevonden, namelijk de relevantie van de CO_2-desorptie van het platinaoppervlak. Tot nu toe werd verondersteld dat deze instantaan is, hetgeen echter niet het geval blijkt te zijn.

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De Ontwikkeling van een nieuw Propeen Epoxidatieproces

In hoofdstuk 4 wordt het adsorptiegedrag van gassen op en in microporeuze materialen beschreven. Aangetoond wordt dat het zeer goed mogelijk is om met behulp van Multitrack de absolute waarden van adsorptie en diffusieparameters te bepalen, die goed overeenstemmen met in de literatuur opgegeven waarden. Het voordeel van deze methode is dat deze zeer snel is en alle relevante parameters simultaan bepaalt.

Propeen epoxidatie

In hoofdstuk 5 wordt een beschrijving gegeven van een aantal mogelijkheden voor nieuwe propeen epoxidatieprocessen. Van deze processen is er slechts een zo ver gevorderd dat het mogelijk is dat het in de nabije toekomst toegepast kan worden: een combinatieproces waarin waterstofperoxide geproduceerd wordt volgens het anthrahydroquinone proces en onmiddellijk wordt benut om met behulp van een TS-1 (titaan silicaliet-1) katalysator propeen te epoxideren. Hoewel dit geen direkt epoxidatieproces is, heeft dit proces wel de voordelen van een direct epoxidatieproces: een schoon proces zonder co-produkt (afgezien van water, wat echter meer een afvalprodukt is dan een co-produkt). Hoewel dit proces, op dit moment in het pilotplantstadium in ontwikkeling bij Enichem, waterstofperoxide gebruikt voor de daadwerkelijke epoxidatie is het toch financieel aantrekkelijk, aangezien de (dure) scheidingsstappen die normaal gesproken noodzakelijk zijn bij de waterstofperoxide-produktie overbodig zijn.

Drie katalytische systemen zijn onderzocht voor de directe epoxidatie van propeen: zilverkatalysatoren, hoog-disperse goud op titaan katalysatoren en de epoxidatie met behulp van gesmolten-zout systemen. Hoofdstuk 6 geeft een korte beschrijving over de epoxidatie met behulp van zilverkatalysatoren, welke industrieel worden toegepast voor de directe epoxidatie van etheeën. Voor de epoxidatie van propeen zijn deze katalysatoren minder geschikt doordat slechts lage selectiviteiten behaald worden. Deze lage selectiviteiten worden voornamelijk veroorzaakt door de reactiviteit van de γ-waterstof atomen van propeen. Indien een van de waterstofatomen met een zuurstofatoom op het zilveroppervlak reageert is een volledige oxidatie onvermijdelijk. Hoewel pogingen deze katalysator te bereiden niet succesvol geweest zijn, zou door informatie uit de literatuur met elkaar te combineren het wel te verwachten moeten zijn dat het mogelijk is om een selectieve zilverkatalysator voor de propeenepoxidatie te bereiden. Een dergelijke katalysator zou dan geïsoleerde zilversites (= clusters van vier zilveratomen) moeten bevatten, waarop atomair zuurstof op aangebracht moet worden, bijvoorbeeld door lachgas op deze sites te ontleden.

Het tweede katalytische systeem, beschreven in hoofdstuk 7, is een disperse goud-katalysator op een titaanhoudend dragermateriaal. Deze katalysator is in staat bij lage temperatuur (323 K) propeen te epoxideren in aanwezigheid van zuurstof en waterstof. De werking van deze katalysator is gebaseerd op een nauwe
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samenwerking tussen goud en titaan, waarbij waarschijnlijk waterstofatomen worden overgedragen van goud deeltjes aan molecule zuurstof geabsorbeerd op titaan. Hierbij wordt dan een soort van peroxide-groep gevormd op een titaansite, die vervolgens propeen epoxideert naar propeenoxide. Dit type katalysator is zeer selectief in de propeenepoxidatie, hoewel er nog wel een aantal verbeteringen op aangebracht kunnen worden. Een van de belangrijkste aandachtspunten is de efficiëntie welke de katalysator heeft voor het gebruik van waterstof. De maximaal bereikte waterstofefficiëntie is tot nu toe 30 %, hetgeen nog onvoldoende is. Een hogere waterstofefficiëntie kan mogelijk bereikt worden door de reactie bij nog lagere temperatuur uit te voeren. Propeenoxide adsorbeert echter zeer sterk aan de katalysator, hetgeen bij lagere temperatuur alleen maar erger wordt. Bij grote hoeveelheden propeenoxide op de katalysator polymeriseert propeenoxide en deactiveert daardoor de katalysator. Als gevolg van deze sterke adsorptie (en daarop volgende polymerisatie) is het niet mogelijk om hogere propeenoxideopbrengsten dan ongeveer 1 % te bereiken. Door echter het proces in een twee- (of meer) staps reactor uit te voeren zijn hogere waterstofefficiënties wel mogelijk en kan ook de propeenoxide in geconcentreerde vorm worden geproduceerd. In één reactor moet dan propeenoxide op de katalysator geproduceerd worden (bij voorkeur bij lage temperatuur) uit propeen, zuurstof en waterstof. De katalysator wordt vervolgens een tweede reactor gebracht, waar de propeenoxide van de katalysator wordt verwijderd door drukverlaging of temperatuurverhoging, waarbij geconcentreerd propeenoxide vrijkomt. Een dergelijk proces kan bijvoorbeeld in een riser-regenerator of een roterende monoliet worden uitgevoerd. Als alternatief kan in plaats van de katalysator ook de gasstroom en temperatuur en/of druk in de reactor worden veranderd, waarbij het proces wordt bedreven in twee of meer reactoren zoals dit ook bij pressure-swing reacties of adsorpties gedaan wordt. Zodra de katalysator in een reactor dan 'vol' zit met propeenoxide wordt er gewisseld van propeenoxide produktie naar propeenoxide desorptie.

Het laatste 'katalytische' systeem wat onderzocht is, is de propeenepoxidatie in gesmolten zouten (hoofdstuk 8). In een aantal patenten (Olin) worden zeer goede resultaten voor dergelijke systemen geclaimd (tot 65 % selectiviteit bij 15 % propeenconversie), echter de werking van dergelijke systemen was onduidelijk. Dergelijke hoge selectiviteiten konden niet geregistreerd worden, hoewel dit mogelijk deels te wijten geweest is aan beperkingen in de experimentele condities. Wat echter wel duidelijk is geworden uit de experimenten, is dat de werking van de zouten niet zozeer katalytisch is, maar dat deze als initiator werken voor een homogene gasfase (radicaal) reactie. Een dergelijk reactiemechanisme is zeer gevoelig voor invloeden van buiten af, waarbij de productenstabiliteit sterk kan variëren. Gezien de complexiteit van een dergelijk systeem en het feit dat op slechts een maximale propeenoxide selectiviteit van 30 % bereikt is, wordt voortzetting van onderzoek naar de mogelijke toepassing van een dergelijk systeem dan ook afgewend.

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Dankwoord

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Curriculum Vitae


Van augustus 1993 tot en met oktober 1997 werd als Assistent in Opleiding in dienst van de TU Delft onder begeleiding van Prof. dr. J.A. Moulijn en Dr. ir. M. Makkee een promotieonderzoek verricht binnen de sectie Industriële Katalyse naar de ‘directe oxidatie van propeen tot propeenoxide’, wat heeft geresulteerd in de totstandkoming van dit proefschrift.
Publications and Presentations

Publications


Contributions to publications


Publications in preparation

T.A. Nijhuis, B.J. Huizinga, M. Makkee, and J.A. Moulijn, 'The direct epoxidation of propene using dispersed gold on titania catalysts', to be submitted to J. Catal.

Publications and Presentations

Publications in preparation (continued)


Orals


T.A. Nijhuis, M. Makkee, A.D. van Langeveld, and J.A. Moulijn, ‘The desorption of CO, from the surface as a kinetically relevant step in the CO oxidation reaction over platinum’, Dynamics of surfaces and reaction kinetics in heterogeneous catalysis, Antwerpen, September 15-17, 1997.